

Prema

Illinois  
Institute of  
Technology  
N - M - R  
Newsletter

No. 95  
AUGUST, 1966

Hampson, Mathias <sup>14</sup> N Chemical Shifts in Primary and Secondary Amides	1
Baldeschwieler Halide Ion Probes for NMR Studies of Antibody-Hapten Binding	4
Snyder Isomerization of Acetone Anils	7
Kanekar, Khetrpal NMR Studies of the Interaction between Polyfluoroacetones and Proton-donors	10
Kranenburg, Sekuur NMR of Cyclopropyl Ions	12
Fraenkel Pyridine, Chemical Decoupling, Computer Analysis with Different Programs	17
Temussi Ring Inversion in Trihetero-Cyclohexanes	18
Hempel Kalibrierung von NMR-Spektrometern unter Verwendung von Lösungsmittelmischungen	20
Porte Observations on Conformations and Configurations in Hg(II) Derivatives of Some Sugars	22
Hirt Simultaneous Measurement of NMR Spectrum and Integral	25
Fritz, H. P., Schwarzhang Variable Frequency Equipment for HR-100	26
Schaefer Signs of Coupling Constants in 2-Bromo-5-chlorotoluene	27
Weigert, Roberts A Two-stage MEF Program; Preliminary Results from the DFS-60	28
Anderson, J. M. NMR of some Substituted Difluorobenzenes; NMR of Ammonia and Phosphine	31
Reeves <sup>29</sup> Si Magnetic Resonance	32
Narasimhan Perturbation Approach to the Proton Spin Coupling in the Ethane Fragment	34
Samek, Spirko, Toman Damped Least Squares Analysis of the NMR Spectra	36
Fiat, Reuben <sup>17</sup> O NMR Studies of Metal-ion Hydration	38
Molin, Zaev, Voevodsky The <sup>59</sup> Ni Shifts in Paramagnetic Complexes of Co <sup>+2</sup> and Ni <sup>+2</sup>	39
Szymanski Correlation of the Position of the Signal for the CH <sub>3</sub> Group Attached to Aromatic Rings with Ring Substituents	42

OVER

Vold, Gutowsky	
Computer Calculation of Spin-Echo Trains	43
Harris	
Are $^{13}\text{C}$ Satellites Always Helpful for Spectral Analysis; Signs of (P,F) Coupling Constants	44
Carter, Crutchfield, Irani	
Chemical Shifts of Nitrilotriacetic and Triphosphonic Acids and their N-Oxides upon Neutralization	46
Brockmann	
Diastereomere 10-Methoxy-methylphosphoribide Zuordnung der Methylsignale	48
Stothers	
8th ENC - Preliminary Announcement	51
Ich, Gagnaire	
Signes Negatifs de Couplages "Benzyliques" Ortho Et Para	52
Collin	
Acid Induced Upfield Shifts in Some Carbonyl Compounds	54
Lawson, Flautt	
C-1024: Use with Fieldial and Read Out of Calibrated Spectra	55
Allerhand	
Performance of a Magnion Spin-Echo Apparatus; Theory of Spin-Echoes in Solids	58

Deadline Dates: No. 96 - 15 September 1966 No. 97 - 15 October 1966
--

A monthly collection of informal private letters from laboratories of NMR. Information contained herein is solely for the use of the reader. Quotation is not permitted, except by direct arrangement with the author of the letter, and the material quoted must be referred to as a "Private Communication".

---



# Imperial Chemical Industries Limited

DYESTUFFS DIVISION

P.O. Box 42, Hexagon House, Blackley, Manchester, 9

Professor E.L. Shapiro,  
Department of Chemistry,  
Illinois Institute of Technology,  
Chicago, 60616,  
U.S.A.

Your Ref:

Our Ref: PL/ARG-B5  
Research Department

6th July, 1966.

Dear Professor Shapiro,

## $^{14}\text{N}$ CHEMICAL SHIFTS IN PRIMARY AND SECONDARY AMIDES

In the past we have submitted contributions to the NMR Newsletter concerning the double resonance method of obtaining  $^{13}\text{C}$  chemical shifts from proton spectra. We have now modified a second probe for our HA-100 spectrometer so that  $^{14}\text{N}$  data can be obtained by similar means. Here the transmitter coil supplies both the 100 Mc/s proton observation frequency and the 7.22 Mc/s  $^{14}\text{N}$  decoupling frequency. The decoupling frequencies for both  $^{13}\text{C}$  and  $^{14}\text{N}$  work are now generated by a Schomandl frequency synthesizer, which gives a continuously variable output frequency from 0-33 Mc/s with a setting accuracy of  $\pm 1$  c/s.

The  $^{14}\text{N}$  nucleus with spin  $I=1$  is expected to split the signal of any attached proton into a triplet. This splitting however, is only seen when the electric field at the nitrogen nucleus is highly symmetrical, e.g. in ammonium ions. In most organic compounds, where the field is asymmetrical,  $^{14}\text{N}$  quadrupole relaxation effects usually cause the attached proton signal to appear as a broadened singlet. Double irradiation at the  $^{14}\text{N}$  resonant frequency removes, or at low  $^{14}\text{N}$  Rf power modifies, the triplet splitting or alternatively sharpens the broadened singlet peak of any attached proton and the  $^{14}\text{N}$  chemical shift can be determined from this critical irradiating frequency.

The double resonance method has advantages of sensitivity, precision, convenience and lower cost over the direct observation method. However, to compensate, it has the following disadvantages, (a) only  $^{14}\text{N}$  nuclei coupled to protons can be investigated, (b) if the  $^{14}\text{N}$  nuclear quadrupole relaxation rate or alternatively the labile NH proton exchange rate is fast enough to effectively decouple the proton and the  $^{14}\text{N}$  nucleus, i.e. an already sharpened proton singlet peak is observed, the  $^{14}\text{N}$  irradiation will have no further effect.

In the amides, the two complicating effects above are not serious and the double irradiation method was successful for all the primary and secondary amides examined. The results are given in the Table. The solvent throughout was  $\text{CDCl}_3$  except for formamide itself which being insoluble in  $\text{CDCl}_3$  was examined in acetone. Tests showed that the results are free of solvent and concentration effects within the present level of experimental error. The  $^{14}\text{N}$  chemical shifts were

RCONH <sub>2</sub>	Shift p.p.m.	Error (±)	RCONHR <sup>1</sup>	Shift p.p.m.	Error (±)
H CONH <sub>2</sub>	267.8	1.5	CH <sub>3</sub> CONHCH <sub>3</sub>	268.7	2.0
CH <sub>3</sub> CONH <sub>2</sub>	269.6	2.0	CH <sub>3</sub> CONHC <sub>2</sub> H <sub>5</sub>	253.3	3.5
C <sub>2</sub> H <sub>5</sub> CONH <sub>2</sub>	272.8	2.5	CH <sub>3</sub> CONHC <sub>3</sub> H <sub>7</sub> (n)	246.6	3.5
n-C <sub>3</sub> H <sub>7</sub> CONH <sub>2</sub>	272.4	2.5	CH <sub>3</sub> CONHC <sub>4</sub> H <sub>9</sub> (n)	248.6	2.0
i-C <sub>3</sub> H <sub>7</sub> CONH <sub>2</sub>	272.8	3.5	C <sub>2</sub> H <sub>5</sub> CONHCH <sub>3</sub>	270.3	2.0
CH <sub>2</sub> ClCONH <sub>2</sub>	278.5	2.5	HCONHCH <sub>3</sub>	264.1	2.0
CHCl <sub>2</sub> CONH <sub>2</sub>	280.8	2.5	HCONHC <sub>2</sub> H <sub>5</sub>	248.7	1.5
CCl <sub>3</sub> CONH <sub>2</sub>	283.3	2.5	HCONHPh	235.0	2.5
PhCH <sub>2</sub> CONH <sub>2</sub>	274.5	2.5	CH <sub>3</sub> CONHPh	243.3	2.0
Ph <sub>2</sub> CHCONH <sub>2</sub>	273.1	3.5	C <sub>2</sub> H <sub>5</sub> CONHPh	243.6	2.0
CH <sub>2</sub> =CHCONH <sub>2</sub>	276.4	2.0	PhCONHPh	251.6	2.0
Ph-CH=CH-CONH <sub>2</sub>	277.1	2.5	o-nitroacetanilide	253.3	2.0
PhCONH <sub>2</sub>	282.1	2.0	m-nitroacetanilide	246.3	5.0
			2,4-dinitroacetanilide	254.1	3.5

obtained experimentally relative to that of the ammonium nitrogen of a 4.5 M solution of Analar NH<sub>4</sub>NO<sub>3</sub> in 3N aqueous HCl. Richards [1] used the nitrate nitrogen chemical shift of this solution as the reference for his collection of <sup>14</sup>N data and our results were converted to the same scale using the value of 353.5 ± 0.5 p.p.m. for the shift difference between the two nitrogen signals. The main source of error in the quoted shift values arises from the uncertainty in determining the optimum <sup>14</sup>N decoupling frequency due to quadrupole broadening of the nitrogen resonance itself. Instrumental instabilities were found to be negligible. The quoted errors are the maximum uncertainties and also include the 0.5 p.p.m. uncertainties in Richards conversion value. Richards [1] has given <sup>14</sup>N chemical shift values for formamide, acetamide and benzamide obtained by direct observation. The agreement between his results and our determinations is satisfactory.

The results shown in the Table indicate that the <sup>14</sup>N chemical shift values of the primary amides cover only a small range. Also if the values in formamide and acetamide are taken as a standard, then all the measured shifts are to higher field as changes are made in the group α to the carbonyl group. The largest shifts (up to 14 p.p.m.) are found when the carbonyl group is conjugated as in acrylamide, cinnamamide and benzamide and when the alkyl protons of acetamide are successively replaced by chlorine atoms. The <sup>14</sup>N chemical shift range in the secondary amides is larger and here downfield shifts are found in all cases relative to the corresponding primary amide. A fairly regular large downfield shift is found (~ 30 p.p.m.) when a primary amide is converted to the anilide, but the changes in the <sup>14</sup>N chemical shift on N-alkylation are surprising. N-methylation has little effect on the <sup>14</sup>N amide chemical shift, but going

- 3 -

from an N-methyl to an N-ethyl derivative produces downfield shifts of about 15 p.p.m. These downfield shifts level off at the N-butyl derivative, to give a final value about 22 p.p.m. downfield from that of the primary amide.

Previous work has indicated that  $^{14}\text{N}$  chemical shift variations are controlled largely by the paramagnetic term  $\sigma_A$ . In the amides, it is proposed that the small changes in  $\sigma_A$  are governed largely by the effect the substituents on the amide unit have upon the nitrogen lone pair of electrons. Tentative explanations of the observed shift variations can be put forward in these terms with the exception of the shifts observed on N-alkylation. A paper has been prepared in which these results are discussed in detail.

Yours sincerely,



P. Hampson.



A. Mathias.

[1] Herbison-Evans and Richards. Mol. Phys. 8, 19, 1964.

## STANFORD UNIVERSITY

STANFORD, CALIFORNIA

DEPARTMENT OF CHEMISTRY

June 30, 1966

Professor B. L. Shapiro  
 Department of Chemistry  
 Illinois Institute of Technology  
 Chicago, Illinois

Title: Halide Ion Probes for NMR Studies of  
 Antibody-Hapten Binding

Dear Barry:

Professor Thomas R. Stengle and I have recently described the use of halide ions as chemical probes for NMR studies of biomolecules in solution. (Proc. Nat. Acad. U.S., Vol. 55, 1020, 1966). Professor Stryer (Stanford Medical School) suggested that the technique might be applied to study antibody-hapten binding and offered to supply us with a sample antibody-hapten combination.

For nuclei with spin greater than  $1/2$  such as  $\text{Cl}^{35}$  the interaction of the nuclear electric quadrupole moment with fluctuating electric field gradients at the nucleus can provide a simple and dominant relaxation mechanism. When a chloride ion is symmetrically hydrated in solution, the electric field gradient at the nucleus is very small, and the corresponding  $\text{Cl}^{35}$  NMR signal is sharp (about 10 cps for 1 M aqueous NaCl.) On the other hand, if  $\text{Cl}$  is chemically bound to a large molecule with a long correlation time, the  $\text{Cl}^{35}$  linewidth can be as much as  $10^6$  cps. If a quadrupolar nucleus can be located at different kinds of sites in solution, then the resulting lineshape depends on the relative concentration of various sites, the values of  $e^2qQ$  and  $\tau_c$  at each site and the exchange rate of  $\text{Cl}^-$  between various sites. In the limit of rapid exchange between two sites, the resultant linewidth is given very simply by

$$\Delta\nu = (\Delta\nu_a)P_a + (\Delta\nu_b)P_b$$

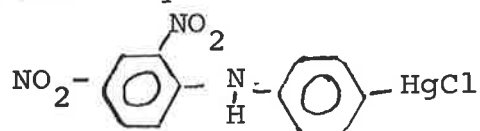
where  $\Delta\nu$  corresponds for example to the linewidth of solvated  $\text{Cl}^-$  (10 cps),  $\Delta\nu_a$  corresponds to the linewidth of chloride bound to a macromolecule ( $10^6$  cps)  $P_a$  is the probability that the chloride ion is in solution and  $P_b$  equals the probability that it is bound to the macromolecule.

From this equation it is apparent that for a 1 M aqueous solution of NaCl a concentration of bound sites of the order of  $10^{-6}$  M is sufficient to give rise to a 1 cps change in the average linewidth. The binding and exchange of chloride ions thus acts as a chemical amplifier and permits various inferences about the gross structure and conformation of macromolecules at very low concentrations.

It is clear that the choice of the chloride binding site on the macromolecule is quite restricted. The ion must form a chemical bond to the macromolecule to give rise to a large value of  $q$ . The Cl must remain bound for a time long relative to  $\tau_c$  but it must exchange rapidly relative to  $\frac{1}{\pi \Delta \nu_b}$ . Various

metal-Cl bonds including Hg-Cl satisfy these conditions. Therefore, if suitable sites on macromolecules can be labelled with Hg, it is then possible to infer the properties of these sites from the  $\text{Cl}^{35}$  NMR spectra of the macromolecule in saline solution. Since the organo-metallic chemistry of mercury is rich, it is possible to prepare a wide variety of labels.

The antibody-hapten binding experiment proceeds as follows: the  $\text{Cl}^{35}$  NMR of a 1.0 M aqueous NaCl solution is shown in Fig. 1a. The linewidth is about 10 cps. The addition of  $1 \cdot 10^{-5}$  M anti-2,4-dinitrophenol antibody gives rise to the  $\text{Cl}^{35}$  signal shown in trace b. Anti-2, 4-dinitrophenol antibody binds specifically with molecules containing the metadinitrophenol group. Addition of the antibody has little apparent effect on the  $\text{Cl}^{35}$  linewidth. However titration of this antibody with a solution of



in acetonitrile yields the traces shown in Figs. 1c and 1d. If the antibody binds the hapten such that the Hg end is exposed to binding and exchange with  $\text{Cl}^-$ , then the  $\text{Cl}^{35}$  linewidth is expected to increase. On the other hand, if the hapten is bound in such a way that the Hg is in a hydrophobic region, then the binding of the hapten should have no effect on the  $\text{Cl}^{35}$  linewidth. Addition of the Hg labelled hapten evidently causes an increase in linewidth, indicating that the label is exposed to binding and exchange with the  $\text{Cl}^-$  in solution. It appears possible in principle to place the label at various interesting places in a hapten molecule, and thus obtain a crude map of the antibody binding site.



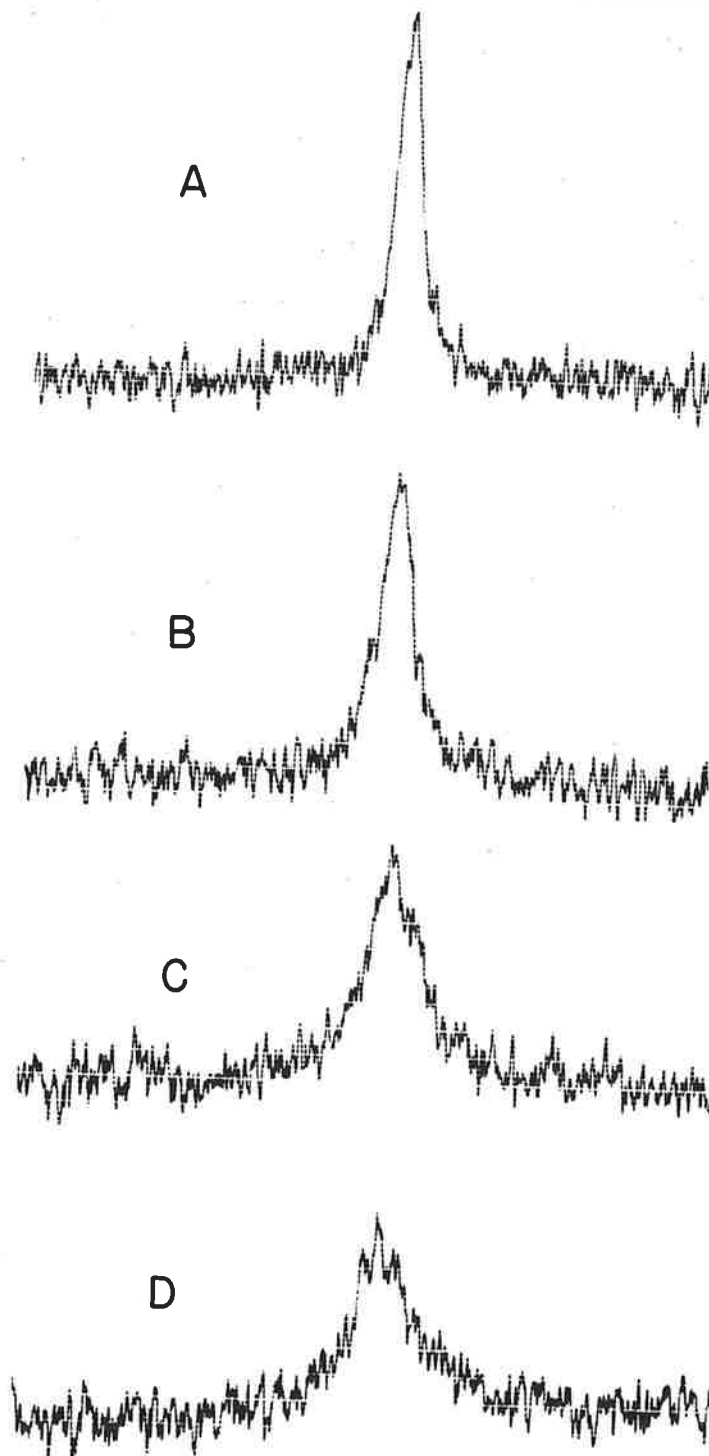
We have not yet been able to obtain a clean cut titration curve since we don't have an antibody fraction of convincing purity. If Professor Stryer's rabbits will cooperate we will soon be able to obtain some more quantitative results.

With best regards,



John D. Baldeschwieler

JDB:1a





THE UNIVERSITY OF CONNECTICUT  
THE COLLEGE OF LIBERAL ARTS AND SCIENCES

July 14, 1966

Dr. B. L. Shapiro  
Department of Chemistry  
Illinois Institute of Technology  
Chicago, Illinois 60616

Dear Dr. Shapiro:

Isomerization of Acetone Anils

In studying the isomerization rates of imines we chose the symmetrical acetone anil system, where the consequences of unequal



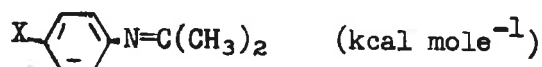
population of different sites could be avoided. Rate constants were measured from line broadening, line separation, and maximum/minimum ratios using Gutowsky's formulation. Data reduction is considerably complicated by a temperature dependent chemical shift, which is easily demonstrable by measuring line separations at the limit of slow exchange. In some of the substituted anils the chemical shift decreases by as much as 3 cps. from 0° to 60°, with the mean shift being 20-25 cps. Such behaviour is at least partly responsible for the relatively large ( $\pm 3$  kcal. mole<sup>-1</sup>) uncertainty in the measured activation energies. Our results are more or less in accord with those of Curtin<sup>1</sup> and the very precise ones of Wettermark<sup>2</sup>, although we are not able to specify a  $p$  for this reaction as the other workers did. The activation energy seems to be decidedly solvent dependent although again the scatter in the data reduces this to a qualitative statement.

Dr. B. L. Shapiro

July 14, 1966

Page 2

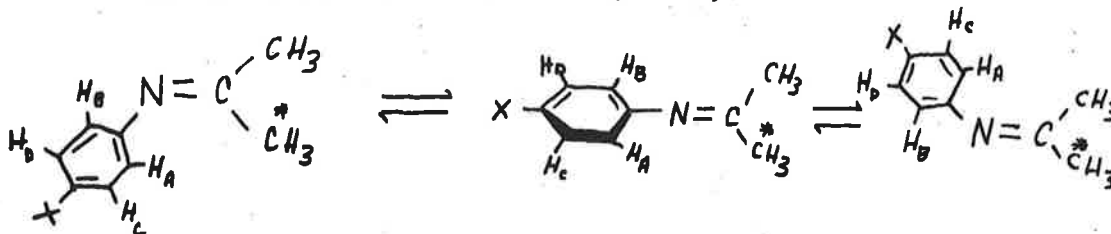
## Measured Activation Energies for



## Solvent

	nitrobenzene	o-dichlorobenzene	quinoline
X=H	8		16.5
Cl	21	21	
Br	20	16	29
CH <sub>3</sub>	16	19	23

Perhaps the most interesting observation of all is that X=Cl the aromatic proton pattern is not  $A_2X_2$ , even up to the point of coalescence of the methyl signals. Since the samples studied had present unreacted amine with the imine/amine ratio about 1, no detailed study of the aromatic portion was possible. However the nonequivalence of the ortho protons requires slow rotation of the aromatic ring about the C-N bond axis. Furthermore, it would require a very special synchronous rotation of the aromatic ring about this axis if the isomerization proceeded via a "wagging" motion of the aromatic, i.e.,



Such a "wagging" motion seems to be the one implied by Curtin when he writes the transition state as  $\text{Ar}-\text{N}=\text{C}^{\ddagger}$ . Perhaps a reasonable alternative, this process is one where the  $\text{Ar}-\text{N}=\text{C}$  angle remains invariant and the motion involved is that of the gem-dimethyls about the  $\text{N}=\text{C}$  bond axis, i.e.,



Dr. B. L. Shapiro  
July 14, 1966  
Page 3

This may not be so implausible as it initially seems, for if the nitrogen is  $sp^2$  hybridized the N=C bond has characteristics both of a C=C bond (high rotational barrier) and a C $\equiv$ C bond (cylindrical symmetry). The transition state could then be one where there is considerable overlap between the N- $sp^2$  orbital and the C-p orbital. The N-p orbital remains in conjugation with the aromatic, but since it is now doubly occupied the delocalization would be favored by electron withdrawing groups and a positive  $\rho$  value would be observed.

This entire hypothesis is quite speculative, but measurement of rotational rates about the aryl-nitrogen bond should help clarify the situation.

Sincerely,

*Eugene I. Snyder*

Eugene I. Snyder  
Assistant Professor of Chemistry

LIS:bld

- (1) D. Y. Curtin, E. J. Grubbs, and C. G. McCarty, J. Am. Chem. Soc., **88**, 2775 (1966).
- (2) G. Wettermark, J. Weinstein, J. Sousa and L. Dogliotti, J. Phys. Chem., 1584 (1965).

## TATA INSTITUTE OF FUNDAMENTAL RESEARCH

*National Centre of the Government of India for Nuclear Science and Mathematics*

Telegrams: ZETESIS

COLABA, BOMBAY 5

Telephone : 213141

Pr/10234

July 16, 1966

Professor B.L. Shapiro  
 Department of Chemistry  
 Illinois Institute of Technology  
 Chicago, Illinois 60616

NMR Studies of the Interaction between Polyfluoroacetones  
 and Proton-donors:

Dear Professor Shapiro,

There is a group in this institute working on the High Resolution NMR and we would like to be included on the mailing list of IIT-NMR Newsletters. As our first contribution, we submit the following work done by us recently.

We have studied the interactions between polyfluoroacetones (1,1,1 trifluoroacetone and Sym. tetrafluorodichloro acetone) and proton donors of the type RH (R being HO, CH<sub>3</sub>S, CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>S, CH<sub>3</sub>O, (CH<sub>3</sub>)<sub>2</sub>N and (CH<sub>3</sub>CH<sub>2</sub>)<sub>2</sub>N) from F<sup>19</sup> and H<sup>1</sup> magnetic resonances. In pure solute only one F<sup>19</sup> line is observed as expected but on addition of the solvent we observe an additional line at higher fields, the relative intensity of which increases with an increase in the amount of the solvent added until the original line disappears. The results have been interpreted in terms of the formation of addition products in which RH group is added to the

- 2 -

carbonyl group (  $>C = O + RH \rightarrow >C \begin{smallmatrix} \text{OH} \\ \text{R} \end{smallmatrix}$  ) because of the enhanced electropositivity of the carbonyl carbon atom due to strong electron-withdrawing capacity of the polyfluoroalkyl group. It may be pointed out that although there are two hydroxyl groups attached to the same carbon atom in the addition products formed by interaction with water, the adducts are so stable that they require very strong dehydrating agents to remove water from them. We also find evidence of hydrogen bonds between fluorine and the hydroxyl group in these compounds. The infra red data obtained on these systems also confirm the NMR results.

Yours sincerely,

*C.R. Kanekar*

( C.R. Kanekar )

*C.L. Khetrapal*

(C.L. Khetrapal)

## ORGANISCH CHEMISCH LABORATORIUM, RIJKSUNIVERSITEIT LEIDEN

Hugo de Grootstraat 25, Leiden

Telefoon 26457

Leyden, July 21. 1966 JH

Afdeling voor

Theoretische Organische Chemie

Telefoon 31106

Prof. dr L. J. Oosterhoff

nr.:

onderwerp: N.M.R. of Cyclopropyl Ions.

Dr. B.L. Shapiro,  
 Department of Chemistry,  
 Illinois Institute of Technology,  
 Technology Center,  
Chicago, Illinois, 60616.  
 U.S.A.

Dear Dr. Shapiro,

Some of the results we obtained in our studies of positive cyclopropyl ions differ from the observations reported by Pittman and Olah (J. Am. Chem. Soc., 87, 5123, (1965)).

The Tables I and II collect our data on the NMR spectra of fifteen cyclopropyl ions, Two of the ions are also described by Pittman and Olah. Our data and spectra on these two ions are different.

The spectrum of the cyclopropyl-p-tolyl-carbinol, in  $\text{HSO}_3\text{F}-\text{SbF}_5-\text{SO}_2$ , recorded at  $-79^\circ\text{C}$  (Fig. 4) is comparatively simple and can be used as a key to the interpretation of the more complicated spectra. The absorption lines can easily be attributed to the different (groups of) protons in the molecule. The signal of the exocyclic proton is found as a doublet at approximately 9.00 ppm downfield from TMS with  $J=13$  cps; the signals from the  $\alpha$ - and  $\beta$ -hydrogens on the cyclopropylring are shifted 2-3 ppm downfield which is about the same value Pittman and Olah report. The phenyl absorptions are noteworthy as they show positively that the hydrogens at the ortho positions are non-equivalent; the non-equivalency of the meta protons is as expected, less pronounced. Here, as in the comparable spectra of the other cyclopropyl aryl ions, the difference of the chemical shift of the ortho protons is about 0.5 ppm. Moreover in all these compounds the doublets of the ortho protons show additional splittings (1-2 cps) because of the different meta couplings. The spectrum of the cyclopropyl phenyl ion is shown in Fig. 1. The absorption lines due to the

Table 1  $\pi$ )

## Chemical Shifts of Cyclopropyl Aryl Carbonium Ions

Starting carbinol	T(°C)	Chemical shifts in ppm from TMS				
		Phenyl protons	H exoc.	Cyclopropyl protons		Subst.
				$\alpha$	$\beta$	
Cyclopropyl phenyl	-70	8.02; 8.17; 8.35; 8.47; 8.77; 8.90	9.23	4.09	3.42; 3.60	-
Cyclopropyl p-tolyl	-60	7.70; 7.82; 8.02; 8.16; 8.57; 8.70	8.94	3.87	sign. from 2.92 to 3.37	CH <sub>3</sub> : 2.67
Cyclopropyl p-anisyl	-70	7.33; 7.43; 8.12; 8.27; 8.63; 8.78	8.41	3.27	sign. from 2.12 to 2.80	OCH <sub>3</sub> : 4.25
Cyclopropyl p-ethylphenyl	-70	7.75; 7.87; 8.10; 8.12; 8.64; 8.77	9.00	3.89	2.97	CH: 2.97 CH <sub>2</sub> : 1.30 CH <sub>3</sub>
Cyclopropyl p-iso- propylphenyl	-70	7.85; 7.95; 8.14; 8.27; 8.69; 8.83	8.97	3.84	3.07 to 3.28	CH: obsc. CH <sub>3</sub> : 1.37 CH <sub>3</sub>
Cyclopropyl 3,4-di- methylphenyl	-70	7.67; 7.82; 7.93; 8.07; 8.50; 8.62	8.89	3.77	2.87 to 3.34	CH <sub>3</sub> : 2.58 CH <sub>3</sub> : 2.42 (doublet)
Cyclopropyl p-fluorophenyl <sup>xx)</sup>	-75	multiplets at 8.88; 8.37 and 7.66	9.08	3.96	sign. from 3.29 to 3.52	-
Cyclopropyl p-chlorophenyl <sup>xx)</sup>	-75	7.87; 8.00; 8.13; 8.30; 8.67; 8.80	9.18	4.07	sign. from 3.42 to 3.65	-
Cyclopropyl p-bromophenyl <sup>xx)</sup>	-80	8.10; 8.10; 8.19; 8.54; 8.69	9.20	4.10	sign. from 3.50 to 3.67	-

<sup>xx)</sup> In HSO<sub>3</sub>F-SO<sub>2</sub>



Table II <sup>\*</sup>)

## Chemical Shifts of Cyclopropyl Aryl Methyl Carbonium Ions

Starting carbinol	T(°C)	Chemical shifts in ppm from TMS				
		Phenyl protons	CH <sub>3</sub> exoc.	Cyclopropyl protons		Other.
				$\alpha$	$\beta$	
Cyclopropyl p-tolyl methyl	-80	7.72; 7.84 8.58(br.doublet)	2.88	4.03	3.05	CH <sub>3</sub> :2.67
Cyclopropyl p-anisyl methyl	-85	7.32; 7.47 8.59; 8.76; 8.90	2.69	3.62	2.51 2.60	COCH <sub>3</sub> :4.22
Cyclopropyl p- ethylphenyl methyl	-85	7.81; 7.91; 8.68(br.sing.)	2.91	4.03	3.06	CH <sub>3</sub> :obsc. CH <sub>2</sub> :1.35
Cyclopropyl p- <u>iso</u> - propylphenyl methyl	-80	7.80; 7.94; 8.66(br.sing.)	2.88	4.06	3.07	CH:obsc. CH <sub>3</sub> :1.38
Cyclopropyl p- <u>tert</u> . butylphenyl methyl	-80	7.94; 8.10; 8.62(br.sing.)	2.89	4.03	3.15	CH <sub>3</sub> :1.45
Cyclopropyl p-chlorophenyl methyl	-70	7.77; 7.92; 8.45; 8.58	2.92	4.06	3.37	-

<sup>\*</sup>) Spectra were recorded at 60 Mc.

The (CH<sub>3</sub>)<sub>4</sub>N<sup>+</sup> ion was used as an internal reference. The difference in chemical shift between the reference and TMS (external) was estimated as -3.20 ppm.

For multiplets centered positions are given.

The compounds were dissolved in mixtures of HSO<sub>3</sub>F and SO<sub>2</sub> containing less than 20% SbF<sub>5</sub> (b.w.).

ORGANISCH CHEMISCH LABORATORIUM, RIJKSUNIVERSITEIT LEIDEN  
Afdeling voor Theoretische Organische Chemie  
Hugo de Grootstraat 25, Leiden, Telefoon 31106

brief nr  
bladzijde  
onderwerp: N.M.R. of Cyclopropyl Ions.

exocyclic proton and to the ortho phenyl hydrogens can be distinguished. Data on the cyclopropyl aryl ions are collected in Table 1.

The spectra recorded at  $-60^{\circ}\text{C}$  are identical with those recorded at lower temperatures, however, as it is our experience that the ions decompose extremely rapidly at this temperature, we think that the different results of Pittman and Olah find their origin in the fact that all their spectra were recorded at  $-60^{\circ}\text{C}$ . At  $-75^{\circ}\text{C}$  decomposition, though less rapid, is still observed. Therefore no temperature dependence of these spectra can be shown, in contrast of those of the cyclopropyl aryl methyl ions.

Fig. 2 shows the spectrum of the cyclopropyl-p-anisyl methyl carbonium ion recorded at  $-85^{\circ}\text{C}$ . The low field signals due to the ortho protons especially are broadened. The phenyl signals narrow again when the temperature is raised. The spectra of the other cyclopropyl aryl methyl ions investigated show the same picture. The difference between our spectrum of the cyclopropyl-p-tolyl methyl ion and that recorded by Pittman and Olah is probably due again to the fact that their spectrum is recorded at a considerably higher temperature. Here the rigidity of the molecule plays the most important role, rather than the decomposition.



(P. Krakenburg.)

Yours Sincerely,



(Th. J. Sekuur.)

FIG. 1

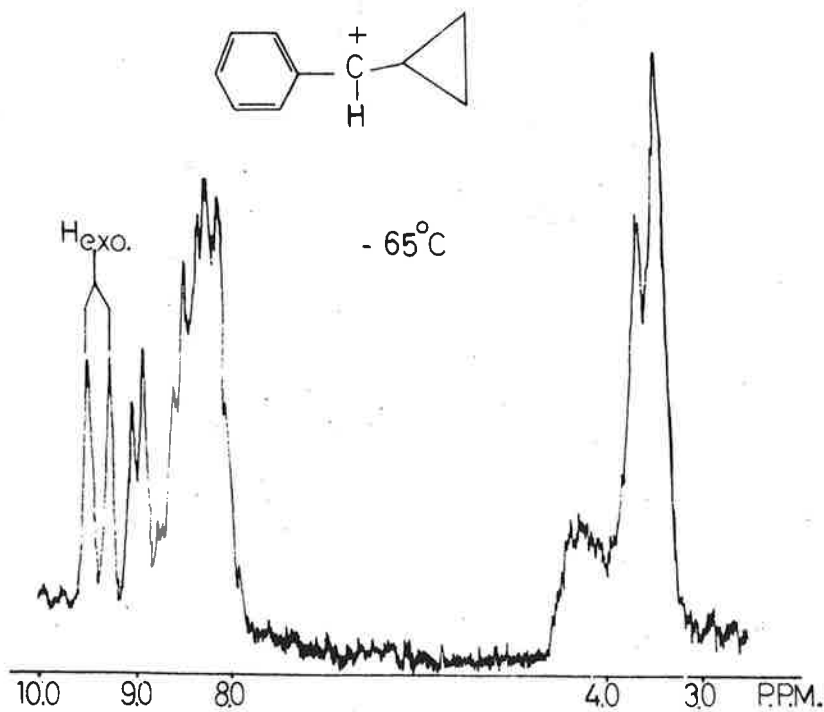


FIG. 2

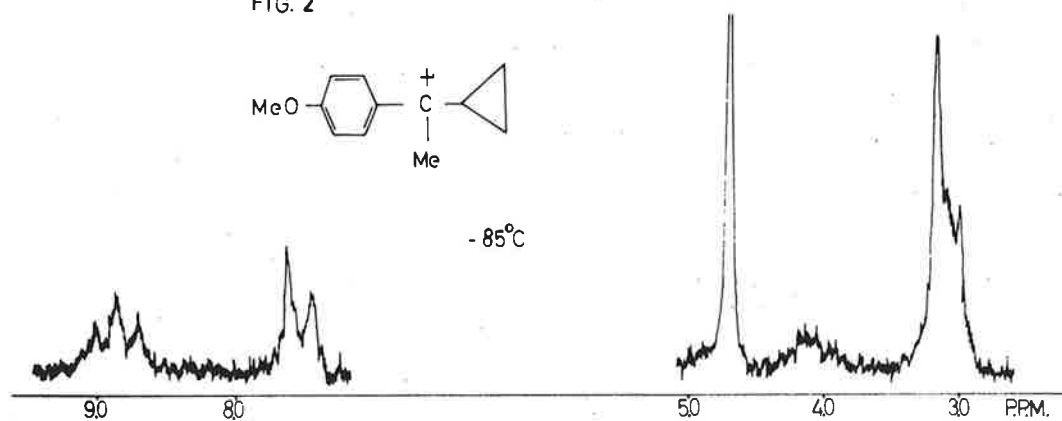
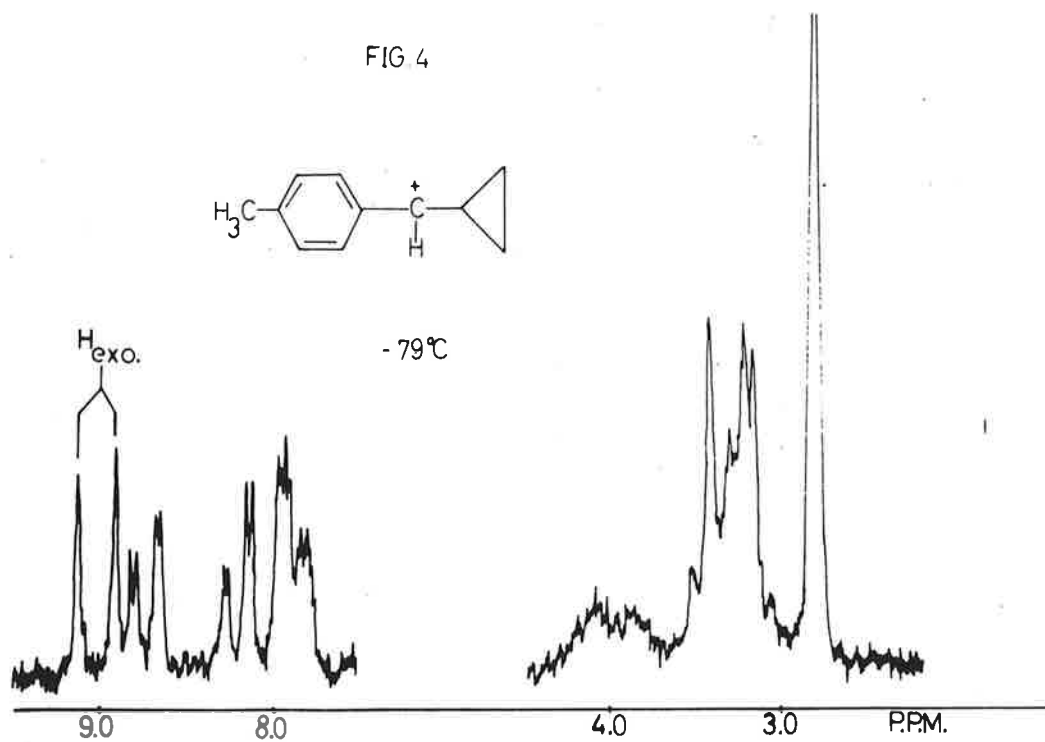


FIG. 4



# THE OHIO STATE UNIVERSITY

DEPARTMENT OF CHEMISTRY  
88 WEST 18TH AVENUE  
COLUMBUS, OHIO 43210

July 22, 1966

Dr. B. L. Shapiro  
Chemistry Department  
Illinois Institute of Technology  
Chicago, Illinois, 60616

Dear Barry:

We have done some work on the n.m.r. spectrum of pyridine and find with Castallano that the results differ somewhat from those in the literature pyridine 5% in ether: Reilly-Swalen program,

W(1) -0.76 Hz  
W(2) 81.78  
W(3) 57.81

J:	1,2	1,3	1,4	1,5	2,3	2,4
	4.82	1.77	0.96	-0.14	7.63	1.24

As is well known the components of the  $\alpha$ -hydrogen multiplet are considerably wider than the other lines in the spectrum. However, we have found several cases where the  $\alpha$ -hydrogen lines are quite narrow in the presence of hydrogen bonding solvents or of small quantities of organometallic compounds. For instance a 1M solution of pyridine in ether containing 0.05 M of bis-(2-methylbutyl)-magnesium yields a single n.m.r. spectrum, due to rapid metal-nitrogen exchange. The  $\alpha$ -lines in this spectrum are about 0.15 Hz wide. Apparently the line-narrowing we observe comes from changes in the  $T_1$  of  $N^{14}$  due in form to different electric field gradients around this nucleus. We are checking this idea with spin-echo measurements of  $T_1$ .

The chemical line-narrowing effect described above is brought about even by ratios of RM/heterocycle of 1 mole percent. Hence the experiment amounts to chemically decoupling  $N^{14}$  from the  $\alpha$ -hydrogens.

Spectral parameters for 1M pyridine + 0.05 M bis-(2-methylbutyl) magnesium in ether were determined with the Reilly-Swalen program and also by Axel Bothner-By

W(1) -0.40 -0.36  
W(2) 69.99 69.89  
W(3) 45.52 45.51  
R-S

J:	1,2	1,3	1,4	1,5	2,3	2,4	
	5.17	1.80	0.94	0.13	7.47	1.38	R-S
	5.29	1.77	0.88	0.19	7.40	1.27	B

Evidently the two programs are sensitive to different kinds of errors which is reasonable since they employ different arithmetical procedures. The inter-program deviation becomes important when the n.m.r. parameters are small.

Sincerely yours,

*Gideon Fraenkel*

Gideon Fraenkel  
Associate Professor of Chemistry

GF/dc

P.S. Note that the programs give identical results in fitting an invented spectrum

## UNIVERSITY OF ILLINOIS

THE WILLIAM ALBERT NOYES LABORATORY

July 25, 1966

Dr. B. L. Shapiro  
 Department of Chemistry  
 Illinois Institute of Technology  
 Technology Center  
 Chicago, Illinois 60616

Re: Ring Inversion in Trihetero-cyclohexanes

Dear Dr. Shapiro:

I hope this note will put my name on the mailing list of your NMR newsletters.

This academic year I have been working in Professor Gutowsky's group, mainly on the ring inversion of symmetrical trihetero-cyclohexanes; in particular, trioxane(I), hexamethyl-trithiane(II), and N-trimethyl-hexahydrotriazine(III).

Only III can be easily studied with steady-state methods. Preliminary results of a high resolution study at different temperatures are reported in this letter.

As expected<sup>1,2,3</sup>, the axial-equatorial chemical shift difference between the methylene protons is quite large:  $0.896 \pm 0.005$  ppm in a 30% v/v solution in  $\text{CH}_2\text{Cl}_2$  at  $240^\circ\text{K}$ . The coupling constant between the axial and equatorial methylene proton, at the same temperature, is  $J_{AB} = 10.4 \pm 0.2$  cps. The rate of ring inversion was determined by a complete lineshape analysis method for temperatures from  $240^\circ$  to  $315^\circ\text{K}$ . The activation parameters, as determined from a least squares treatment of the data, are given in the following table:

$T_c$ $^\circ\text{K}$	$E_a$ (kcal)	$A$ ( $\text{sec}^{-1}$ )	$\Delta H_{cc}^+(T_c)$ (kcal)	$\Delta G_{cc}^+(T_c)$ (kcal)	$\Delta S_{cc}^+$ (eu)
267.9	$15.6 \pm 0.2$	$(6 \pm 2) \times 10^{14}$	$15.1 \pm 0.2$	$13.2 \pm 0.2$	7.3

University of Illinois  
Page No. 2

July 25, 1966

Dr. B. L. Shapiro--

While this work was being completed, a note has appeared<sup>4</sup> in which a value for the free energy of activation, as determined from the coalescence temperature, is reported. This datum is in fairly good agreement with the value reported in this letter. In fact, a still better agreement is obtained if the correct expression

$$\Delta G_c^+ = 4.57 T_c \left[ 10.274 + \log \frac{T_c}{(\delta^2 + 6J^2)^{1/2}} \right]$$

is used.

Sincerely yours,

*Piero A. Temussi*  
Piero A. Temussi

Permanent address:

Istituto di Chimica Generale  
via Mezzocannone 4, Napoli, Italy

---

<sup>1</sup>H. P. Homlow, S. Okuda, N. Nakagawa,  
Tetrahedron Letters N. 37, 2553 (1964).

<sup>2</sup>F. Bohlmann, D. Schumann, C. Arndt  
ibid, N. 31, 2705

<sup>3</sup>J. B. Lambert, R. G. Keske  
J. Am. Chem. Soc. 88, 620 (1966)

<sup>4</sup>F. G. Riddell and J. M. Lehn  
Chem. Comm. No. 72, 375 (1966).

Dr. B. Hampel  
i.Fa.  
**E. MERCK · DARMSTADT**  
AKTIENGESELLSCHAFT  
FORSCHUNGS-ABTEILUNGEN  
Hauptlaboratorium

61 Darmstadt, 22. Juli 1966

Herrn

Professor Dr. B. L. Shapiro  
Department of Chemistry,  
Illinois Institute of Technology,  
Technology Center  
Chicago, Illinois 60616

Sehr geehrter Herr Professor Shapiro!

Für die Aufnahme in die mailing list der IIT-NMR-Newsletters danke ich Ihnen ebenso herzlich wie für die ersten beiden Hefte!

Im Zusammenhang mit der Aufnahme der NMR-Spektren von Steroiden in verschiedenen Lösungsmitteln haben wir uns auch mit der

Kalibrierung von NMR-Spektrometern unter  
Verwendung von Lösungsmittelmischungen

beschäftigt. Wie viele organisch-chemische Laboratorien haben wir nicht die Möglichkeit, unser A 60-Spektrometer durch einen Frequenzstandard zu kalibrieren. Wir waren daher sehr daran interessiert, die von Jungnickel<sup>1)</sup> angegebene und genau vermessene Lösungsmittelmischung auf ihre Zuverlässigkeit zu prüfen.

Ich habe eine größere Menge dieses Gemisches der Zusammensetzung: 3 % Tetramethylsilan, 2 % Cyclohexan, 3 % Aceton, 9 % 1,1,1-Trichloräthan, 2 % p-Dioxan, 8 % Dichlormethan und 18 % Chloroform (Volumenprozent) hergestellt und an drei Kollegen verschickt, die die Möglichkeit zur Kalibrierung ihrer Geräte durch Seitenhandmethode bzw. Frequenzzähler hatten. Die anliegende Tabelle der Ergebnisse zeigt, daß trotz der Bedenken, die sich auf die Anwesenheit von Chloroform und Aceton in dieser Lösung beziehen, ein brauchbarer Standard vorgeschlagen worden ist. Die Mittelwerte der vier Meßreihen sollten bis auf  $\pm 0,005$  ppm sicher sein.

1) Analyt.Chem. 35, 1985 (1963)



Empfänger

Unsere Zeichen

Tag

Blatt 2

Den Kollegen, die auf meine Wünsche eingegangen sind, möchte ich auch an dieser Stelle noch einmal herzlich danken.

Mit den besten Grüßen und

vorzüglicher Hochachtung

Ihr

B. Jampel

Komponente	Bearbeiter:	J	W	M	B	Mittel
TMS		0	0	0	0	0
Cyclohexan		1,433	1,433	1,433	1,433	1,433
Aceton		2,112	2,113	2,108	2,111	2,111
1,1,1-Trichloräthan		2,731	2,730	2,729	2,730	2,730
p-Dioxan		3,621	3,621	3,620	3,623	3,621
Dichlormethan		5,301	5,297	5,296	5,298	5,298
Chloroform		7,330	7,325	7,322	7,327	7,326

Chemische Verschiebung der Lösungsmittelkomponenten in der Referenzlösung nach Jungnickel<sup>1)</sup> in ppm (von Tetramethylsilan).

J : J.L. Jungnickel, A 60-Spektrometer; angegebene Genauigkeit  $\pm 0,03$  Hz; Meßtemperatur  $37^\circ \text{C}$ .

W : G. Walz, Farbenfabriken Bayer. A 60-Spektrometer;  $\pm 0,1$  Hz; Meßtemperatur nicht angegeben.

M : A. Melera, Varian AG, Zürich. HA-100-Spektrometer; Meßgenauigkeit nicht angegeben;  $27^\circ \text{C}$ .

B : W. Brügel, BASF. Meßbedingungen: A 60-Spektrometer;  $\pm 0,05$  Hz;  $43^\circ \text{C}$ .

Mittel : Aus den Ergebnissen der vier Beobachter gebildeter Mittelwert.

Alle Werte sind - soweit möglich - auf  $37^\circ$  Meßtemperatur umgerechnet.

Department of Chemistry,  
The University,  
GLASGOW, W.2.  
Scotland.

22nd July, 1966.

Professor B.L. Shapiro,  
Illinois Institute of Technology,  
Chicago,  
Illinois, 60616,  
U.S.A.

Dear Barry,

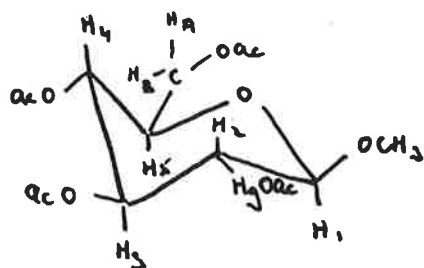
The following information might interest some of the sugar chemists of the I.I.T.N.M.R. brotherhood. The problem originated with, and the compounds were supplied by, Dr. Peter Schwarz of the University of Edinburgh, and most of the hard work in interpreting the spectra was done by Mr. Kenneth W. Moore of this department.

Observations on conformations and configurations in  
Hg(II) derivatives of some sugars

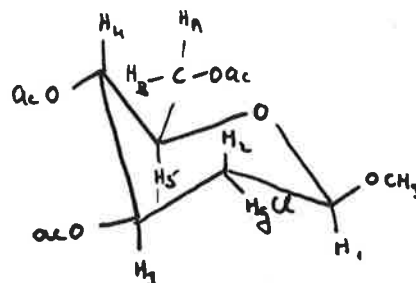
Proton magnetic resonance spectra of saturated  $\text{CDCl}_3$  solutions of the following four compounds have been analysed.

- A. The mercuriacetate of 1-methyl-3,4,6-triaceto- $\beta$ -glucose.
- B. The mercurichloride of 1-methyl-3,4,6-triaceto- $\beta$ -glucose.
- C. The mercurichloride of 1-methyl-3,4,6-triaceto- $\alpha$ -mannose.
- D. The mercurichloride of 1-methyl-3,4,6-triaceto- $\alpha$ -talose.

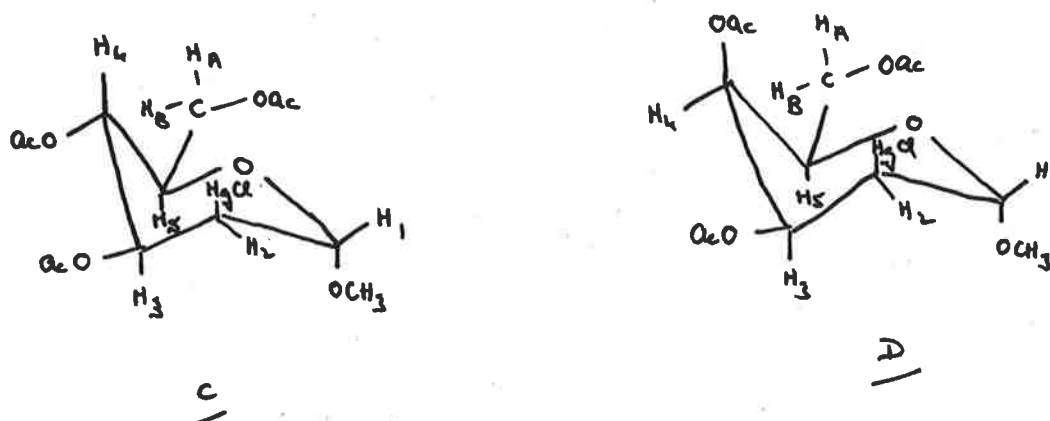
The proton chemical shifts and coupling constants extracted from these spectra are listed in Table I. In all cases, the  $\text{C}_1$  conformations A, B, C and D, shown below, predominate.



A



B



The peaks in the spectra of compounds A, B and C are quite sharp and these compounds appear to be conformationally pure, although breathing motions must occur since the spectra are not quite as sharp as should be expected from the homogeneity of the magnetic field that was used. In this context, ring system C appears to be the most rigid of the four systems studied.

In each case, that part of the spectrum which arises from H(3) occurs at lowest applied field, and this provides a very simple and rapid method of distinguishing between the glucose, mannose and talose systems, since in these compounds H(4), H(3) and H(2) are in aaa, aae, and eae relationship respectively, in the C1 conformations. In all of the compounds examined, the mercury atom substitutes at position 2 of the pyranoside system, with retention of configuration at C(2). The H(2) resonance is displaced upfield by the Hg(II) substitution. That part of the spectrum due to H(2), when taken in conjunction with that part due to H(3), immediately distinguishes between the  $\alpha$ - and  $\beta$ - anomeric forms. The anomeric form is of course specified once the absorptions due to H(1) have been identified, but these would not be immediately obvious from a simple inspection of the spectra.

$^{199}\text{Hg}(I=\frac{1}{2})$  and  $^{201}\text{Hg}(I=\frac{3}{2})$ , occur in natural abundance of 16.86% and 13.24% respectively. The expected couplings of H(1), H(2) and H(3) with these ~~nuclei~~ mercury isotopes have not been observed, almost certainly as a result of solubility difficulties in the case of  $^{199}\text{Hg}$  and a combination of solubility difficulties and quadrupolar relaxation effects in the case of  $^{201}\text{Hg}$ .

With best wishes,

*Andrew*

Andrew L. Porte

TABLE 1. PROTON CHEMICAL SHIFTS<sup>a</sup> AND COUPLING CONSTANTS<sup>b</sup>  
FOR SOLUTIONS OF COMPOUNDS A,B,C and D IN  $\text{CDCl}_3$

Compound	A	B	C	D
H <sub>1</sub>	5.33	5.23	4.89	4.95
H <sub>2</sub>	7.40	7.38	6.69	7.17
H <sub>3</sub>	4.78	4.72	4.15	4.28
H <sub>4</sub>	5.05	4.99	5.01	4.71
H <sub>5</sub>	6.29	6.13	5.96	5.75
H <sub>A</sub>	5.68	5.60	5.76	5.93
H <sub>B</sub>	5.88	5.78	5.76	5.93
OCH <sub>3</sub>	6.49	6.39	6.61	6.68
-COOCH <sub>3</sub>	7.92 } 7.96 }	7.82 }	7.89 } 7.94 }	7.75 } 7.98 }
J <sub>12</sub>	10.0 <sub>1</sub>	9.7 <sub>8</sub>	1.5 <sub>0</sub>	~ 0 <sup>c</sup>
J <sub>23</sub>	10.9 <sub>3</sub>	11.2 <sub>6</sub>	5.3 <sub>5</sub>	5.1 <sub>6</sub>
J <sub>34</sub>	8.9 <sub>0</sub>	9.4 <sub>9</sub>	9.0 <sub>5</sub>	3.0 <sub>9</sub>
J <sub>45</sub>	9.0 <sub>0</sub>	7.3 <sub>8</sub>	9.3 <sub>5</sub>	~ 0 <sup>c</sup>
J <sub>5A</sub>	5.8 <sub>0</sub>	4.6 <sub>1</sub>	~ 8 <sup>d</sup>	7.0
J <sub>5B</sub>	3.2 <sub>3</sub>	2.7 <sub>8</sub>	~ 8 <sup>d</sup>	7.0
J <sub>AB</sub>	11.9 <sup>d</sup>	12.5 <sup>d</sup>	- e	- e

a. Chemical shifts in  $\tau$  units are given to the nearest 0.01 $\tau$  unit.

b. Coupling constants are in units of c./s., and except for those marked c,d and e are accurate to within  $\pm 0.2$  c./s.

c. Less than 10.3/c./s.

d. These coupling constants can be altered by relatively large amounts without sensibly affecting the calculated spectrum.

e. Not available from the spectrum.

# GENERAL ELECTRIC COMPANY

WATERFORD, NEW YORK 12188 . . . . . AREA 518—TELEPHONE 237-3330

SILICONE  
PRODUCTS  
DEPARTMENT

July 25, 1966

## Simultaneous Measurement of NMR Spectrum and Integral

Professor B.L. Shapiro  
Dept. of Chemistry  
Illinois Institute of Technology  
Chicago, Illinois 60616

Dear Professor Shapiro:

Recently we had an opportunity to try some digital integrators designed for measuring area of chromatographic peaks.

Two pieces of equipment made by Infotronics Corp., 7800 Westglen Drive, Houston, Texas, 77042 were connected to our A-60. Both integrators are based on the technique of voltage to frequency conversion. The CRS-11H is fully automatic. It detects the peak and prints out a number proportional to peak area. The electronics are designed so that the integrator prints out after the slope logic changes in the following sequence: zero, positive, zero, negative, zero. Thus on sharp peaks where ringing is observed a print out is observed for each "peak" due to ringing. In order to obtain the correct peak area the integrals of the ringing "peaks" must be added to that obtained for the main peak.

The CRS-30 prints out integral data after specified time intervals. Thus all "peaks" due to ringing are automatically added to the main peak. Although the CRS-30 can be used to obtain integral data it is not too practical to use. The time interval for integrations must be longer than the time required to scan a given peak. If there are two closely spaced peaks the sweep must be stopped between peaks until the integral is obtained.

The following data was obtained:

<u>Mixture</u>		<u>Relative Area</u>		
		CRS-11H	CRS-30	A-60 Theory
I	$\text{Cl}_3\text{CMe}$	1.00		1.00
	Acetone	0.89		.87
	$\text{C}_6\text{H}_{12}$	0.73		.73
II	$\text{CH}_3\text{CH}$	2.98		3.0
	$\text{CH}_3/\text{H}$	2.97		3.0
III	$\text{CH}_2=\text{C}(\text{Cl})-\text{CH}_2$		0.493	0.536
	$\text{C}-\text{H}=\text{CH}_2$		0.473	0.464

From a price standpoint neither of these integrators is practical unless a large number of integrals must be measured. The CRS-30 sells for about \$2700.00 and the CRS-11H sells for about \$6,000.00 including printers. If the price can be reduced there would be an advantage in being able to simultaneously measure spectra and integrals.

Sincerely yours,

*Carl A. Hirt*

Carl A. Hirt

ANORGANISCH-CHEMISCHES LABORATORIUM  
DER  
TECHNISCHEN HOCHSCHULE MÜNCHEN

8 MÜNCHEN 2, den 26.7.1966  
Arcisstraße 21  
Ruf-Nr. 5592/330  
331

Herrn

Professor B.L. S h a p i r o  
Chemistry Department  
Illinois Institute of Technology  
C h i c a g o , Ill., 60616  
USA

"Variable frequency equipment for HR-100"

Sehr geehrter Herr Professor S h a p i r o !

Gemeinsam mit der Fa. S c h o m a n d l KG., München 8, Belfortstrasse 6-8, wurde unser HR-100 für variable Frequenzen von 2,5 - 35 MHz bei 23,480 KG umgerüstet. Die Frequenzen der den Sende- und Mischquarz im V4311 ersetzenden "Schomandl-Frequenzdekaden" ND30MQ4 und ND30M können in 1 Hertz-Schritten bei einer Konstanz von  $5 \cdot 10^{-8}$  pro Monat über den angegebenen Bereich variiert werden. Die Schwingkreise im Sender und Empfänger werden mit 4 Sätzen von je 4 geeichten Steckspulen über den angegebenen Bereich abgestimmt-. Als Probenköpfe genügen für den angegebenen Bereich ein  $^{14}\text{N}$ - und ein  $^{13}\text{C}$ -Kopf der Firma Varian. Zwischen 7 und 30 MHz wurde mit 5 verschiedenen Frequenzen Protonenresonanz betrieben, ferner wurde bereits  $^{14}\text{N}$ ,  $^{59}\text{Co}$ , und  $^{11}\text{B}$ -Resonanz gemessen. Die Empfindlichkeit wurde mit einer Varian-V-4311 für  $^{14}\text{N}$  verglichen und war bei dieser Frequenz (7,22 MHz) mehr als doppelt so groß.

Mit freundlichen Grüßen

*Hans P. Fritz*      *Karl Schwarzhans*  
(H.P.Fritz)      (K.E.Schwarzhans)



## THE UNIVERSITY OF MANITOBA

DEPARTMENT OF CHEMISTRY

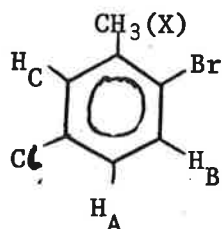
WINNIPEG, CANADA

July 25th, 1966

Professor B.L. Shapiro  
 Department of Chemistry  
 Illinois Institute of Technology  
 Chicago, Illinois 60616

Dear Barry:

Perhaps you will accept the following as a contribution to the IIT NMR Newsletter. We have finally gotten an internal lock on our DP-60 and have tested it by doing tickling and decoupling experiments on 2-bromo-5-chlorotoluene (10 mole % in CS<sub>2</sub>). The shifts (relative to internal TMS) and coupling constants go as follows:



$$\begin{array}{l} \nu_A = -6.919 \pm 0.005 \text{ ppm} \\ \nu_B = -7.317 \pm 0.005 \text{ ppm} \\ \nu_C = -7.097 \pm 0.005 \text{ ppm} \end{array} \left\{ \begin{array}{l} \text{ABC analysis} \\ \text{on decoupled} \\ \text{spectrum} \end{array} \right.$$

$$J_{AB} = +8.48 \pm 0.03 \text{ c/s (taken positive)}$$

$$J_{AC} = +2.55 \pm 0.03 \text{ c/s}$$

$$J_{BC} = +0.33 \pm 0.03 \text{ c/s}$$

$$J_{CX} = -0.63 \pm 0.03 \text{ c/s}$$

$$J_{BX} = +0.40 \pm 0.03 \text{ c/s}$$

$$J_{AX} = -0.58 \pm 0.03 \text{ c/s}$$

Note that all signs are relative to  $J_{AB}$ . The methyl-ring proton splittings have the signs expected from theory - I don't think they had actually been determined before.

Yours sincerely,

Ted Schaefer

TS/ds



SEVENTY-FIFTH ANNIVERSARY  
1891-1966

## CALIFORNIA INSTITUTE OF TECHNOLOGY

PASADENA, CALIFORNIA 91109

GATES AND CRELLIN LABORATORIES OF CHEMISTRY

July 27, 1966

Professor B. L. Shapiro  
Department of Chemistry  
Illinois Institute of Technology  
Chicago, Illinois 60616

Dear Barry:

## A Two-stage MEF Program

## Preliminary Results from the DFS-60

We have recently modified the Ferguson magnetic equivalence factoring program (1), so that it can be used in two stages instead of three. The first stage is unchanged while the input to the second stage includes the assignment of the transitions in the observed spectrum as well as the usual parameters which are included in stage three. After a check is made on the correctness of the energy-level solution, the program goes directly to stage three without operator intervention. If the solution appears to be incorrect, the iterative portion is suppressed and the program continues on to the next problem. No intermediate storage on magnetic tape or punched output is required. The system requires three scratch tapes in addition to the standard FORTRAN I/O package. A listing of the program is available upon request.

Some preliminary results from the Varian-produced DFS-60 (Digital Frequency Sweep) spectrometer may be of interest. The sample arrangement in this spectrometer is something like that described by Shoolery (2). With its internal-lock system the spectrometer is stable enough to be used in conjunction with a time-averaging computer to obtain slow passage, high-resolution  $^{13}\text{C}$  and  $^{15}\text{N}$  spectra. In light of a recent report by Bernstein (3) we would like to present a preliminary natural abundance  $^{13}\text{C}$  spectrum of benzene. The spectrum is basically a doublet,  $J_{\text{C}^{13}\text{H}} = 159 \text{ Hz}$ , but shows a great deal of fine structure presumably due to long-range C-H couplings.

The spectrometer is now being modified to sweep both up and down frequency and, hopefully, this will allow us to estimate saturation

B. L. Shapiro

2

July 27, 1966

effects and complete an analysis of the spectrum.

Because of this fine structure the center of each of the two multiplets is uncertain and the use of benzene as a standard for  $^{13}\text{C}$  chemical shifts is not advised. Carbon disulfide gives a single peak and is more suitable.

- (1) R. C. Ferguson and D. W. Marquardt, J. Chem. Phys., 41, 2087 (1964).
- (2) J. N. Shoolery, IITNMRN, 42, 8 (1962).
- (3) H. J. Bernstein, IITNMRN, 92, 12 (1966).

Sincerely yours,

*Frank J. Weigert*

Frank J. Weigert

*Jack*

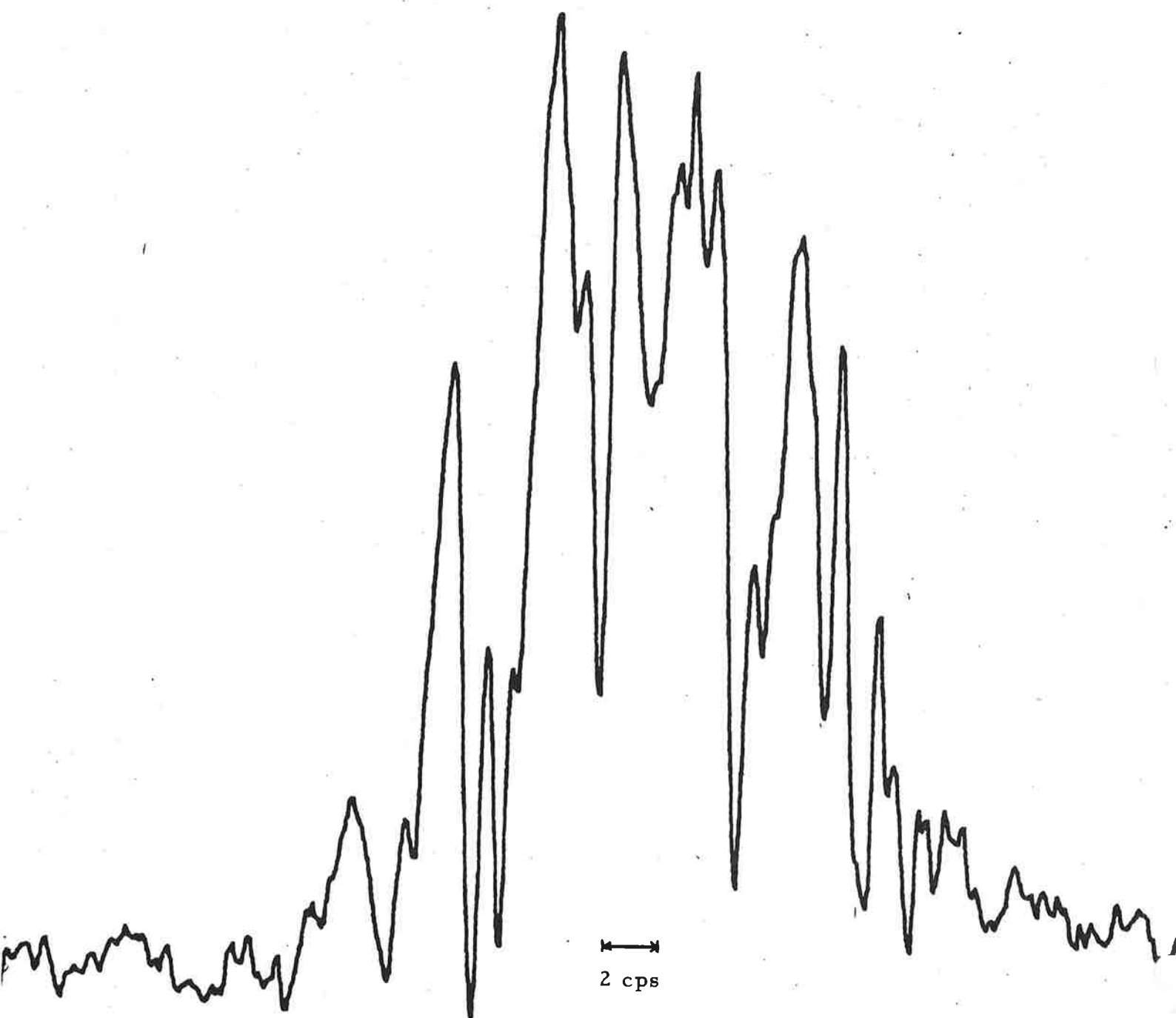
John D. Roberts

JDR:bi

Encl.

95-30

The low frequency half of the benzene spectrum:  
Sweep width 100 cps  
Sweep time 50 sec  
170 scans



**BRYN MAWR COLLEGE**  
BRYN MAWR, PENNSYLVANIA 19010, USA

DEPARTMENT OF CHEMISTRY

TEL: (215) LA 5-1000

30 July 1966

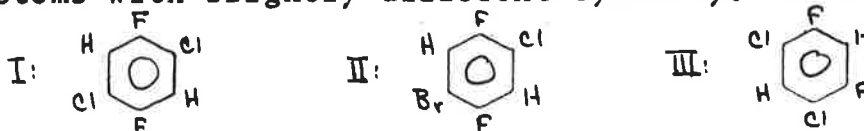
Prof. B. L. Shapiro  
Department of Chemistry  
Illinois Institute of Technology  
Chicago, Illinois 60616

Dear Barry:

Your reminder about our contribution to IITNMR Newsletter caught us in the middle of some new work; this letter will therefore be only a progress report and a sketch of our plans. Our work has become more experimental (at last!) with the installation of a new A-56/60A spectrometer here.

NMR of some Substituted Difluorobenzenes

The three compounds shown below have been synthesized (by us physical chemists!) as illustrations of four-spin systems with slightly different symmetry. We are just beginning




the analysis of their NMR spectra. The AA'XX' system (I) happens accidentally to be an A<sub>2</sub>X<sub>2</sub> system: that is, by chance the ortho and meta H-F coupling constants are identical, and both fluorine and proton spectra give a 1:2:1 triplet. Analysis of the ABXY and ABX<sub>2</sub> systems (II and III) are under way. Our ultimate plan is to do some relaxation time measurements in these molecules with the idea of seeing what relaxation mechanisms are operative, and to what extent the symmetry of the molecule affects the relaxation.

NMR of Ammonia and Phosphine

We are just beginning new NMR and NMDR studies of ammonia and phosphine. We'd like to follow the relaxation mechanism from near the melting point through the critical point and into the gas phase to look for a change in mechanism between liquid and gas, and what that all might mean. We are having some difficulty in containing gas samples at high pressure, and would appreciate any helpful hints on this sort of technique.

Sincerely yours,

  
Jay Martin Anderson  
Assistant Professor

## THE UNIVERSITY OF BRITISH COLUMBIA

VANCOUVER 8, CANADA

DEPARTMENT OF CHEMISTRY

July 28, 1966

Dr. Bernard L. Shapiro  
Department of Chemistry  
Illinois Institute of Technology  
Chicago, 60616

Short Title -  $^{29}\text{Si}$  magnetic resonance

Dear Barry,

We are doing quite a bit of work on a neglected nucleus  $^{29}\text{Si}$ , in natural abundance. We use the rapid passage methods introduced by Lauterbur for  $^{13}\text{C}$ . Our frequency is 7.95 M.Hz and field 9.41 K. gauss. Signals are very good as you can see from the enclosed figure. The samples are 15 mm O.D. tubes and the signal for hexamethyl disiloxane is taken for the pure compound. Using an 8 m.m. tube of T.M.S. as an external standard the signal to noise is still impressive. The chemical shift of tetraethoxysiloxane is  $84 \pm 1$  ppm. to high field of T.M.S. as measured in the lower of the two spectra in the figure. At the present time we can only use this demonstration as a general request to anyone who is interested to send silicon compounds which are liquids or easily soluble in greater than 1 gram quantities to us for measurement. We will be pleased to return shift measurements to them. The only reference I have on  $^{29}\text{Si}$  chemical shifts is that of Holzman, Lauterbur, Andersen and Koth, J. Chem. Phys. 25, 172-3 (1956).

All best wishes



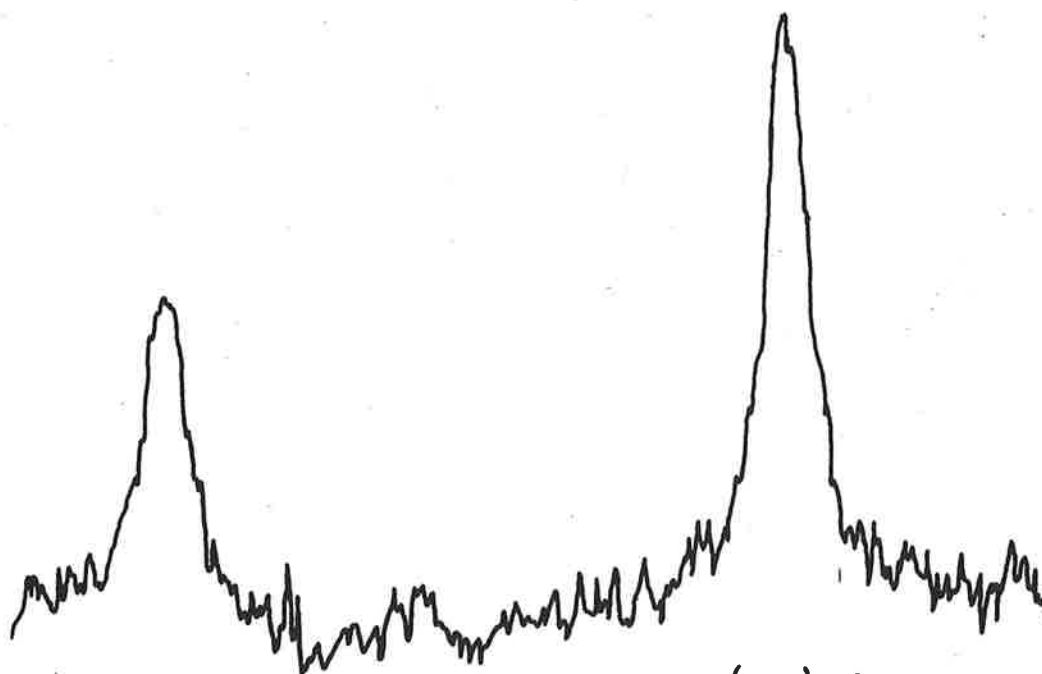
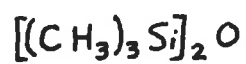
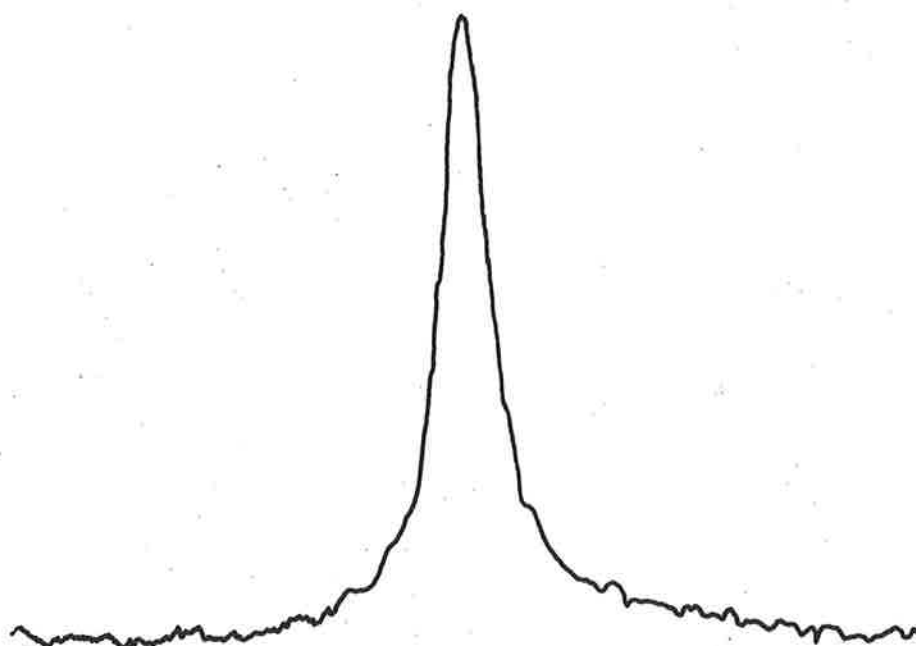
LWR/lu

L. W. Reeves  
Professor of Chemistry

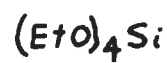
## THE UNIVERSITY OF BRITISH COLUMBIA

VANCOUVER 8, CANADA

DEPARTMENT OF CHEMISTRY



T.M.S.



## INDIAN INSTITUTE OF TECHNOLOGY KANPUR

 I. I. T. Post Office  
 KANPUR July 26 1966

Professor B.L. Shapiro  
 Department of Chemistry  
 Illinois Institute of Technology  
 Chicago  
 Illinois 60616

Dear Professor Shapiro:

Hope this letter will serve as my subscription for the  
~~N~~letter.

Perturbation Approach to the Proton Spin Coupling in the Ethane  
 Fragment

Recently, Mr. P. Chandra and myself have been able to derive a general expression for the long-range proton spin-spin coupling constant ( $J_{HH'}$ ) in a six-electron (three bond) case by V.B. perturbation theory.

We use the Dirac vector model [ S. Alexander, J. Chem. Phys., 34, 106 (1961); S. Koide and E. Duval, ibid., 41, 315 (1964) ] and treat the exchange interactions between electrons in inter-bond orbitals as a perturbation ( $\mathcal{H}'$ ) on the main part of the Hamiltonian, which consists of intra-bond exchange interactions ( $\mathcal{H}_0$ ). An expression for

$\langle \Psi | \vec{S}_H \cdot \vec{S}_{H'} | \Psi \rangle$  is thus obtained and  $J_{HH'}$  calculated.

The earlier work of Koide and Duval, who considered the



three bond case, failed to bring out the dependence of  $J_{HH'}$  on the dihedral angle ( $\Phi$ ) since they included only intra-bond and intra-atomic exchange interactions. They also used only four singlet functions and evaluated  $\langle \Psi | \vec{S}_H \cdot \vec{S}_{H'} | \Psi \rangle$ . However, the correct basis set for the singlet state consists of five functions. We use, in our treatment, all these five functions and extend the perturbation upto fourth order in  $\mathcal{H}'$ . Values of  $\langle \Psi | \vec{S}_H \cdot \vec{S}_{H'} | \Psi \rangle$  for all these orders can be expressed in terms of all the appropriate exchange integrals.

Using this perturbation approach we investigated the dependence of  $J_{HH'}$  on dihedral angle in the ethane fragment. An analytical expression for  $J_{HH'}$  as a function of  $\Phi$  can be given considering contributions upto third order in  $\mathcal{H}'$ . In the Ramsey formalism we get (with  $\Delta E = 9\text{e.v.}$ ) for the ethane fragment the following expression:

$$J_{HH'} = -0.2033 - 0.6275 \cos \Phi + 8.4869 \cos^2 \Phi \quad (\text{c.p.s.}).$$

This equation is in good agreement with the earlier V.B. results of Karplus (J. Amer. Chem. Soc., 85, 2870 (1963)). Details of our calculations are to be found in a forthcoming paper.

[P. Chandra and P.T. Narasimhan, Mol. Phys., 1966 (in print)].

Our perturbation results are valid for the general three bond case and we are at present investigating proton spin couplings in fragments of the type  $H - X - Y - H$  where  $X, Y = C, N, O$  etc.

Sincerely yours,

*P.T. Narasimhan*

P.T. Narasimhan  
Professor of Chemistry

**CZECHOSLOVAK ACADEMY OF SCIENCE  
INSTITUTE OF ORGANIC CHEMISTRY AND BIOCHEMISTRY,**

Na cvičišti 2.

**PRAHA 6**

July 29, 1966

Dr. B.L. Shapiro  
Department of Chemistry  
Illinois Institute of Technology  
Technology Center  
Chicago, Illinois 60616  
USA

Dear Dr. Shapiro:

Thank you for sending the recent issues of IITNMR-Letters. I have been unable to send the address form required before the deadline May 1 st since I only received No.90 on May 6th and since I was absent from the Institute for some time, I am sending it only now.

On this occasion I am sending another contribution and I should appreciate it if you could accept it to appear in a further series of IITNMR-Letters.

In the course of our investigations of the methods of analysis of NMR spectra, my colleagues studied the convergence properties of the currently used procedures. In the standard least squares analysis of the NMR spectrum of an N-spin system the minimization of the function  $\Phi$  leads to a system of nonlinear equations

$$\Phi(q_1, q_2, \dots, q_M) = \sum_{i=1}^n w_i (p_i^{\text{calc}} - p_i^{\text{obs}})^2$$

which is linearized to yield the system of normal equations in the form (see ref.1,2)

$$J^T W J \Delta = J^T W R$$

(J - rectangular nx M Jacobian matrix, W -weighting matrix, R- column vector of residuals,  $\Delta$  - column vector of corrections). The conventional iteration process based on repeatedly solving this equation (Castellano-Bothner-By (ref. 1), Arrata-Shimizu-Fujiwara (ref. 2) and Swallen-Reilly (ref. 3) for the corrections  $\Delta$  converges only if the corrections to the initial values of the parameters  $q_i$  are small and if the matrix  $J^T W J$  is regular. Otherwise the process will oscillate or diverge. Levenberg (ref. 4) has shown how both of these restrictions can be removed; in this formulation (the method of damped least squares see ref. 5) the above equation takes on the form,

$$(J^T W J + pE) \Delta = J^T W R$$

in which  $p > 0$  is the damping factor and E the unit matrix. The Matrix  $(J^T W J + pE)$  will be regular for appropriate  $p > 0$ . For  $p \rightarrow \infty$  this modified equation can be written in the form

/Continued.....

(gradient-method)

$$\Delta \doteq (\frac{1}{p}) J^T W R \sim \text{grad } \Phi$$

in which the condition for small values of the components of the column vector  $\Delta$  is fulfilled.

It was found, if the damping factor is choosen as  $p = \text{const.}$   $\Phi$  rapid convergence can be achieved even in the cases where the initial estimates of the NMR parameters were quite rough. For the case where the columns of the matrices are normalized to unity, appropriate values of the proportionality constant were found to be about 0,5 to 0,1. This method proved especially valuable in investigating multiple solution in NMR analyses (see ref.6).

A slightly more detailed account of this method will appear in the J.Mol.Spectry.

Yours sincerely,

Z. Samek

V. Špirko

S. Toman

(Department of Instrumental  
Analysis, Institute of  
Chemical Technology, Prague)

(Institute of Physical  
Chemistry, Czechoslovak  
Academy of Science,  
Prague)

#### REFERENCES

1. S.Castellano, and A.A.Bothner-By, J.Chem.Phys. 41, 3863 (1964)
2. Y.Arrata, H.Shimizu, and S.Fujiwara, J.Chem.Phys. 36, 1951 (1962)
3. J.D.Swallen, and C.A.Reilly, J.Chem.Phys. 37, 21 (1962).
4. K.Levenberg, Quart.Appl.Math. 2, 164 (1944)
5. D.Papoušek, S.Toman, and J.Plíva, J.Mol.Spectry 15, 502, (1965)
6. S.Toman, V.Špirko, and J.Plíva, to be published

suggested title : Damped least squares analysis of the NMR spectra.



מכון ויצמן למדע  
THE WEIZMANN INSTITUTE OF SCIENCE

REHOVOTH • ISRAEL  
P.O. B. 26 • PHONE: 951721-7

ISOTOPE DEPARTMENT

רחובות • ישראל  
ת.ד. 26 • טלפון: 951721-7

מחלקת האיזוטופים

July 31, 1966

Prof. B.L. Shapiro  
Department of Chemistry  
Illinois Institute of Technology  
Chicago, Illinois 60616  
U.S.A.

Dear Professor Shapiro,

We are engaged for some time in  $^{17}\text{O}$  NMR studies of metal-ion hydration. Using the method of "molal shifts" [Alej and Jackson, J. Chem. Phys., 41, 3402 (1964)] for the determination of coordination numbers, some interesting results were obtained.

For the  $\text{VO}^{++}$  ion a hydration number of 4 was obtained, which was assigned to the four molecules in the equatorial plane of the complex. Their life-time in the first coordination sphere was determined using the line-broadening method of Swift and Connick [J. Chem. Phys., 37, 307 (1962)] and found to be  $1.3 \times 10^{-3}$  sec (at  $300^\circ\text{K}$ ).

In the method of molal shifts the water  $^{17}\text{O}$  chemical shift due to  $\text{Dy}^{3+}$  is measured in absence and in presence of the ion, the hydration number of which is to be determined. We found that the shifts due to  $\text{Dy}^{3+}$  are very sensitive to the anion present. Thus, for example, the molal shift is reduced by 33% in presence of an excess of nitrate or of sulfate ions. We are now investigating the nature of the complexes formed in solution. The results suggest that the presence of anions other than perchlorate should be avoided while using this method.

We hope that this contribution will put us again on the mailing list of your very helpful News letter.

Yours sincerely,  
*Daniel Fiat*  
Daniel Fiat and Jack Reuben

JR/sa

Institute of Chemical  
Kinetics and Combustion  
Siberian Department  
Academy of Sciences of USSR  
Novosibirsk - 90

Professor B.L.Shapiro  
Department of Chemistry  
Illinois Institute of Technology  
Technology Center  
Chicago, Illinois 60616  
USA

Dear Professor Shapiro!

We want to communicate some new data on the unpaired spin delocalisation in paramagnetic coordination compounds studied by NMR. We measured the  $N^{14}$  shifts and calculated the hyperfine splitting constants  $A$  and nitrogen spin densities  $\rho^N$  in four paramagnetic complexes of  $Ni^{+2}$  and  $Co^{+2}$  (see table).

No	Complex	Solvent	Shift $-\frac{H_x}{H} 10^3$	A Mc/sec	$\rho^N$
1.	Co (en) <sub>3</sub> (NO <sub>3</sub> ) <sub>2</sub>	H <sub>2</sub> O	14,4	7,9	0,061
2.	Ni (en) (NO <sub>3</sub> ) <sub>2</sub>	H <sub>2</sub> O	12,6	12,9	0,067
3.	CoPy <sub>6</sub> (NO <sub>3</sub> ) <sub>2</sub>	CH <sub>3</sub> NO <sub>2</sub> +Py	9,6	5,3	0,031
4.	CoCl <sub>2</sub> · 2 α-MePy	CH <sub>3</sub> NO <sub>2</sub> +α-MePy	9,6	5,3	0,031

en-ethylenediamine, Py-pyridine, α-MePy - α-picoline.

The relation between the spin density attenuation for different ligands  $\frac{\rho^N}{\rho_{H_2}}$  and for free radicals with a similar structure  $\frac{\rho^N}{\rho_{H_2}} = \frac{500}{A_{H_2}}$  is shown fig 1. The splitting in the methyl radical has been corrected for  $sp^3$  hybridisation following Schrader and Karplus [1]. The  $\beta$ -protons splitting in the ethyl radical has been taken for the same conformation as in ethylen diamine complexes with  $Ni^{+2}$  and corrected for  $sp^3$  hybridisation. From fig.1 we con-

clude that spin delocalisation in molecules acting as ligands in paramagnetic complexes and in corresponding free radicals is similar. It is interesting to point out although the data are given for three different ions ( $\text{Cu}^{+2}$ ,  $\text{Co}^{+2}$  and  $\text{Ni}^{+2}$ ) and the delocalisation is transmitted through two different atoms (N in complexes and C in radicals) the correlation tangent is close to unity.

A detailed accounts of this work are to be published in J. Struct. Chem. USSR and DAN USSR.

We are indebted to Dr. Proctor (Varian AG, Zürich) for giving one of us (Yu. M.) the possibility to measure  $\text{N}^{14}$  shifts in his laboratory.

*Molin* Yu. N. Molin

*E. Zaev* E. E. Zaev

*V. Voevodsky* V. V. Voevodsky

Short Title: The  $\text{N}^{14}$  shifts in paramagnetic complexes of  $\text{Co}^{+2}$  and  $\text{Ni}^{+2}$ .

#### R e f e r e n c e s:

1. D. M. Schrader, M. Karplus, J. Chem. Phys., 40, No 6, 1593 (1964).
2. R. W. Fessenden, R. H. Schuler, J. Phys. Chem., 68, No 2, 347 (1964).
3. V. A. Tolkachev, I. I. Chkeidze, N. Ya. Buben, J. Struct. Chem., USSR, 3, No 6, 709 (1962).
4. J. R. Morton, Chem. Rev., 64, 453 (1964).
5. G. M. Larin, J. Struct. Chem., USSR, 6, No 4, 548 (1965).
6. E. E. Zaev, G. I. Skoobnewskay, Yu. M. Molin, J. Struct. Chem. USSR, 6, No 4, 639 (1965).
7. K. I. Zamaraev, Yu. N. Molin, G. I. Skoobnewskay, J. Struct. Chem., USSR, (to be published).

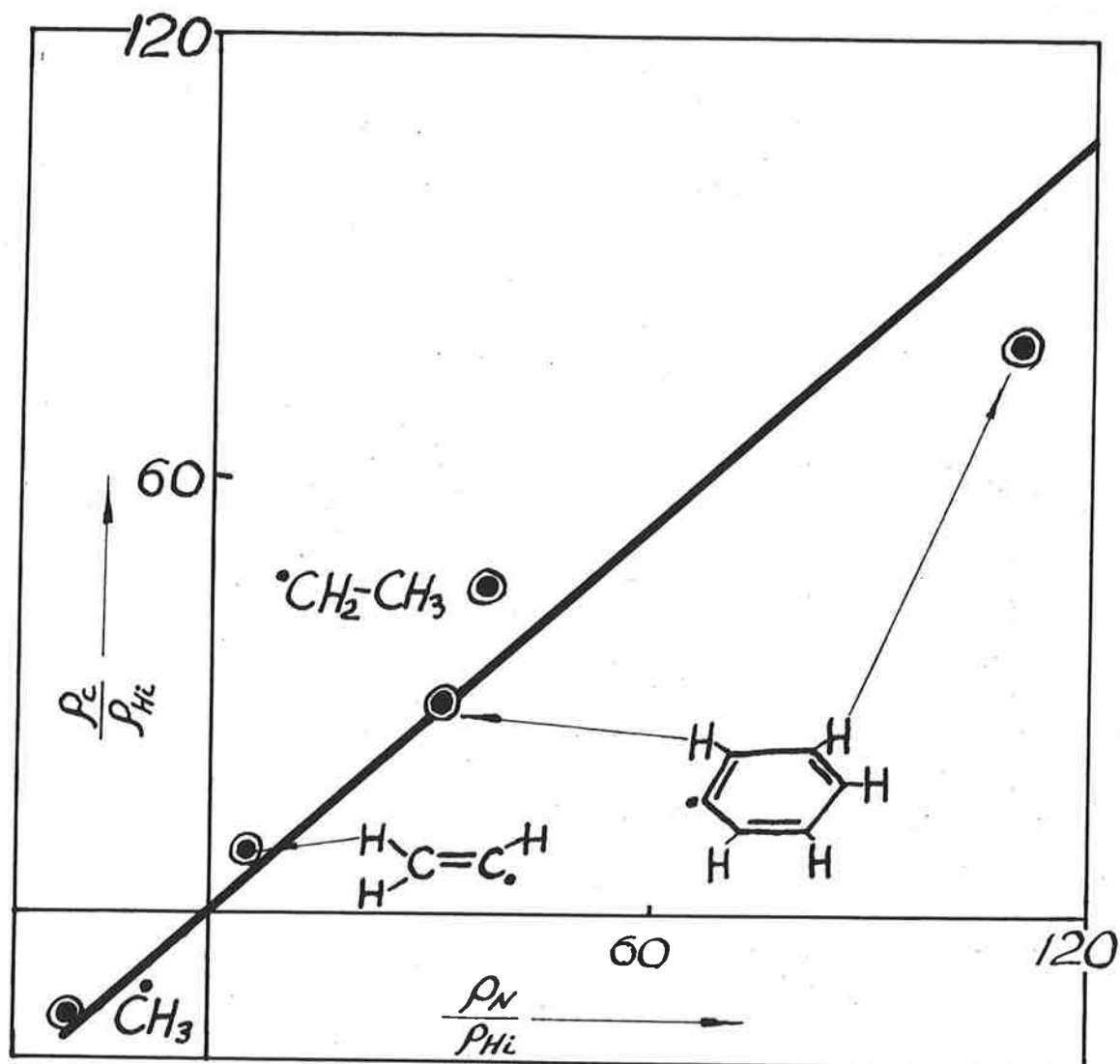


Fig. 1

Radical	Ref.	Fragment of complex	Ref.
$\dot{H}C=CH_2$	2	$\begin{matrix} R'' \\ \vdots \\ Cu^{+2} \vdots N=C-H^* \\ \vdots \\ R' \end{matrix}$	5
$\cdot C_6H_5$	3	$\begin{matrix} R'' \\ \vdots \\ Co^{+2} \vdots \text{C}_6H_5^* \\ \vdots \\ R' \end{matrix}$	6
$\dot{C}H_2-\dot{C}H_3$	4	$Ni^{+2} \vdots NH_2-\dot{C}H_2-$	7
$\dot{C}H_3$	1	$Ni^{+2} \vdots NH_2-$	7



## CANISIUS COLLEGE

BUFFALO, NEW YORK 14208

DEPARTMENT OF CHEMISTRY

August 2, 1966

Dr. Bernard Shapiro  
Department of Chemistry  
Illinois Institute of Technology  
Chicago, Illinois 60616

Dear Dr. Shapiro:

As our contribution to the Newsletter, I would like to give the results we obtained in correlating the position of the signal of the  $\text{CH}_3$  group attached to the aromatic ring with various substituents on the ring. We did of course compare the position under the same sample conditions. Some of the spectra were run at Canisius while others were from the various reference spectra. The correlations listed below are all for the  $\text{CH}_3$  signal only and we use the delta scale with TMS signal as zero. Some of the correlations listed are well-known but others may be new to some of your readers.

1. Comparing liquids to solutions the shift is to higher ppm values for the solutions.
2. Using the  $\text{CH}_3$  signal of toluene as a reference if the substituent is an activating group the shift is to lower ppm and if deactivating to higher.

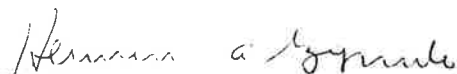
3. Activating groups in order of decreasing shift are;  $\text{NH}_2$ ,  $\text{NR}_2$ ,  $\text{OH}$  >  $\text{SH}$  >  $\text{OR}$  >  $\text{R}$ .

Deactivating groups in order of decreasing shift are;  $\text{NO}_2$ ,  $\text{C}\equiv\text{N}$  >  $\text{SO}_3\text{H}$  > halogen.

4. Activating groups in the ortho position shift the  $\text{CH}_3$  signal to lower ppm values to a greater degree than if the activating group is in the meta or para position. The meta and para substituents shift the signal about the same magnitude.
5. Deactivating groups in the ortho position shift the  $\text{CH}_3$  signal to higher ppm values to a greater degree than if the deactivating group is in the meta or para position. The meta and para substituents shift the signal about the same magnitude.

These correlations were from the work of a summer research student who will enter his junior year in September 1966. His name is L. Marabella.

Sincerely,

  
Dr. Herman A. Szymanski  
Chairman  
Department of Chemistry



UNIVERSITY OF ILLINOIS

DEPARTMENT OF CHEMISTRY  
THE WILLIAM ALBERT NOYES LABORATORY

August 8, 1966

Dr. B. L. Shapiro  
Department of Chemistry  
Illinois Institute of Technology  
Chicago, Illinois 60616

Dear Barry:

At long last we have gotten around to observing Carr Purcell spin echo (CPSE) trains in systems somewhat more complicated than the equally populated two site uncoupled system. Unless the A matrix for the system (see J. Chem. Phys. 43, 4107 (1965)) is symmetric and two by two, we have not been able to derive analytical formulae for the echo amplitudes in terms of chemical shifts, coupling constants, exchange rates, etc. which apply over the entire range of exchange rates and pulse rates.

Therefore we have developed a fortran program, ECHO-G, for calculating transverse relaxation rates as a function of rf pulse repetition frequency (which we call a "relaxation curve") from a given set of input parameters. The program proceeds by diagonalizing the complex, non-hermitian A matrix, and is limited by time considerations to systems with fifteen or less first order lines in the spectrum (a simple modification allows combination lines to be treated as well). In addition to simple test cases, we have used the program for a number of two spin substituted ethanes, and for the case of  $n$  spin  $\frac{1}{2}$  nuclei coupled to a spin 1 quadrupole or a spin  $\frac{3}{2}$  quadrupole.

A limited number of fortran source decks and instruction sheets are available.

Yours truly,

Robert L. Vold  
H. S. Gutowsky

RLV:ljz

## University of East Anglia

From Dr. R.K. Harris.

School of Chemical Sciences  
Wilberforce Road, Norwich NOR 77H  
Telephone Norwich 52651

4th August, 1966.

Dear Barry,

Thank you for the reminder. The trouble with your system is that it's too efficient! About a month ago it occurred to me that it was time I contributed to IIT (née MELLO) NMR, but my lack of initiative came to the rescue and I re-assured my conscience by saying "I'll wait for Barry's reminder". Anyway, now I have no excuse for further prevarication, so here goes. Among quite a few topics of current interest here there are two which perhaps merit mention. To prevent possible sub-titles by BLS, I'll give each a clear heading. I should add that Elliot Finer is my colleague in this work.

CONTRIBUTION. PART A. ARE  $^{13}\text{C}$  SATELLITES ALWAYS HELPFUL FOR SPECTRAL ANALYSIS?

Answer - No. We have been examining the problem of tetramethyl diphosphine, which gives a deceptively simple  $\text{X}_2\text{AA}'\text{X}_2'$  spectrum, from which at first glance only  $|J_{\text{AX}} + J_{\text{AX}}'| = 14.15 \text{ c/s}$  can be obtained. The proton spectrum is a triplet, although the central line is broader than the outer ones. The obvious solution to the problem of obtaining all the coupling constants is to look at  $^{13}\text{C}$  satellites, which "should" be first order. Unfortunately they again are triplets, though with even broader central lines. From this I previously drew an erroneous conclusion, but in fact it is clear that, for example, if  $^1J_{\text{PC}} = ^2J_{\text{PC}} = 0$ , then the  $^{13}\text{C}$  satellites would still be deceptively simple. We decided to investigate the conditions under which the  $^{13}\text{C}$  satellites would be triplets i.e. when there is no splitting in the central line of each  $^{13}\text{C}$  satellite. The answer is that this is so for :-

$$\left| \frac{L_{\text{C}}}{2J_{\text{PP}}} \right| < \Delta\nu_{\frac{1}{2}}, \text{ where } L_{\text{C}} = |^1J_{\text{PC}} - ^2J_{\text{PC}}|$$

$$L = |^2J_{\text{PH}} - ^3J_{\text{PH}}|$$

and  $\Delta\nu_{\frac{1}{2}}$  is the natural line-width.

Happily we have solved our problem in other ways and have obtained  $|^1J_{\text{PP}}| = 179.6 \text{ c/s}$ ,  $^2J_{\text{PH}} = + 2.95 \text{ c/s}$ ,  $^3J_{\text{PH}} = + 11.2 \text{ c/s}$ , i.e. the signs of two (P,H) coupling constants are the same. Moreover we find by heteronuclear double resonance that  $^1J_{\text{PP}}$  is negative with respect to  $^{13}\text{CH}$ .

As far as we are aware, (P,P) coupling constants are the only directly-bonded ones which have been shown to be negative except for those involving fluorine. Naturally we have had some thoughts on the subject and results will appear when these thoughts are formalised.

CONTRIBUTION. PART B. SIGNS OF (P,F) COUPLING CONSTANTS

As is apparent from PART A, we are interested in the magnitudes and signs of any coupling constants involving phosphorus. Among the compounds whose spectra we have studied are  $(\text{CF}_3)_2\text{PF}$  and  $(\text{CF}_3)_2\text{PSCF}_3$ . The latter involves a single-bond P-S linkage, i.e. the phosphorus is trivalent. Partial decoupling and tickling show that for these molecules the relative signs of the coupling constants are as follows :-

$$^1J_{\text{PF}} = 1013 \text{ c/s} \quad ^2J_{\text{PF}} = 83.8 \text{ and } 89.6 \text{ c/s} \quad ^3J_{\text{PF}} = 21.9 \text{ c/s}$$

$$^3J_{\text{FF}} = 3.46 \text{ c/s} \quad ^5J_{\text{FF}} = 1.11 \text{ c/s}$$

We hope in the future to relate these signs to a known absolute sign such as  $^1J_{\text{CF}}$ .

The heteronuclear double resonance experiments were carried out at the National Physical Laboratory. We are extremely grateful for use of the NPL facilities, for discussion with Dr. D.H. Whiffen and, especially for being taught the heteronuclear business by Dr. W. McFarlane.

Best wishes,

*Robin*

R.K. Harris.

Dr. B.L. Shapiro,  
Illinois Institute of Technology,  
Department of Chemistry,  
Chicago, 60616,  
U.S.A.

# Monsanto

C O M P A N Y

INORGANIC CHEMICALS DIVISION

800 N. Lindbergh Boulevard  
St. Louis, Missouri 63166  
(314) WYdown 3-1000

August 9, 1966

Dr. B. L. Shapiro  
Department of Chemistry, IIT NMR  
Illinois Institute of Technology  
Chicago, Illinois 60616

Dear Barry:

We wish to report some  $^{31}\text{P}$  and  $^1\text{H}$  nmr measurements on nitrilotrismethylenetriphosphonic acid [0.33 M] and nitrilotriacetic acid [0.25 M] and their N-oxides [0.10 M,  $\text{D}_2\text{O}$ ] at  $25^\circ$ . The data are summarized in the attached figure, which shows the changes in chemical shifts as a function of the extent of neutralization of the parent acids with sodium hydroxide. In conjunction with acid-base titration curves, the data permit some conclusions as to the relative acidity of alternate proton sites in these molecules. The largest changes in shift are attributed to equilibria involving dipolar ions with protons bound to nitrogen. This is confirmed by the measurements on the corresponding N-oxides which cannot bind protons directly to the nitrogen, and thus do not exhibit the sudden changes in chemical shift which are observed with the parent nitrilo compounds.

The use of nmr to detect subtle changes in molecular structure as a function of ionization, complexing, solvation, etc. is an application which we feel has not yet received sufficient attention, even though there have been a number of published studies of this general kind.

Full details of the present work are contained in a paper which has been submitted for publication. A limited number of preprints are available.

Sincerely,

R. P. Carter

R. P. Carter

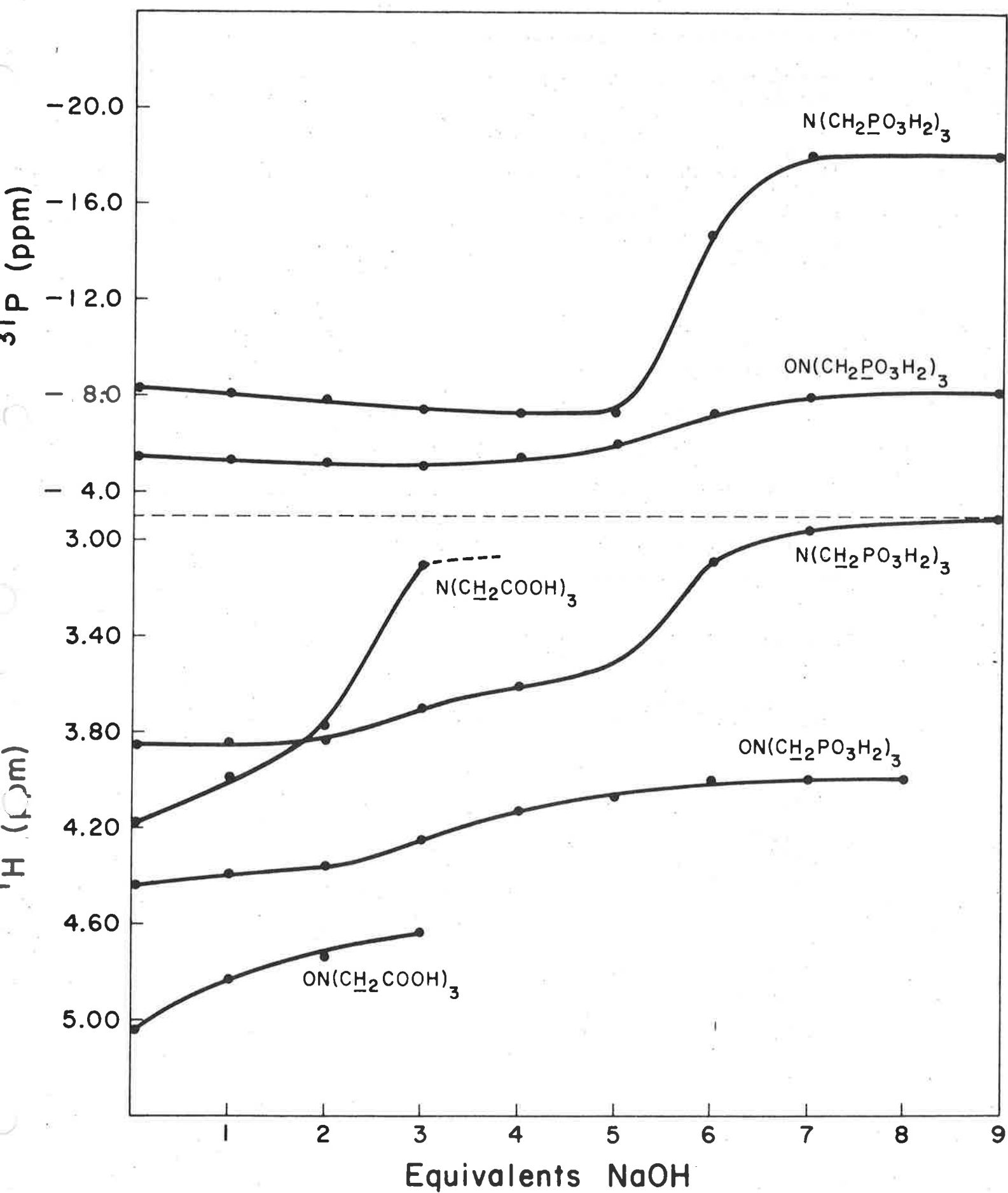
M. M. Crutchfield

M. M. Crutchfield

R. R. Irani

R. R. Irani

/cm  
Atta ch.



INSTITUT FÜR ORGANISCHE CHEMIE DER TECHNISCHEN HOCHSCHULE BRAUNSCHWEIG

PROF. DR. PHIL., DR. MED. h. c. H. H. INHOFFEN  
Dr. Hans Brockmann jr.

33 BRAUNSCHWEIG  
SCHLEINITZSTRASSE  
Tel. Hochschule 4761  
Durchwahl Institut 478 22 25  
Vorwahl 05 31

3. August 1966

Herrn  
Professor Dr. Bernard L. Shapiro  
Department of Chemistry  
Illinois Institute of Technology  
CHICAGO, Ill. 60616  
=====

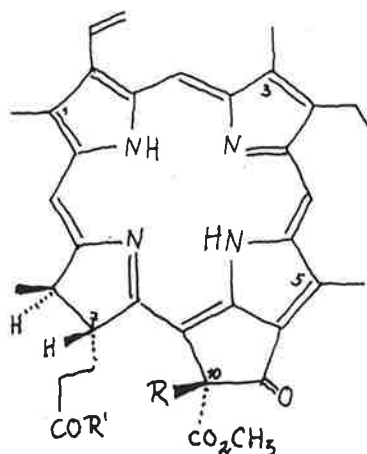
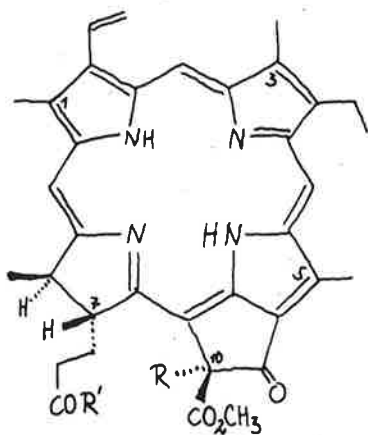
U. S. A.

Sehr geehrter Herr Professor Shapiro!

Diastereomere 10-Methoxy-methylphäophorbide

Zuordnung der Methylsignale

Im Zusammenhang mit stereochemischen Untersuchungen an den im hiesigen Institut (1) erstmals hergestellten 10-Methoxy-methylphäophorbiden a (2 und 3) durch ORD- und NMR-Messungen war es notwendig, in den NMR-Spektren von 2 und 3 die sechs scharfen Methylsignale im Bereich von 3.10 bis 3.75 ppm den sechs in Frage kommenden Methylgruppen eindeutig zuzuordnen.



- |          |                                      |                                     |
|----------|--------------------------------------|-------------------------------------|
| <u>1</u> | R = H;                               | R' = OCH <sub>3</sub>               |
| <u>2</u> | R = OCH <sub>3</sub> ;               | R' = OCH <sub>3</sub>               |
| <u>4</u> | R = OCH <sub>3</sub> ;               | R' = OC <sub>2</sub> H <sub>5</sub> |
| <u>6</u> | R = OC <sub>2</sub> H <sub>5</sub> ; | R' = OCH <sub>3</sub>               |

- |          |                                      |                                     |
|----------|--------------------------------------|-------------------------------------|
| <u>3</u> | R = OCH <sub>3</sub> ;               | R' = OCH <sub>3</sub>               |
| <u>5</u> | R = OCH <sub>3</sub> ;               | R' = OC <sub>2</sub> H <sub>5</sub> |
| <u>7</u> | R = OC <sub>2</sub> H <sub>5</sub> ; | R' = OCH <sub>3</sub>               |

Derartige Probleme sind bei Chlorin- und Porphyrin-NMR-Spektren recht häufig und können, da Weitbereichskopplungen kaum auftreten, nur durch den Vergleich von Spektren strukturell ähnlicher Verbindungen gelöst werden.

Gestützt auf Angaben von Closs et al. (2) und eigene Korrelationen scheint die Interpretation des NMR-Spektrums von Methylphäophorbid a (1) im zu untersuchenden Bereich gesichert. Die Einführung einer 10-Methoxygruppe wird die C-Methylgruppen nur durch allgemeine Ringstromeffekte, z.B. Einebnung oder Verzerrung des Macrocyclus beeinflussen. Daher werden die in den Spektren beider Diastereomere (2 und 3) bei gleichen Feldstärken auftretenden Signale (3.15, 3.37, 3.72 ppm) offenbar durch die Methylgruppen an C-3, C-1 und C-5 hervorgerufen.

Die starken sterischen Wechselwirkungen zwischen der Methoxy- und den Methoxycarbonylgruppen verursacht jedoch Abschirmeffekte, die nicht ohne weiteres vorausgesagt werden können. Gelöst haben wir unser Problem durch Darstellung von vier weiteren Verbindungen, den diastereomeren 10-Methoxy-äthylphäophorbiden a (4 und 5) sowie den diastereomeren 10-Äthoxy-methylphäophorbiden a (6 und 7).

Der Vergleich der NMR-Spektren von 2, 4 und 6 einerseits und von 3, 5 und 7 andererseits gestattet nun, wie aus der Tabelle ersichtlich ist, die eindeutige Zuordnung aller Signale.

Dr. H. Brockmann jr. c/o

Prof. Dr. H. H. Inhoffen · Technische Hochschule Braunschweig

Blatt 3 zum Schreiben 3.8.1966

Chemische Verschiebung (ppm) der Methylprotonen in  $\text{CDCl}_3$ 

	<u>1</u>	<u>2</u>	<u>4</u>	<u>6</u>	<u>3</u>	<u>5</u>	<u>7</u>
3- $\text{CH}_3$	3.11	3.15	3.15	3.15	3.15	3.15	3.15
1- $\text{CH}_3$	3.33	3.37	3.37	3.37	3.37	3.38	3.37
5- $\text{CH}_3$	3.64	3.72	3.72	3.71	3.72	3.72	3.71
10- $\text{OCH}_3$	---	3.45	3.45	---	3.31	3.31	---
10- $\text{CO}_2\text{CH}_3$	3.86	3.63	3.64	3.62	3.68	3.68	3.67
7''- $\text{CO}_2\text{CH}_3$	3.56	3.55	---	3.56	3.50	---	3.50

- (1) H. H. Inhoffen, H. Biere, H. Brockmann jr. und H. Wolf,  
Liebigs Ann. Chem. in Vorbereitung
- (2) G. L. Closs, J. J. Katz, F. C. Pennington, M. R. Thomas  
und H. H. Strain, JACS 85, 3809 (1963).

Mit vorzüglicher Hochachtung

Ihr

*H. Brockmann jr.*



THE UNIVERSITY OF WESTERN ONTARIO  
FACULTY OF ARTS AND SCIENCE  
COLLEGE OF SCIENCE



DEPARTMENT OF CHEMISTRY

LONDON, CANADA

August 8, 1966

Dr. B. L. Shapiro,  
Dept. of Chemistry,  
Illinois Institute of Technology,  
Chicago, Illinois 60616, U.S.A.

Dear Barry,                      8th ENC - Preliminary Announcement

Following the lead provided by Herb Retcofsky in the preceding newsletter, I should like to take this opportunity to announce formally that the 8th ENC will be held at the Mellon Institute, Pittsburgh, Pa., March 2-4, 1967. These dates are the end of the week preceding the 1967 Pittsburgh Conference on Anal. Chem. and Appl. Spec.

As in the past, the Conference is devoted to advances in instrumentation, experimental design and techniques and does not compete with Workshops or courses offering an introduction to the field. It's a little early to construct an outline of the sessions which will be held but I wish to make the time for the meeting known to all so that you can reserve these dates.

A detailed first announcement will appear in the November issue of the IITNMR newsletter.

Sincerely,

A handwritten signature in cursive script, appearing to read "J. B. Stothers".

J. B. Stothers  
Chairman, 8th ENC

JBS:v1

RÉPUBLIQUE FRANÇAISE  
PREMIER MINISTRE

COMMISSARIAT A L'ÉNERGIE ATOMIQUE

CENTRE D'ÉTUDES NUCLÉAIRES DE GRENOBLE

RUE DES MARTYRS - 38 - GRENOBLE

ADRESSER LA CORRESPONDANCE :  
BOITE POSTALE 269 - GRENOBLE

TÉL. 07-59-11

Dr. B.L. SHAPIRO  
Illinois Institute of Technology  
Department of Chemistry

CHICAGO, Ill., 60616  
U.S.A.

GRENOBLE, LE 9 août 1966

RÉFÉRENCE A RAPPELER :  
a/COP.1/66-642

VOTRE RÉP. :

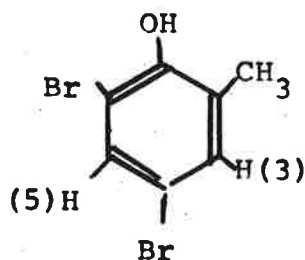
VOTRE LETTRE DU

Cher Professeur SHAPIRO,

"SIGNES NEGATIFS DE COUPLAGES "BENZYLIQUES" ORTHO  
ET PARA"

Toutes nos excuses pour le délai d'envoi de cette lettre qui résume une communication à paraître au Bulletin de la Société Chimique de France.

Dans le dibromo-4,6-O-crésol existent deux couplages à longue distance ("benzyliques") entre le méthyle et les protons aromatiques :



$$\begin{aligned} |J_{H_3-CH_3}| &= 2,3 \text{ c.n.s.} \\ |J_{H_5-CH_3}| &= 0,6 \text{ c.n.s.} \\ |J_{H_3-H_5}| &= 0,8 \text{ c.n.s.} \end{aligned}$$

En solution dégazée, et en présence d'acide trifluoroacétique, le spectre est du type  $AKX_3$ .

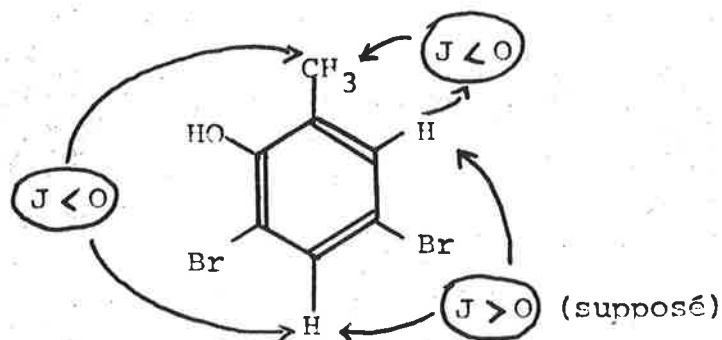
../.

Par deux expériences de double irradiation sélective, on peut obtenir les signes relatifs des couplages, soit :

$$- J_{H_3-H_5} \cdot J_{H_3-CH_3} < 0$$

$$- J_{H_3-H_5} \cdot J_{H_5-CH_3} < 0$$

En supposant le couplage  $J_{H_3-H_5}$  positif, on trouve donc que les deux couplages à longue distance  $^4J$  et  $^6J$ , entre le  $CH_3$  et les protons aromatiques ortho ou para, sont tous deux positifs, soit :



Les signes négatifs obtenus pour ces couplages benzyliques  $^4J$  et  $^6J$  sont ceux que l'on peut prévoir théoriquement par la théorie de Mc CONNELL sur la contribution au couplage de l'interaction  $\sigma - \pi$ .

Nous vous prions de bien vouloir agréer, cher Monsieur SHAPIRO, l'assurance de nos sentiments les meilleurs.

TRINH-HUU ICH

D. GAGNAIRE

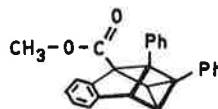
10th August, 1966

Professor B.L. Shapiro,  
 Dept. of Chemistry,  
 Illinois Institute of Technology,  
 Technology Center,  
 CHICAGO, ILLINOIS 60616, U.S.A.

Dear Professor Shapiro,

ACID INDUCED UPFIELD SHIFTS IN SOME CARBONYL COMPOUNDS

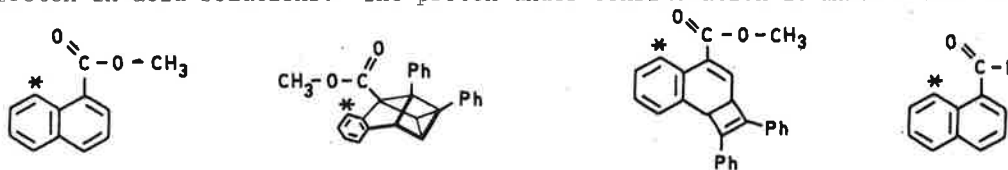
During work on some acid-catalysed rearrangements it was observed that in the p.m.r. spectrum of the compound



one aromatic proton showed a marked upfield shift in acid solution. This prompted examination of the spectra of a few "shelf" chemicals in a 10% v/v solution of CF<sub>3</sub>COOH in CDCl<sub>3</sub>, and again after the extraction of the acid with water. All compounds studied exhibit complex aromatic patterns and the chemical shift(s) of the proton(s) under consideration are only approximate.

The results obtained may be summarized as follows:

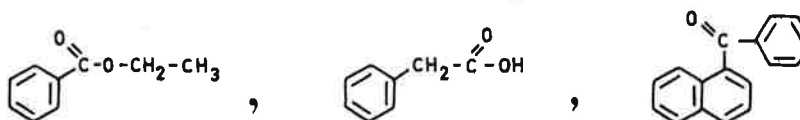
1. Compounds that showed a marked upfield change in the chemical shift of one proton in acid solutions. The proton under consideration is marked with an \*.



2. Compounds that showed a small upfield change in the chemical shift of one proton in acid solution.



3. Compounds that showed no change in chemical shift in acid solutions.



It will be noted that the compounds which exhibit the large changes in chemical shift have at least four connecting bonds in a common plane between the hydrogen atom under consideration and the carbonyl group. Therefore co-planarity of the carbonyl group and the C-H bond could be a prerequisite for this effect. This hypothesis could explain the apparently exceptional behaviour of 1-benzoyl-naphthalene.

A plausible explanation is that in neutral solutions a weak hydrogen bond exists between the peri-aromatic proton and the coplanar carbonyl group, and on the addition of the acid the preferred bonding is between the carbonyl group and a proton derived from the acid, thus causing the observed upfield shifts in acid solution.

Yours faithfully,

*P. Collin*  
 P. Collin



## THE PROCTER &amp; GAMBLE COMPANY

MIAMI VALLEY LABORATORIES

P.O. BOX 39175  
CINCINNATI, OHIO 45239

August 12, 1966

Dr. Barry Shapiro  
Department of Chemistry  
Illinois Institute of Technology  
Chicago, Illinois 60616

Dear Barry:

We have a few comments on the use of the C-1024 which might be of interest to some of the readers. We have recently been using the C-1024 in conjunction with our wide-line spectrometer which is equipped with the Fieldial sweep unit. It is quite easy to accommodate the C-1024 to the Fieldial. The x-drive pot on the sweep unit provides a linear voltage output of 0 to -15 volts over the sweep range. This voltage is used to trigger an electronic relay which closes an additional 110 V relay to trigger the C-1024 at the beginning of the sweep. We have found that the Sargent S-81990 thermoregulating relay works very nicely but there are probably others which will do just as well.

The sweep times of the Fieldial and C-1024 are different but this presents no great problem. The Fieldial sweeps in multiples of 30 seconds and the C-1024 sweeps in multiples of 25 seconds. As a result the C-1024 will end its sweep before the Fieldial and must wait for a period before retriggering. The only disadvantage in this is that a portion of the range covered by the sweep unit will not be read into the computer and the signal position must be positioned accordingly.

The stability of the Fieldial regulator is such that no broadening of lines 0.5-1.0 gauss wide has been noted for overnight runs. For most wide-line spectra the readout of the C-1024 can be calibrated accurately enough by simply scanning a line of known width for a couple of times, reading out the spectrum and obtaining the scale in gauss/length from the chart. For more accurate calibration the method described below can be used.

One caution we will mention about averaging wide-line spectra. Most of the commercial inserts contain enough residual protons to produce a significant signal after a few scans. The signal from one of our 15 mm, 40 MHz inserts is shown in the enclosed Figure (A) for a single scan and after 179 scans. Other inserts, both 15 mm and 5 mm show similar signals. These signals are out of phase with respect to any signal from a sample.

We have found that the insert signal can be removed by simply subtracting it with the C-1024. Shown in the Figure (B) are spectra

Dr. Barry Shapiro

Page 2

August 12, 1966

obtained before and after subtracting the insert signal. This method of removing the insert signal does produce some problems however. First, the amount of time necessary to obtain a spectrum is increased by a factor of two. Secondly, the signal-to-noise suffers by a factor of  $\sqrt{2}$  since twice as many noise spectra as signal spectra are averaged.

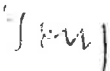
Reading Out Calibrated Spectra. There has been much discussion concerning the best way to calibrate the read out of the C-1024 in past issues of the NMR Newsletter. The way which we feel is superior is to use the "read out while reading in" capability of the C-1024. This feature is discussed in the C-1024 manual in paragraph 4.4.3 "Simultaneous Data Accumulation and Read Out." For read out, merely add one more spectrum to the computer (this spectrum may be a zero signal) and flip the spectrometer switch on the HA-100 to WL/EPR. (For other spectrometers, there are probably analogous settings.) This places the analog signal from the computer on the recorder of the spectrometer. Since all conditions are the same as when the spectrum is read in, the record produced is identical in scale calibration, and more importantly, in offset so that the chemical shift may be read directly from the recorder read out. The only caution to be observed is to make sure that the spectrum is on scale properly for the last reading. This can be done by checking the appearance of the spectrum using the C-1024 oscilloscope. Reading out in this manner will raise the dc level of the spectrum slightly above its value in the display mode, but it should not be objectionable if many spectra have been added.

Sincerely,

THE PROCTER & GAMBLE COMPANY  
Research & Development Department



K. D. Lawson

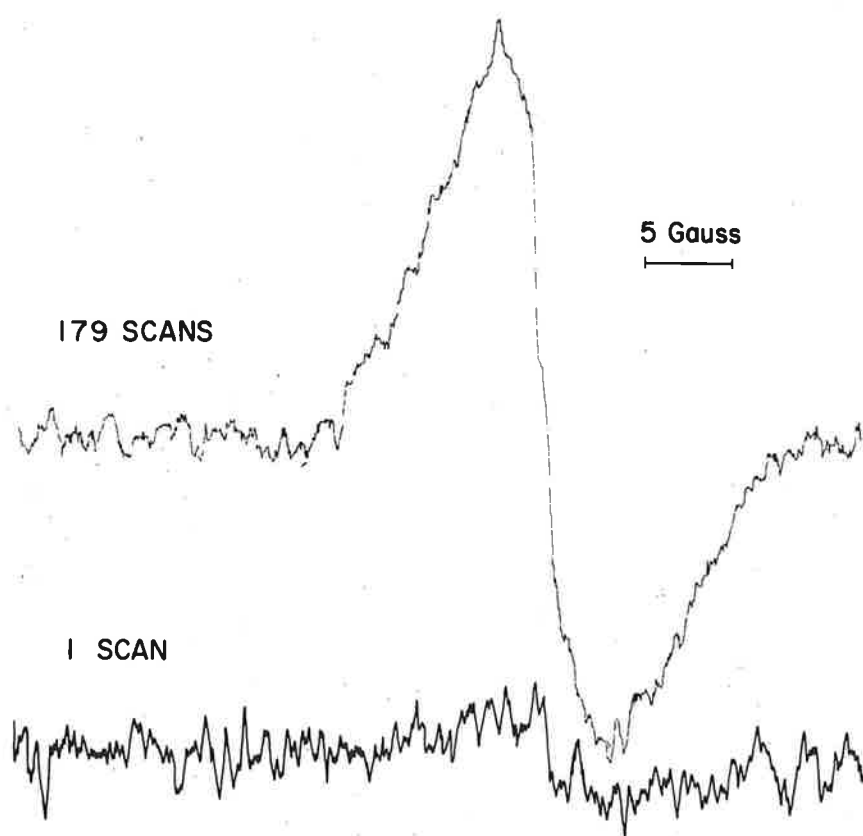


T. J. Flautt  
Research Division

CW

Enc.

Suggested Title: C-1024: Use with Fieldial and Read Out of Calibrated Spectra



A

B

10 ADDITIONS OF SAMPLE +  
INSERT SIGNAL

10 SUBTRACTIONS OF  
INSERT SIGNAL



THE JOHNS HOPKINS UNIVERSITY • BALTIMORE 18, MARYLAND

DEPARTMENT OF CHEMISTRY

August 14, 1966

Professor B. L. Shapiro  
IITNN  
Department of Chemistry  
Illinois Institute of Technology  
Chicago, Illinois 60616

Dear Barry,

I hope this letter reaches you before my name is removed from the IITNN mailing list! I wish to report on some of my NMR activities:

Performance of a Magnion Spin-Echo Apparatus -- Theory of Spin-Echoes in Solids

A. Spin-Echo Apparatus.

I have recently received a Magnion Spin-Echo system operating at 10, 30, and 60 MHz. I have very little to report on it yet. It seems to be of a basically good design. Although it is a "low power" system, I have obtained 90 degree pulses of less than 10 microseconds at 60 MHz, and I suspect it will be possible to do quite a bit better with a few minor modifications. On the other hand, there are a large number of minor "bugs" and inconveniently located adjustable components. As received, I consider the system far from satisfactory but potentially very good. I hope to be able to report on some experiments in the near future.

B. Theoretical Aspects of Spin-Echoes in Solids.

Recently Ostroff and Waugh<sup>1</sup> observed that in a modified Carr-Purcell experiment\* on a solid in which dipolar interactions are dominant, the magnetization may be observed for periods much longer than in an induction decay experiment (homogeneous broadening!). A similar effect was previously observed in single echo (two pulses) experiments.<sup>2,3</sup>

Here I wish to report briefly on some calculations for a few model systems for which closed solutions are easily obtained, and on a perturbation treatment for modified Carr-Purcell experiments\* with fast pulse repetition rates (small  $\gamma$ ).

The exact calculations were performed using a procedure previously employed<sup>4</sup> for Carr-Purcell experiments on liquid systems with scalar coupling. We assume "strong rf pulses" and neglect dipolar interactions during pulses. The following results are obtained if only dipolar interactions are present between pulses.



For an isolated two-spin system in a rigid lattice (both spins  $\frac{1}{2}$ ), the effect of the dipolar interactions disappears at the echo maxima (Time  $=2n\tau$ ). This effect is independent of  $\gamma$  and is an extension of the result of Powles and Mansfield<sup>2a</sup> for two pulse experiments.

For an isolated system of three spins  $\frac{1}{2}$  at the corners of an equilateral triangle reorienting rapidly about the  $C_3$  axis, the amplitude of the  $n$ th echo is proportional to

$$1 + 2 \frac{1 + \cos 3A\tau}{3 + \cos^2 3A\tau} + (-1)^n \frac{(1 - \cos 3A\tau)^2}{3 + \cos^2 3A\tau} \cos 2n\lambda \quad (1)$$

where  $A = \frac{1}{4}(\gamma\hbar)^2 r^{-3}(1 - 3\cos^2\theta)$ ,  $\theta$  is the angle the normal to the triangle makes with the static magnetic field and the other quantities have their customary meaning. Also,  $\lambda$  is defined by  $\sin \lambda = -\frac{1}{2}\sin 3A\tau$ ,  $-\frac{1}{2}\tau \leq \lambda \leq \frac{1}{2}\tau$ .

It is amusing that at least three spins  $\frac{1}{2}$  are needed for the dipolar interactions to affect the echo maxima at large and medium  $\gamma$ . Approximate methods must of course be used for large spin systems. If one wished to apply the type of expansion used by Lowe and Norberg<sup>5</sup> for induction decays, and extend it to spin echoes as was done by Powles and Strange,<sup>2b</sup> it would be necessary to repeat the procedure  $n$  times successively for the  $n$ th echo, with inherent difficulties in the derivation of general expressions.

I have used a somewhat different perturbation expansion based on the Baker-Hausdorff theorem. It appears to be more suitable to the analysis of Carr-Purcell experiments on solids. One result that comes out nicely is, that the effect of dipolar interactions on the echo maxima of a modified\* Carr-Purcell train of echoes can always be made to disappear by making  $\gamma$  sufficiently small, in agreement with the results of Ostroff and Waugh<sup>1</sup>.

More details and other results will soon be available in preprint form.

With best wishes,



Adam Allerhand

\* Pulse spacings are the same as in an ordinary Carr-Purcell train, but all pulses are of the 90 degree variety. There is a 90° phase shift between the initial pulse and the rest. The spacing between the first two pulses is  $\tau$ .

1. E. D. Ostroff and J. S. Waugh, Phys. Rev. Letters 16, 1097(1966).
2. (a)J. G. Powles and P. Mansfield, Phys. Letters 2, 58 (1962); (b)J. G. Powles and J. H. Strange, Proc. Phys. Soc. (London) 82, 6 (1963).
3. D. S. Metzger and J. R. Gaines, Phys. Rev. 147, 644 (1966).
4. A. Allerhand, J. Chem. Phys. 44, 1 (1966).
5. I. J. Lowe and R. E. Norberg, Phys. Rev. 107, 46 (1957).

# MELLON INSTITUTE

## BIBLIOGRAPHY

"Nuclear Magnetic Resonance Detector for Demonstrations or Magnetic Field Measurements"  
M. R. Proffitt and W. C. Gardiner, Jr.  
Am. J. Phys. 34, 163 (1966)

"Proton Magnetic Resonance Spectra of Unsaturated Fatty Acids"  
J. M. Purcell, S. G. Morris and H. Susi  
Anal. Chem. 38, 588 (1966)

"Fluorisoprenole"  
H. Machleidt und W. Grell  
Ann. Chem. 690, 79 (1965)

"Umsetzung von Ubichinon(35) mit Lithiumalanat und Natriumborhydrid"  
H. Morimoto, I. Imada und M. Sasaki  
Ann. Chem. 690, 115 (1965)

"1,3,4-Oxiazoline und Hydrazondicarbonsäureester aus der Umsetzung von Diazoessigsäureestern mit Azodicarbonsäureestern: IR- und <sup>1</sup>H-NMR-spektroskopische Untersuchung"  
E. Fahr, K. Königsdorfer und F. Scheckenbach  
Ann. Chem. 690, 138 (1965)

"Guaianolides from the Was of Calocephalus Brownii F. Muell. (Compositae)"  
T. J. Batterham, N. K. Hart and J. A. Lamberton  
Australian J. Chem. 19, 143 (1966)

"6,7,8,9-Tetrahydropyridoquinazolines, A New Class of Alkaloids from Mackinlaya Species (Araliaceae)"  
J. S. Fitzgerald, S. R. Johns, J. A. Lamberton and A. H. Redcliffe  
Australian J. Chem. 19, 151 (1966)

"Iodoamidation of Cyclohexene: Failure to Repeat a Fluorination Reaction"  
R. H. Andreatta and A. V. Robertson  
Australian J. Chem. 19, 161 (1966)

"The Hydrolysis of Piperazine-2,5-dione"  
B. D. Sykes, E. B. Robertson, H. B. Dunford, and D. Konasewich  
Biochemistry 5, 697 (1966)

"Synthesis and Some Properties of N<sup>α</sup>-Glycyl-N<sup>ε</sup>-[β-(glycyl-α-L-aspartylglycine)]-L-lysylglycine and Related Peptides"  
J. E. Shields  
Biochemistry 5, 1041 (1966)

"NMR Spectrum of Dibenzyl Mercury"  
I. P. Beletskaya, L. A. Fedorov, V. A. Moskalenko and O. A. Reutov  
Bull. Acad. Sci., USSR Div. Chem. Sci. (English Transl.) 907 (1965)

"Nuclear-Magnetic-Resonance Studies of Polyisobutylene Solutions"  
W. P. Slichter and D. D. Davies  
Bull. Am. Phys. Soc. 11, 166 (1966)

"Nuclear-Magnetic-Resonance Studies of Li<sup>7</sup> in Lithium Nitride"  
S. G. Bishop, P. J. Ring, and P. J. Bray  
Bull. Am. Phys. Soc. 11, 171 (1966)

"NMR Study of Exchange Interaction in Thallium Chloride Crystals"  
S. Clough and W. I. Goldberg  
Bull. Am. Phys. Soc. 11, 171 (1966)

"Pulsed NMR of Na<sup>23</sup> in Rapidly Rotated NaCl"  
S. M. Day and A. C. Cunningham  
Bull. Am. Phys. Soc. 11, 171 (1966)

"Pulsed NMR Study of CsF"  
D. Hutchins and S. M. Day  
Bull. Am. Phys. Soc. 11, 171 (1966)

"Nuclear Double-Resonance Studies of Substantial Ag<sup>+</sup> in Single-Crystal Sodium Chloride"  
G. T. Mallick, Jr. and R. T. Schumacher  
Bull. Am. Phys. Soc. 11, 171 (1966)

"Nuclear Magnetic Resonance in NaTl and Related Phases"  
L. H. Bennett  
Bull. Am. Phys. Soc. 11, 172 (1966)

"Nuclear Magnetic Resonance of CH<sub>3</sub>F and CF<sub>3</sub>H Dissolved in Liquid Crystal"  
R. A. Bernheim and B. J. Lavery  
Bull. Am. Phys. Soc. 11, 172 (1966)

"Nuclear-Magnetic-Resonance Studies of TlSe, TlTe, and Tl<sub>3</sub>Te<sub>2</sub>"  
K. C. Brog and W. H. Jones, Jr.  
Bull. Am. Phys. Soc. 11, 172 (1966)

"Interpretation of NMR Data in Solid Hydrogen"  
A. B. Harris  
Bull. Am. Phys. Soc. 11, 172 (1966)

"P<sub>31</sub>, As<sup>75</sup>, r<sup>89</sup>, and La<sup>139</sup> NMR in the Paramagnetic State of the fcc Rare-Earth Intermetallic Phosphides and Arsenides"  
E. D. Jones and J. E. Hesse  
Bull. Am. Phys. Soc. 11, 172 (1966)

"Nuclear Magnetic Resonance of Fe<sup>57</sup> in α-Fe<sub>2</sub>O<sub>3</sub> at 4°K"  
M. Rubinstein, G. H. Stauss, and D. H. Anderson  
Bull. Am. Phys. Soc. 11, 172 (1966)

"Sensitive Low-Level Transistorized NMR Spectrometer Employing Frequency Modulation"  
V. Hugo Schmidt, and F. J. Blankenburg  
Bull. Am. Phys. Soc. 11, 172 (1966)

"Al<sup>27</sup> and r<sup>89</sup> Nuclear Magnetic Resonance in Yttrium Aluminum Garnet"  
C. M. Verber, K. C. Brog, and W. H. Jones, Jr.  
Bull. Am. Phys. Soc. 11, 172 (1966)

"Dynamic Nuclear Polarization in Hexafluorobenzene"  
E. H. Poindexter, J. R. Stewart and D. D. Thompson  
Bull. Am. Phys. Soc. 11, 201 (1966)

"Knight Shift and Nuclear-Spin-Lattice Relaxation in FeAl, RuAl, and OsAl Intermetallic Compounds"  
D. O. Van Ostenburg, J. J. Spokas, and C. H. Showers  
Bull. Am. Phys. Soc. 11, 219 (1966)

"Nuclear Resonance in Dilute Alloys of Transition Metals in Al"  
J. M. Brettell and A. J. Heeger  
Bull. Am. Phys. Soc. 11, 219 (1966)

"Synthese und Struktur von Isomeren des Chlordans"  
K. H. Michel, A. E. Ginsberg und R. Fischer  
Chem. Ber. 99, 421 (1966)

"Der sterische Verlauf von Additionen an die Dreifachbindung"  
E. Winterfeldt und H. Preuss  
Chem. Ber. 99, 450 (1966)

"Gold(I)-chlorid-Komplexe cyclischer Mono-, Di- und Triolefine"  
R. Mittel, H. Reinheimer und H. Dietl  
Chem. Ber. 99, 462 (1966)

"Isolierung von zwei weiteren Abbauphenolen mit einer 1.2-Diaryl-propan-Struktur"  
H. Nimz  
Chem. Ber. 99, 469 (1966)

"Triazoline aus organischen Aziden und  $\alpha,\beta$ -ungesättigten Carbonylverbindungen oder Nitrilen"  
R. Huisgen, G. Szeimies und L. Möbius  
Chem. Ber. 99, 475 (1966)

"Thermolyse der  $\Delta^2$ -1.2.3-Triazolin-4-carbonester; Chemismen des Triazolin-Zerfalls"  
G. Szeimies und R. Huisgen  
Chem. Ber. 99, 491 (1966)

"Darstellung von N,N'-Bis-arylsulfonyl-formamidinen"  
I. Hagedorn, H. Etling und K. E. Lichtel  
Chem. Ber. 99, 520 (1966)

"Darstellung von Tetrakis-(N-alkyl-anilino)-äthylene"  
I. Hagedorn und K. E. Lichtel  
Chem. Ber. 99, 524 (1966)

"Untersuchungen mit Cumaranon-epoxiden"  
A. Schönberg und K. Junghans  
Chem. Ber. 99, 531 (1966)

"Synthese und Struktur von Chinoxalin-glucosiden"  
F. Reisser und W. Pfeleiderer  
Chem. Ber. 99, 547 (1966)

"6H-1.2-Oxazine durch 1.4-Addition an konjugierte Diene"  
D. Klamann, M. Fligge, P. Weyerstahl und J. Kratzer  
Chem. Ber. 99, 556 (1966)

"Protonmagnetische Resonanzspektren von cis- und trans-2.3-Dichlor-dioxan"  
D. Jung  
Chem. Ber. 99, 566 (1966)

"Hypoxanthin- und Uracil-Nucleoside der 3-Nitro- und 3-Amino-3-desoxy-glucopyranose"  
F. W. Lichtenthaler und H. P. Albrecht  
Chem. Ber. 99, 575 (1966)

"Struktur und Synthese einiger Acetylenverbindungen aus Chrysanthemum maximum Ramond"  
F. Bohlmann, H. Mönch und U. Niedballa  
Chem. Ber. 99, 586 (1966)

"Die Polyine aus Cousinia hystrix C. A. May"  
F. Bohlmann und K.-M. Kleine  
Chem. Ber. 99, 590 (1966)

"Photo- $C_4$ -Cyclodimerisation von Cumarin"  
C. H. Krauch, S. Farid und G. O. Schenck  
Chem. Ber. 99, 625 (1966)

"Synthese und Eigenschaften substituierter Divinyläther und Divinylthioäther"  
K. Dimroth, H. Follmann und G. Pohl  
Chem. Ber. 99, 642 (1966)

"A Novel Synthesis of 1,2-Dithiol-3-Thione"  
R. N. Warrenner and E. N. Cain  
Chem. Ind. (London) 289 (1966)

"Conformational Analysis of 8-Oxa-1-azabicyclo[4.3.0]nonanes using Geminal Coupling Constants"  
T. A. Crabb and R. F. Newton  
Chem. Ind. (London) 339 (1966)

"4-Indenol and 7-Indenol Structure Determination"  
H. L. Retcofsky, J. A. Queiser and R. A. Friedel  
Chem. Ind. (London) 340 (1966)

"Carbon-bonded Acetylacetone Derivatives of Gold(I) Complexes"  
D. Gibson, B. F. G. Johnson, J. Lewis and C. Oldham  
Chem. Ind. (London) 342 (1966)

"Formation and Fission of 2,3-Dihydropyrazine by Pyrolysis of Pyrazine-2,3-Dicarboxylic Anhydride"  
R. F. C. Brown, W. D. Crow and R. K. Solly  
Chem. Ind. (London) 343 (1966)

"N.M.R. Spectra of C(20)-Substituted Pregnanes"  
C. H. Robinson and P. Hofer  
Chem. Ind. (London) 377 (1966)

"Comportamento di composti organometallici alogenati di alluminio in presenza di basi di Lewis. Nota II - Dismutazione dell'  $[AlCH_3Cl_2]_2$ , in soluzione toluenica, in presenza di basi di Lewis in difetto"  
A. Zambelli, A. L. Segre, A. Marinangeli, G. Gatti  
Chim. Ind. (Milan) 48, 1 (1966)

"A Study of Low Molecular Weight Asphaltic Hydrocarbons"  
D. E. Wetmore  
Dissertation Abstr. 26, 3609 (1966)

"Spettri di R. M. N. e stereoregolarita di bromuro di polivinile preparato a diverse temperature"  
M. Frata, G. Vidotto, G. Talamini  
Chim. Ind. (Milan) 48, 42 (1966)

"Étude de la relaxation des protons de  $CuCl_2 \cdot 2H_2O$  anti-ferromagnétique. Influence des impuretés et de la taille des échantillons"  
H. Benoit et J.-P. Renard  
Compt. Rend. 262B, 450 (1966)

"Étude par résonance magnétique nucléaire de dérivés de la 2H-benzothiazine-1.4. La non-équivalence des protons du substituant 2-méthylène"  
J. Bourdais  
Compt. Rend. 262C, 495 (1966)

"Conformation du diacétate de Westphalen."  
M. Mousseron-Canet et J.-C. Guilleux  
Compt. Rend. 262C, 509 (1966)

"Double Résonance Hétéronucléaire  $^{31}P - ^1H$ . Couplage à longue distance dans le triméthyl-phosphonoacétate"  
J.-J. Dunand, A. Rousseau et P. Servox-Gavin  
Compt. Rend. 262B, 515 (1966)

"The Periodate Oxidation of Nitrones"  
A. K. Qureshi and B. Sklarz  
J. Chem. Soc. (C) 412 (1966)

"The Reductive Fission of Methyl Sulphides, 1,3-Dithiolans, and a 1,3-Oxathiolan by Sodium in Liquid Ammonia"  
E. D. Brown, S. M. Iqbal, and L. N. Owen  
J. Chem. Soc. (C) 415 (1966)

"Reactions of Cyclohexadienes. Part V. A New Synthesis of 4-Substituted Cyclohexenones"  
A. J. Birch and J. S. Hill  
J. Chem. Soc. (C) 419 (1966)

"Extractives from Guttiferae. Part II. The Isolation and Structure of Four Polyhydroxyxanthenes in Symphonia globulifera L"  
H. D. Locksley, I. Moore, and F. Scheinmann  
J. Chem. Soc. (C) 430 (1966)

"The Reaction of Methadone and Methadone Nitrile with Cyanogen Bromide"  
N. J. Harper, D. Jones, and A. B. Simmonds  
J. Chem. Soc. (C) 438 (1966)

"Unsaturated Carbohydrates. Part IV. Allylic Rearrangement Reactions of 3,4,6-Tri-O-acetyl-D-galactal"  
D. M. Ciment and R. J. Ferrier  
J. Chem. Soc. (C) 441 (1966)

"Light-induced and Related Reactions of Quinones. Part I. The Mechanism of Formation of Acetylquinol from 1,4-Benzoquinone and Acetaldehyde"  
J. Malcolm Bruce and E. Cutts  
J. Chem. Soc. (C) 449 (1966)

"On the Structure of the Sex Attractant of the American Cockroach"  
A. C. Day and M. C. Whiting  
J. Chem. Soc. (C) 464 (1966)

"Cinnolines. Part VIII. Methylation of Some Substituted Cinnolines"  
D. E. Ames, R. F. Chapman and D. Waite  
J. Chem. Soc. (C) 470 (1966)

"Some Substitution Reactions of 1-Methyl- and 2-Methoxy-fluorene"  
E. O. Arene and D. A. H. Taylor  
J. Chem. Soc. (C-Organic) 481 (1966)

"The Reactions of Thiourea with Some Chloropyrazines and their N-oxides"  
J. Cullen and D. Harrison  
J. Chem. Soc. (C) 495 (1966)

"New Metabolites of Gibberella fujikuroi. Part XI. Gibberellin A<sub>14</sub>"  
B. E. Cross  
J. Chem. Soc. (C) 501 (1966)

"West African Timbers. Part XIII. Extracts from the Heartwood of Amphimas pterocarpoides and Pterocarpus erinaceus"  
C. W. L. Bevan, D. E. U. Ekong, M. E. Obasi and J. W. Powell  
J. Chem. Soc. (C) 509 (1966)

"The Acid-catalysed Rearrangement of Tetrahydroquinoline Derivatives"  
W. H. Cliffe, D. Dodman and O. Meth-Cohn  
J. Chem. Soc. (C) 514 (1966)

"A Re-examination of the Friedel-Crafts Acetylation of 2-Bromo-naphthalene"  
R. B. Girdler, P. H. Gore, and J. A. Hoskins  
J. Chem. Soc. (C) 518 (1966)

"The Preparation of Some Polyamino-Compounds"  
A. M. Roe and D. R. Reavill  
J. Chem. Soc. (C) 527 (1966)

"The Stereochemistry and Conformation of (±)-6a,12a-Dihydrorotoxen-12(6H)-one and Natural Rotenoids from Spin-coupling Considerations"  
D. J. Adam, L. Crombie and D. A. Whiting  
J. Chem. Soc. (C) 542 (1966)

"Novel Features in the Chemistry of (±)-6a,12a-Dihydrorotoxen-12(6H)-one, Synthetic Parent Compound of the Natural Rotenoids"  
D. J. Adam, L. Crombie, K. S. Siddalingaiah and D. A. Whiting  
J. Chem. Soc. (C) 544 (1966)

"Aspects of the Chemistry of 6,6a-Dehydrorotenol, Rotenononic Acid and Isoderrisic Acid Acetates"  
D. J. Adam, L. Crombie and D. A. Whiting  
J. Chem. Soc. (C) 550 (1966)

"The Photoisomerisation of Phorone"  
K. J. Crowley, R. A. Schneider and J. Meinwald  
J. Chem. Soc. 571 (1966)

"Mouvements des Molécules d'eau dans les Hydrates. Comparaison des Résultats de RMN et de Diffraction"  
M. Van Meerssche et J.-M. Depreppe  
J. Chim. Phys. 63, 17 (1966)

"Developments in the Nuclear Magnetic Resonance Study of Molecular Motion in Solids"  
E. R. Andrew and F. S. Allen  
J. Chim. Phys. 63, 85 (1966)

"Résonance Magnétique Protonique Mouvements et Changements de Phase de L'Hexaméthylbenzène et du Paradichlorobenzène"  
B. Lemanceau, J.-M. Chezeau et J.-Y. Hache  
J. Chim. Phys. 63, 94 (1966)

"Liberté D'Orientation dans Quelques Benzènes Hexasubstitués Polycristallins"  
C. Brot et I. Darmon  
J. Chim. Phys. 63, 100 (1966)

"Étude Comparée des Mouvements de Réorientation Moléculaire des Benzènes Penta et Hexasubstitués à L'État Solide: I. — Examen du spectre de résonance magnétique Protonique"  
M. Eveno et J. Meinnel  
J. Chim. Phys. 63, 108 (1966)

"Analyse du Spectre de Résonance Magnétique Nucléaire d'un Système de Six Noyaux de Spin  $\frac{1}{2}$  Chimiquement Équivalents Deux à Deux"  
C. Barbier, H. Faucher, D. Gagnaire et A. Rousseau  
J. Chim. Phys. 63, 283 (1966)

"Synthesis and Some Physical and Chemical Properties of 3-Alken-1-Ynylgermanes"  
M. D. Stadnichuk and A. A. Petrov  
J. Gen. Chem. USSR (English Transl) 35, 448 (1965)

"Arylcarbenes from Aryllithiums and Methylene Chloride"  
O. M. Nefedov, V. I. Shiryaev, and A. S. Khachaturov  
J. Gen. Chem. USSR (English Transl) 35, 509 (1965)

"Structure of Grosshemin, A Sesquiterpene Lactone from Grossheimia macrocephala (MUSS.-PUSCHK.) D. Sosn. Et Takht."  
K. S. Rybalko and V. I. Sheichenko  
J. Gen. Chem. USSR (English Transl) 35, 578 (1965)

"Unsaturated Organogermanium Compounds. II. Course of the Bromination of 1, 3-Enynic Germa-hydrocarbons"  
M. D. Stadnichuk and A. A. Petrov  
J. Gen. Chem. USSR (English Transl) 35, 701 (1965)

"Fused Small-Ring Compounds. II. Solvolysis Reactions of Some *cis*- and *trans*-Bicyclo[3.2.0]heptane Derivatives"  
J. Meinwald, P. Anderson and J. J. Tufariello  
J. Am. Chem. Soc. 88, 1301 (1966)

"Structure and Synthesis of the Major Components in the Hairpencil Secretion of a Male Butterfly, *Lycorea ceres* *ceres* (Cramer)"  
J. Meinwald and Y. C. Meinwald  
J. Am. Chem. Soc. 88, 1305 (1966)

"Novel Reactions of Olefin-Metal Carbonyl Complexes"  
H. D. Kaesz, S. Winstein, and C. G. Kreiter  
J. Am. Chem. Soc. 88, 1319 (1966)

"Stereochemistry of the Grignard Reagents from *exo*- and *endo*-Norbornyl Chlorides"  
N. G. Krieghoff and D. O. Cowan  
J. Am. Chem. Soc. 88, 1322 (1966)

"Characterization of Functional Groups by Nuclear Magnetic Resonance. I. Classification of Alcohols from the Fluorine-19 Spectra of Trifluoroacetates"  
S. L. Manatt  
J. Am. Chem. Soc. 88, 1323 (1966)

"[2.2]Metaparacyclophane, a Highly Strained Ring System"  
D. J. Cram, R. C. Helgeson, D. Lock and L. A. Singer  
J. Am. Chem. Soc. 88, 1324 (1966)

"Intermediates in the Conversion  $\pi$ - to  $\sigma$ -Allylic Complexes of Palladium"  
G. L. Statton and K. C. Ramey  
J. Am. Chem. Soc. 88, 1327 (1966)

"A Convenient Synthesis of the Cubane System"  
J. C. Barborak, L. Watts and R. Pettit  
J. Am. Chem. Soc. 88, 1328 (1966)

"Photoreduction of a  $\beta,\gamma$ -Unsaturated Ketone"  
R. L. Cargill, J. R. Damewood and M. M. Cooper  
J. Am. Chem. Soc. 88, 1330 (1966)

"The Addition of  $B_2Cl_4$  to 1,3-Cyclohexadiene and the Structural Similarity of the Adduct to That Formed between  $B_2/Cl_4$  and Naphthalene"  
M. Zeldin and T. Wartik  
J. Am. Chem. Soc. 88, 1336 (1966)

"Stereochemistry of the Glutamate Mutase Reaction"  
M. Sprecher, R. L. Switzer, and D. B. Sprinson  
J. Biol. Chem. 241, 864 (1966)

"Kinetic and Magnetic Resonance Studies of the Pyruvate Kinase Reaction"  
A. S. Mildvan and M. Cohn  
J. Biol. Chem. 241, 1178 (1966)

"Instructional NMR Instrument"  
M. H. Proffitt and W. C. Gardiner, Jr.  
J. Chem. Educ. 43, 152 (1966)

"The Nuclear Magnetic Resonance Spectra of Cyclopentenones"  
C. H. Depuy, C. E. Lyons and L. B. Rodewald  
J. Chem. Eng. Data 11, 102 (1966)

"NMR Studies of Inorganic Fluorides. I. High-Resolution  $^{19}F$  Spectra of  $Si_2F_6$  and  $(SiF_3)_2O$ "  
R. B. Johannesen, T. C. Farrar, F. E. Brinckman and T. D. Coyle  
J. Chem. Phys. 44, 962 (1966)

"NMR Spectrum of a Nearly Linear Five-Spin System: Hydrogen Bonding in  $KH_2F_3$ "  
R. Blinc, Z. Trontelj, and B. Volavsek  
J. Chem. Phys. 44, 1028 (1966)

"Spin-Rotation Interactions in Polyatomic Molecules"  
R. G. Gordon  
J. Chem. Phys. 44, 1184 (1966)

"Oxygen-17 NMR in Polycrystalline  $H_2O$  and  $D_2O$  Ice"  
S. W. Rabideau and P. Waldstein  
J. Chem. Phys. 44, 1302 (1966)

"Erratum: Nuclear Magnetic Shielding Constants and X-Ray Atomic Scattering Factors for Two-, Three-, and Four-Electron Systems by Means of Analytic Hartree-Fock Wavefunctions"  
M. L. Rustgi and P. Tiwari  
J. Chem. Phys. 44, 1310 (1966)

"NMR Study of Electron Transfer Rates and Spin Densities in *p*-Xylene and *p*-Diethylbenzene Anions"  
E. de Boer and C. MacLean  
J. Chem. Phys. 44, 1334 (1966)

"Nuclear Magnetic Relaxation in Ionic Solution. I. Relaxation of  $^{23}Na$  in Aqueous Solutions of NaCl and  $NaClO_4$ "  
M. Eisenstadt and H. L. Friedman  
J. Chem. Phys. 44, 1407 (1966)

"Nuclear Magnetic Relaxation of Polymer Solutions, Side-Chain Motion"  
R. Ullman  
J. Chem. Phys. 44, 1558 (1966)

"Spin Delocalization in the Allyl and Ethyl Radicals"  
D. Lazzdins and M. Karplus  
J. Chem. Phys. 44, 1600 (1966)

"Metal Carbonyl Chemistry. Part I. The Reactions of Phosphorus-containing Ligands with Hydridopentacarbonylmanganese"  
B. L. Booth and R. N. Haszeldine  
J. Chem. Soc. (A) 157 (1966)

" $\sigma$ -Bonded Organotransition-Metal Ions. Part II. Kinetics and Mechanism of the Aerobic Acidolysis of Penta-aquo (pyridimethyl)chromium(III) Ions"  
R. G. Coombes and M. D. Johnson  
J. Chem. Soc. (A) 177 (1966)

"Pyrolysis of Di(isobutylamino)phenylboron"  
J. A. Semlyen and P. J. Flory  
J. Chem. Soc. (A) 191 (1966)

"Metal Carbonyl Chemistry. Part II. The Reaction of Phenyl- or Methyl-manganese Carbonyl with Butadiene"  
W. D. Bannister, M. Green and R. N. Haszeldine  
J. Chem. Soc. (A) 194 (1966)

"The Reaction between Difluorotrichloromethylphosphine and Secondary Amines: A New Synthesis of Aminodifluorophosphines"  
C. G. Barlow and J. F. Nixon  
J. Chem. Soc. (A) 228 (1966)

"Polyene Acids. Part IX. Proton Magnetic Resonance Parameters of the Muconic Esters and Mucononitriles"  
J. A. Elvidge and P. D. Ralph  
J. Chem. Soc. (C) 387 (1966)

"Studies in the Synthesis of Terpenes. Part IX. The Reactions of Formaldehyde and Acetaldehyde with Ethyl Cyclohexanone-2-glyoxylate"  
T. G. Halsall and J. M. Mellor  
J. Chem. Soc. (C) 397 (1966)

- "Pressure Dependence of the Knight Shift in Lead, Platinum, and Tin"  
G. A. Matzkanin and T. A. Scott  
Bull. Am. Phys. Soc. 11, 220 (1966)
- "Nuclear Magnetic Resonance in Titanium Metal"  
A. Narath  
Bull. Am. Phys. Soc. 11, 220 (1966)
- "Reaction of Phenylmagnesium Bromide with Six- and Five-Membered Steroid Lactones"  
M. M. Rogic  
Bull. Chem. Soc. Belgrade (English Transl.) 29, 57 (1964)
- "Studies of Organic Catalytic Reactions. III. The Hydration Mechanism of Nitriles to Amides with Nickel Catalysts"  
K. Watanabe and K. Sakai  
Bull. Chem. Soc. Japan 39, 8 (1966)
- "Organic Syntheses by Means of Noble Metal Compounds. XIV. The Carbonylation of Cyclooctadienes"  
J. Tsuji, S. Hosaka, J. Kiki and T. Susuki  
Bull. Chem. Soc. Japan 39, 141 (1966)
- "Organic Syntheses by Means of Noble Metal Compounds. XV. The Carbonylation of 1, 5, 9-Cyclododecatriene Catalyzed by Palladium"  
J. Tsuji and T. Nogi  
Bull. Chem. Soc. Japan 39, 146 (1966)
- "Shift Values of Aromatic Aldehyde Protons"  
M. Anteunis and Y. Rommelaere  
Bull. Soc. Chim. Belges 75, 89 (1966)
- "Triterpenes V. Spectroscopie de Résonance Magnétique Nucléaire de Composés Triterpéniques. Les Groupes Méthyles en Série Oléanénique"  
B. Tursch, R. Savoir et G. Chiurdoglu  
Bull. Soc. Chim. Belges, 75, 107 (1966)
- "Aminocyclitols. VIII. A Synthesis of Inosamines and Inosadamines"  
T. Suami, F. W. Lichtenthaler and S. Ogawa  
Bull. Chem. Soc. Japan 39, 170 (1966)
- "The Base-catalysed Oxidation of Friedelin with Molecular Oxygen"  
T. Nishihama and T. Takahashi  
Bull. Chem. Soc. Japan 39, 200 (1966)
- "Préparation d'hétérocycles encombrés: di-t-butyl-2,5 furanne, pyrrole et thiophène"  
R. Ramasseul et A. Rassat  
Bull. Soc. Chim. France 3136 (1965)
- "Réduction alcoylation des cétones à caractères aromatiques"  
J. A. Gautier, M. Miocque, C. Fauran, M. D. D'Engenieres  
Bull. Soc. Chim. France 3162 (1965)
- "Sur la préparation des alcools  $\alpha$ - $\alpha$ -dichlorés"  
R. Nouri-Bimorghi  
Bull. Soc. Chim. France 3178 (1965)
- "Extension des règles de Zurcher aux spectres de RMN de diméthyl-4,4 stéroïdes"  
M. Fetizon, M. Golfier et P. Laszlo  
Bull. Soc. Chim. France 3205 (1965)
- "Dérivés du 5 $\alpha$ -Cholestane portant en position 4 $\beta$  une fonction aldéhyde, acide, ester, nitrile ou alcool primaire"  
S. Julia et C. Moutonnier  
Bull. Soc. Chim. France 3211 (1965)
- "Alcaloïdes stéroïdiques. XLII.— Synthèse des quatre diméthylamino-3 hydroxy-4 pregnane-5 $\alpha$  diastéréoisomères"  
P. Longevialle et R. Goutarel  
Bull. Soc. Chim. France 3225 (1965)
- "Le longifolène (XIII) (I). Hydrogénation due longifolène"  
J. Carnduff et G. Ourisson  
Bull. Soc. Chim. France 3297 (1965)
- "Réduction de la fenchone, épimérisation des fenchols"  
A. Coulombeau et A. Rassat  
Bull. Soc. Chim. France 3338 (1965)
- "Synthèse et réactions des époxydes de benzyloxy-2\* chalcones"  
J. Chopin et P. Durual  
Bull. Soc. Chim. France 3350 (1965)
- "Préparation et propriétés de deux cyano- benzothiazolines homologues"  
H. Wahl et J.-J. Vorsanger  
Bull. Soc. Chim. France 3359 (1965)
- "Isomérisations photochimiques et chimiques d'un dérivé du cyclohexadiène-1,3, 1'acide trans-cyclohexadiène-3,5 dicarboxylique-1,2"  
P. Courtot et J.-M. Robert  
Bull. Soc. Chim. France 3362 (1965)
- "Benzophenone-Sensitized Photolysis of Cyclopentene. Preparation of meso- and DL-3,3'-Bicyclopentenyl"  
K. S. Sidhu, O. P. Strausz and H. E. Gunning  
Can. J. Chem. 44, 531 (1966)
- "Hydroxyl Proton Magnetic Resonance in Relation to Ring Size, Substituent Groups, and Mutarotation of Carbohydrates"  
A. S. Perlin  
Can. J. Chem. 44, 539 (1966)
- "The Correlation of Chasmanine with Browniine"  
O. E. Edwards, L. Fonzes and L. Marion  
Can. J. Chem. 44, 583 (1966)
- "The Reaction of Caryophyllene and Diazoacetic Ester; Some Observations on Cyclopropanes"  
E. W. Warnhoff and V. Dave  
Can. J. Chem. 44, 621 (1966)
- "On the Condensation of p-Cresol with Glyoxal"  
B. S. Thyagarajan, K. K. Balasubramanian, and R. Bhima Rao  
Can. J. Chem. 44, 633 (1966)
- "The Preparation and Characterization of cis- and trans-2-Hydro-3-Chlorohexafluoro-2-Butene"  
D. J. Burton, R. L. Johnson, and R. T. Bogan  
Can. J. Chem. 44, 635 (1966)
- "Die Struktur des Triphenylallen-Dimeren"  
K. Rewicki  
Chem. Ber. 99, 392 (1966)
- "Eine Allylwanderung der Nitrogruppe bei der Reaktion 2.4.6-triarylierter Pyryliumsalze mit Phenylnitromethan"  
K. Dimroth und H. Wache  
Chem. Ber. 99, 399 (1966)
- "Synthese und Struktur von Heptachlor-methano-tetrahydro-indanen"  
K. H. Michel, A. E. Ginsberg und R. Fischer  
Chem. Ber. 99, 405 (1966)

"Synthese und Eigenschaften von Aziridincarbonstureestern"  
E. Kyburz, H. Els, St. Majnoni, G. Englert, C. von Planta,  
A. Fürst und Pl. A. Plattner  
Helv. Chim. Acta 49, 359 (1966)

"Synthesen in der Carotinoid-Reihe. 20. Mitteilung. Neue  
Synthesen von Apocarotinoiden"  
U. Schwieter, H. Gutmann, H. Lindlar, R. Marbet, N. Rigassi,  
R. Rüegg, S. F. Schaefer und O. Isler  
Helv. Chim. Acta 49, 369 (1966)

"Synthesen in der Isochinolinreihe. Zur Darstellung 6,7,8-  
Hydroxy-dimethoxy-substituierter 1,2,3,4-Tetrahydro-  
isochinoline aus 3-Benzoyloxy-4,5-dimethoxy-phenethylamin und  
Bericht über die Resultate der pharmakologischen Prüfung  
von Anhalamin, Anhalidin, rac. Anhalonidin und rac. Pellotin"  
A. Brossi, F. Schenker, R. Schmidt, R. Banziger und W.  
Leimgruber  
Helv. Chim. Acta 49, 403 (1966)

"Réactions du phényl-3-chlorométhyl-5-oxadiazole-1,2,4 dans  
le diméthylsulfoxyde"  
R. Jaunin  
Helv. Chim. Acta 49, 412 (1966)

"Reaktionen von Steroid-Hypojoediten VIII) 1,3-Verschiebung  
der Nitrilgruppe) (18-Cyano-pregnane)"  
J. Kalvoda, Ch. Meystre und G. Anner  
Helv. Chim. Acta 49, 424 (1966)

"Synthese und Eigenschaften eines Spirotetrens. Spiro[5.5]  
undeca-1,4,7,10-tetraen-3,9-dion"  
G. Farges und A. S. Dreiding  
Helv. Chim. Acta 49, 552 (1966)

"Über Muscarin. 14 Mitteilung. Konfigurative Zusammenhänge"  
E. Hardegger, N. Chariatte und N. Halder  
Helv. Chim. Acta 49, 580 (1966)

"Über zwei cycloisomere Triglycyl-tri-L-alanyle"  
H. Gerlach, G. Haas und V. Prelog  
Helv. Chim. Acta 49, 603 (1966)

"Etudes sur les matières végétales volatiles CXC VII [1]  
Sur la structure du «diépoxyde d'allo-ocimène», les  
«légénols et les légénones»  
Y.-R. Naves et P. Ardizio  
Helv. Chim. Acta 49, 617 (1966)

"Zur Kenntnis der Hexalkylbenzole. 9. Mitteilung. Zur  
Cyclisierung polyalkylierter o-Benzoylbenzoesäuren"  
H. Hopff und A. Gati  
Helv. Chim. Acta 49, 644 (1966)

"3-Hydroxy-1,2,4-benzotriazin-1-oxid-7-carbonsäure und  
verwandte Verbindungen"  
K. Brenneisen, O. Thumm und J. Benz  
Helv. Chim. Acta 49, 651 (1966)

"Stoffwechselprodukte von Mikroorganismen. 50. Mitteilung.  
Die Konfiguration der Arcanose"  
G. Roncari und W. Keller-Schierlein  
Helv. Chim. Acta 49, 705 (1966)

"Die absolute Konfiguration von 1-<sup>2</sup>H<sub>1</sub>-Äthanol"  
H. Weber, J. Seibl und D. Arigoni  
Helv. Chim. Acta 49, 741 (1966)

"Recherches sur la formation et la transformation des esters  
LXIV[1]. Acides aminocoylsulfuriques et isothiocyanates:  
N-thiocarbamylation sans ou avec alcoylation cyclisante  
intramoléculaire"  
E. Cherbuliez, Br. Baehler, S. Jaccard, H. Jindra, G. Weber,  
G. Wyss et J. Rabinowitz  
Helv. Chim. Acta 49, 807 (1966)

"Une Méthode de Mesure des Temps de Relaxation Nucléaire  
pour Signaux Très Faibles"  
P. Cornaz  
Helv. Phys. Acta, 38, 813 (1966)

"Relaxation Magnétique Nucléaire par Contact Avec des  
Surfaces Solides"  
P. Cornaz  
Helv. Phys. Acta, 38, 813 (1966)

"Phenoxylation and Aminolysis of Diphenyltetrachlorotri-  
phonitrile. The Use of Nuclear Magnetic Resonance for  
Structural Determination"  
C. T. Ford, J. M. Barr, F. E. Dickson and I. I. Bezman  
Inorg. Chem. 5, 351 (1966)

"Studies on the Hydrolysis and Structure of the Aquodimethyl-  
lead(IV) Ion by Electromotive Force Measurements and by  
Raman and Proton Nuclear Magnetic Resonance Spectroscopy"  
C. E. Freidline and R. S. Tobias  
Inorg. Chem. 5, 354 (1966)

"Infrared and Nuclear Magnetic Resonance Spectra of Hydro-  
xytrimethylplatinum(IV)"  
G. L. Morgan, R. D. Rennick and C. C. Soong  
Inorg. Chem. 5, 372 (1966)

"The Coordinate Bonding in Transition Metal Complexes of  
2-Carbamoyldimedone"  
E. P. Dudek and M. L. Snow  
Inorg. Chem. 5, 395 (1966)

"The Reaction of Hexacarbonylvanadium with Aromatic Compounds.  
III. Reduction of the [V(CO)<sub>6</sub>arene]<sup>+</sup>Cations to Tetracarbonyl  
- $\eta$ -cyclohexadienylvanadium Derivatives"  
F. Calderazzo  
Inorg. Chem. 5, 429 (1966)

"Deuterio Derivatives of 2,3-Dicarbahehexaborane(8). Forma-  
tion of 2,3-Dicarbaheptahydrohexaborate(1-)"  
T. Onak and G. B. Dunks  
Inorg. Chem. 5, 439 (1966)

"Borazines Stable to Hydrolysis"  
K. Nagasawa  
Inorg. Chem. 5, 442 (1966)

"A Nuclear Magnetic Resonance Study of Hydrogen Bonding in  
Tris(2-N-methylaminoethyl) Borate and Similar Compounds"  
D. W. Meek and C. S. Springer, Jr  
Inorg. Chem. 5, 445 (1966)

"Reactions of Hexachloro- and 2,2,4,4-Tetrachloro-6,6-  
diphenylcyclotriphosphazatrienes with Sodium Phenoxide"  
E. T. McBee, K. Okuhara and C. J. Morton  
Inorg. Chem. 5, 450 (1966)

"Fluorosulfuric Acid Solvent System. III. Cryoscopic  
Measurements"  
R. J. Gillespie, J. B. Milne, and R. C. Thompson  
Inorg. Chem. 5, 468 (1966)

"Group III Alkyl Adducts of Transition Metal Cyclopenta-  
dienides"  
E. Brunner, P. C. Wailles and H. D. Kaesz  
Inorg. Nucl. Chem. Letters 1, 125 (1965)

"On the Structure of Dimethylthallium Acetylacetonate in  
Solution"  
H. Kurosawa, K. Yasuda, R. Okawara  
Inorg. Nucl. Chem. Letters 1, 131 (1965)

"Chemistry of Boranes. XXVI. Inner Diazonium Salts 1,10-B<sub>10</sub>  
H<sub>2</sub>(N<sub>2</sub>)<sub>2</sub>, -B<sub>10</sub>Cl<sub>8</sub>(N<sub>2</sub>)<sub>2</sub>, and -B<sub>10</sub>I<sub>8</sub>(N<sub>2</sub>)<sub>2</sub>"  
W. H. Knoth  
J. Am. Chem. Soc. 88, 935 (1966)

"The Preparation of a Compound Containing Silicon, Boron and  
Nitrogen in the Same Small Ring"  
R. L. Wells and R. W. Nelson  
Inorg. Nucl. Chem. Letters 1, 149 (1965)

"Fluorinated 1,2,3-Triazolines"  
W. Carpenter, A. Haymaker, and D. W. Moore  
J. Org. Chem. 31, 789 (1966)

"A New General Synthesis of Benzo[a]quinolizines, Dibenzo[a],  
f,quinolizines, and Related Compounds"  
M. von Strandtmann, M. P. Cohen, and J. Shavel, Jr.  
J. Org. Chem. 31, 797 (1966)

"3-Aryl-1,2-dihydroquinoxalines"  
J. Figueras  
J. Org. Chem. 31, 803 (1966)

"Ten- -Electron Nitrogen Heterocyclic Compounds. IV. The  
Synthesis, Bromination, and Nuclear Magnetic Resonance  
Spectra of Some Imidazo[1,2-a]pyrimidines"  
W. W. Paudler and J. E. Kuder  
J. Org. Chem. 31, 809 (1966)

" $\beta$  Elimination of Glycoside Monosaccharide from a 3-O-(2-  
Amino-2-deoxy-D-glucopyranosyl)serine. Evidence for an  
Intermediate in Glycoprotein Hydrolysis"  
J. R. Vercellotti and A. E. Luetzow  
J. Org. Chem. 31, 825 (1966)

"Organic Sulfur Compounds. XVIII. Selective Addition of  
Thiols and Thiol Acids to Diallyl Maleate and Fumarate"  
A. A. Oswald and W. Naegele  
J. Org. Chem. 31, 830 (1966)

"The Mechanism of the Alkyl Sulfide-Sulfinic Acid Reaction.  
The Direction of Cleavage of Unsymmetrical Sulfides"  
J. L. Kice, B. R. Toth, D. C. Hampton and J. F. Barbour  
J. Org. Chem. 31, 848 (1966)

"Reactions of Phosphorus Compounds. VIII. Preparation of  
Pyrrolizidine Compounds from Vinyltriphenylphosphonium  
Bromide"  
E. E. Schweizer and K. K. Light  
J. Org. Chem. 31, 870 (1966)

"Ring-Size Effects in the Neophyl Rearrangement. VI. The  
1-Phenylcycloheptylcarbinyl System"  
J. W. Wilt, J. F. Zawadzki, and D. G. Schultenover, S. J.  
J. Org. Chem. 31, 876 (1966)

"Synthesis of 1-Demethyltoxoflavin (8-Demethylfervenulin)"  
T. K. Liao, F. Baiocchi, and C. C. Cheng  
J. Org. Chem. 31, 900 (1966)

"Rearrangement Products of 9-Acetoxy- and 9-Hydroxy-2,5,9-  
trimethyl-6,7-benzomorphan"  
R. T. Parfitt, E. M. Fry, and E. L. May  
J. Org. Chem. 31, 903 (1966)

"Alkyl- and Aryltricyanomethanes. Synthesis and Properties"  
J. K. Williams, E. L. Martin, and W. A. Sheppard  
J. Org. Chem. 31, 919 (1966)

"Reactions of Tetraalkyl-2-tetrazenes with Tetranitromethane"  
W. E. Thun, D. W. Moore, and W. R. McBride  
J. Org. Chem. 31, 923 (1966)

"New Friedel-Crafts Chemistry. XVII. Synthesis of Some  
Pure Di- and Triphenylalkanes. Identification of By-  
products from Carbonium Ion Processes"  
A. A. Khalaf and R. M. Roberts  
J. Org. Chem. 31, 926 (1966)

"Free-Radical Reactions of Fluoroalkanesulfenyl Halides.  
II. Free-Radical Reactions of Trifluoromethanesulfenyl  
Chloride with Alkanes"  
J. F. Harris, Jr.  
J. Org. Chem. 31, 931 (1966)

"Studies on the Azidoazomethine-Tetrazole Equilibrium. IV.  
Azidopurines"  
C. Temple, Jr., M. C. Thorpe, W. C. Coburn, Jr., and J. A.  
Montgomery  
J. Org. Chem. 31, 935 (1966)

"The Chemistry of Pyridine. IV. The Substitution of  
Quinoline 1-Oxide by Mercaptans"  
L. Bauer and T. E. Dickerhofe  
J. Org. Chem. 31, 939 (1966)

"Ketenes. VIII. Some Reactions of 1-(Dimethylamino)-4-  
methyl-1-penten-3-one"  
J. C. Martin, K. R. Barton, P. Glenn Gott, and R. H. Meen  
J. Org. Chem. 31, 943 (1966)

"Sterically Hindered Group IV-A Organometallics. V. Prep-  
aration and Properties of Certain Neopentyl- and Neo-  
phylls"  
H. Zimmer and O. A. Homberg  
J. Org. Chem. 31, 947 (1966)

"Preparation and Proton Magnetic Resonance of Some Neopentyl  
Derivatives of Lead. Long Range  $Pb^{207}-H^1$  Coupling"  
G. Singh  
J. Org. Chem. 31, 949 (1966)

"3d-Orbital Resonance in Trivalent Organophosphines. II.  
Additions of Organolithium Compounds to Vinylphosphines"  
D. J. Peterson  
J. Org. Chem. 31, 950 (1966)

"Fluoride Ion Initiated Reactions of Perfluoro  $\alpha$ -Olefins.  
I. Reaction of the Pentafluoroethyl Carbanion with  
Tetrafluoroethylene"  
D. P. Graham  
J. Org. Chem. 31, 955 (1966)

"Fluoride Ion Initiated Reactions of Perfluoro  $\alpha$ -Olefins.  
II. The Condensation of Tetrafluoroethylene with  
Perfluoro Ketones to Yield Perfluoro Tertiary Alcohols"  
D. P. Graham and V. Weinmayr  
J. Org. Chem. 31, 957 (1966)

"Fluoride Ion Initiated Reactions of Perfluoro  $\alpha$ -Olefins.  
III. The Condensation of Perfluoro  $\alpha$ -Olefins with Carbon  
Dioxide to Yield Perfluoro Carboxylic Acids"  
D. P. Graham and W. B. McCormack  
J. Org. Chem. 31, 958 (1966)

"The Reductive Dimerization of Tropylium Ion by Cycloocta-  
tetraene Dianion"  
R. W. Murray and M. L. Kaplan  
J. Org. Chem. 31, 962 (1966)

"1,3-Di-t-butylcyclohexene"  
R. D. Stelow and J. A. Ward  
J. Org. Chem. 31, 965 (1966)

"An Efficient Synthesis of cis-Jasmone"  
G. Buchi and H. Wuest  
J. Org. Chem. 31, 977 (1966)

"Synthesis of Menthenone and Dihydro Rose Oxide"  
K. C. Brannock and H. E. Davis  
J. Org. Chem. 31, 980 (1966)

"Synthesis of  $\beta$ -Substituted Alkylamines via Alkylation  
of N,N-Disubstituted Amides"  
P. G. Gassman and B. L. Fox  
J. Org. Chem. 31, 982 (1966)

"Alkylation of N,N-Dimethylamides via Carbanion Intermediates"  
H. L. Needles and R. E. Whitfield  
J. Org. Chem. 31, 989 (1966)



"Metall-Bor-Verbindungen. I. Bis(Dimethylamino)Bor-Mangan-carbonyl und Einige Seiner Derivate"  
H. Nöth und G. Schmid  
J. Organometal. Chem. 5, 109 (1966)

"An NMR Study of Arenechromium Tricarbonyl Complexes"  
W. McFarlane and S. O. Grim  
J. Organometal. Chem. 5, 147 (1966)

"Résonance Magnétique Nucléaire des Dérivés Acétyléniques des Éléments des Colonnes IVb, Vb et VIb. Déplacements Chimiques et Constantes de Couplage Hétéroatome-Proton À Longue Distance"  
M.-P. Simonnin  
J. Organometal. Chem. 5, 155 (1966)

"Spektroskopische Untersuchungen an Organometallischen Verbindungen. XXXV. <sup>1</sup>H-NMR-, IR- und UV-Spektren von Cyclopentadienyl-Platin-Verbindungen"  
H. P. Fritz und K.-E. Schwarzthans  
J. Organometal. Chem. 5, 181 (1966)

"Halomethyl-metal compounds. III. The Reaction of Phenyl (trihalomethyl)- and Phenyl(dihalomethyl)mercury Compounds with Trialkyl Phosphites"  
D. Seyferth, J. Yick-Pui Mui, and G. Singh  
J. Organometal. Chem. 5, 185 (1966)

"A Nuclear Magnetic Resonance Study of Diethylamine Hydrogen Bonding"  
C. S. Springer, Jr., and D. W. Meek  
J. Phys. Chem. 70, 481 (1966)

"Water <sup>17</sup>O Nuclear Magnetic Resonance Shift in Aqueous Solutions of 1:1 Electrolytes"  
Z. Luz and G. Yagil  
J. Phys. Chem. 70, 554 (1966)

"Phosphorus-31 Chemical Shifts of Quaternary Phosphonium Salts"  
S. O. Grim, W. McFarlane, E. F. Davidoff, and T. J. Marks  
J. Phys. Chem. 70, 581 (1966)

"Self-Diffusion in Cyclohexane-Benzene Solutions"  
D. W. McCall and E. W. Anderson  
J. Phys. Chem. 70, 601 (1966)

"Correlation of Nuclear Magnetic Resonance and Infrared Spectra in Two Cyanophosphines"  
I. B. Johns, H. R. DiPietro, R. H. Nealey, and J. V. Pustinger, Jr.  
J. Phys. Chem. 70, 924 (1966)

"Keto-Enol Tautomerism in  $\beta$ -Dicarbonyls Studied by Nuclear Magnetic Resonance Spectroscopy. III. Studies of Proton Chemical Shifts and Equilibrium Constants at Different Temperatures"  
J. L. Burdett and M. T. Rogers  
J. Phys. Chem. 70, 939 (1966)

"The Interpretation of Secondary Transitions in Polymers"  
D. W. McCall  
J. Phys. Chem. 70, 949 (1966)

"Nuclear Magnetic Relaxation in Liquid Metals, Alloys and Salts"  
M. Hanabusa and N. Bloembergen  
J. Phys. Chem. Solids 27, 363 (1966)

"Narrowing of Nuclear Magnetic Resonance Lines in a Double Frequency RF Field"  
S. S. Jha  
J. Phys. Soc. Japan 21, 42 (1966)

"NMR Study of Ferroelectric Diglycine Nitrate"  
K. R. K. Easwaran  
J. Phys. Soc. Japan 21, 61 (1966)

"Nuclear Magnetic Resonance in Co Alloys"  
S. Kobayashi, K. Asayama and J. Itoh  
J. Phys. Soc. Japan 21, 65 (1966)

"Temperature Effects on the Nuclear Magnetic Resonance Lines in Borates"  
V. Saraswati and R. Vijayaraghavan  
J. Phys. Soc. Japan 21, 74 (1966)

"Spin Echo Modulation Caused by the Quadrupole Interaction and Multiple Spin Echoes"  
H. Abe, H. Yasuoka and A. Hirai  
J. Phys. Soc. Japan 21, 77 (1966)

"Nuclear Magnetic Resonance in Ferroelectric Sodium Nitrite"  
H. Betsuyaku  
J. Phys. Soc. Japan 21, 187 (1966)

"NMR Spectra of Polyacrylonitriles"  
K. Matsuzaki and M. Takeuchi  
J. Polymer Sci. B4, 93 (1966)

"Über die katalytische Wirksamkeit tertiärer Amine bei der Addition von Äthylenoxid an Phenol"  
F. Patat und R. Erlmeier  
Makromol. Chem. 91, 231 (1966)

"A Nuclear Magnetic Resonance Study of Mercury Dimethyl"  
K. A. McLaughlan and D. H. Whiffen  
Mol. Phys. 10, 131 (1966)

"Non-aqueous Solutions of Electrolytes. I. The <sup>75</sup>As Nuclear Magnetic Spin-lattice Relaxation Times of the Hexafluoroarsenate Ion"  
M. St. J. Arnold and K. J. Packer  
Mol. Phys. 10, 141 (1966)

"Molecular Motion in Liquid Benzene by Nuclear Magnetic Resonance"  
J. G. Powles and R. Figgins  
Mol. Phys. 10, 155 (1966)

"Study of an External Spherical Reference System for N.M.R. Spectroscopy"  
D. J. Frost and G. E. Hall  
Mol. Phys. 10, 191 (1966)

"Electrical Conductivity and Nuclear Magnetic Resonance Chemical Shift in Caesium Silicate Glasses"  
M. E. Milberg, K. Otto and T. Kushida  
Phys. Chem. Glasses 7, 14 (1966)

"<sup>27</sup>Al and <sup>89</sup>Y Nuclear Magnetic Resonance in Yttrium-Aluminum Garnet"  
K. C. Brog, W. H. Jones, Jr. and C. M. Verber  
Physics Letters 20, 258 (1966)

"Nuclear Magnetic Resonance of Indium Metal at 4.2°K"  
J. E. Adams, L. Berry, and R. R. Hewitt  
Phys. Rev. 143, 164 (1966)

"Spin-Lattice Coupling of a Kramers Doublet: Co<sup>2+</sup> in MgO"  
E. B. Tucker  
Phys. Rev. 143, 264 (1966)

"Nuclear Spin Relaxation in Gallium Metal"  
R. H. Hammond, E. G. Wikner, and G. M. Kelly  
Phys. Rev. 143, 275 (1966)

"The Structures of Fatty Acids Elaborated by Avirulent Strains of Tubercle Bacillus"

J. D. Burke  
Dissertation Abstr. 26, 2636 (1966)

"The Chemistry of N-Halohexamethyldisilazanes and Base Catalyzed Rearrangements of Organosilylhydrazines"

R. E. Bailey  
Dissertation Abstr. 26, 3620 (1966)

"Temperature Dependence of Transverse Relaxation Time of Oxygen-17 in Aqueous Solutions Containing Cupric and Chromous Ions"

C. W. Merideth  
Dissertation Abstr. 26, 3622 (1966)

"Synthesis and Reactions of 7-Azabenzonorbornadiene and Related Compounds"

D. E. Barr  
Dissertation Abstr. 26, 3626 (1966)

"The Synthesis and Reactions of Aziridinones ( $\alpha$ -Lactams)"

J. J. Fuerholzer  
Dissertation Abstr. 26, 3629 (1966)

"The Synthesis of 1-,2-,3- and 4-Chloroanthrone"

E. D. Bergmann, J. Blum and E. Kariv  
Israel J. Chem. 3, 91 (1965)

"Nucleophilic Substitution Reactions of Isomeric Propargyl and Allenyl Halides- The Mechanism of the Base-Catalyzed Solvolyses of 3-Bromo-3-Methyl-1-Butyne and 1-Bromo-3-Methyl-1,2-Butadiene"

J. S. Humphrey  
Dissertation Abstr. 26, 3632 (1966)

"A Study of the Carbonyl Doublet in 2-Indanone and trans-Hexahydro-2-Indanone; Conformational Problems"

J. P. St. George  
Dissertation Abstr. 26, 3636 (1966)

"New Concepts in Organo-Boron Chemistry"

L. H. Toporcer  
Dissertation Abstr. 26, 3640 (1966)

"Part I; Physical Chemical Study of the Hydrogen Bonded Binary System 2,2,3,3-Tetrafluoro-1-Propanol-Water.

Part II: Adsorption Studies of Atactic Poly-(Isopropyl Acrylate) from Solution onto a Silica Surface"

G. E. Gajnos  
Dissertation Abstr. 26, 3647 (1966)

"Dilute Solution Properties of Poly(P-Isopropylstyrene) and its Graft Copolymer with Poly(ethyl Methacrylate)"

F. S. Holahan  
Dissertation Abstr. 26, 3649 (1966)

"cis-Azoxybenzenes"

D. L. Webb  
Dissertation Abstr. 26, 3657 (1966)

"Nuclear Spins and Moments of  $Sc^{43}$  and  $Ti^{45}$ "

R. G. Cornwell  
Dissertation Abstr. 26, 4018 (1966)

"The Influence of Paramagnetic Impurities on Nuclear Magnetic Resonance Lines"

F. Biggs  
Dissertation Abstr. 26, 4024 (1966)

"On the Mechanism of the Protolysis of Cis- and Trans-  $\beta$ -Chlorovinylmercury Chlorides Under the Influence of HCl and DCl"

I. P. Beletskaya, V. I. Karpov, V. A. Moskalenko and O. A. Reutov  
Dokl. Chem. (English Transl.) 162, 444 (1965)

"Chemical Shifts and Activities of Dienophiles in the Diels-Alder Reaction"

A. I. Kononov  
Dokl. Chem. (English Transl.) 162, 464 (1965)

"A Study of Trihalogermane Etherates by NMR Spectroscopy"

O. M. Nefedov, S. P. Kolensnikov, V. I. Sheichenko and Yu. N. Sheinker  
Dokl. Chem. (English Transl.) 162, 510 (1965)

"Synthesis of 3-Vinylquinuclidine"

L. N. Yakhontov, L. I. Mastafanova, S. L. Portnova and M. V. Rubtsov  
Dokl. Chem. (English Transl.) 162, 577 (1965)

"Fluorocarbon Derivatives of Transition Metals"

F. G. A. Stone  
Endeavour 25, 33 (1966)

"Die Herzglykoside der roten Meerzwiebel (Scilla maritima): Scillirubrosid"

A. von Wartburg  
Helv. Chim. Acta 49, 30 (1966)

"Trennung und stereochemische Zuordnung von zwei substituierten isomeren Thioxanthinoxiden"

W. Michaelis, O. Schindler und R. Signer  
Helv. Chim. Acta 49, 42 (1966)

"Synthese von 2,5-Dimethyl-3-hydroxy- $\Delta^2$ -furenidon-(4), einer Aromakomponente der Ananasfrucht"

A. Hofmann und C. H. Eugster  
Helv. Chim. Acta 49, 53 (1966)

"Regel zur Abschätzung der chemischen Verschiebung von Protonen an einer Doppelbindung"

C. Pascual, J. Meier und W. Simon  
Helv. Chim. Acta 49, 164 (1966)

"Préparations et configurations des esters  $\alpha, \alpha'$ -diméthoxy-muconiques [1]"

A. Gabbaï, A. Melera, D. Janjic et Th. Posternak  
Helv. Chim. Acta 49, 168 (1966)

"Die Konstitution von Epoxydon"

A. Closse, R. Mauli und H. P. Sigg  
Helv. Chim. Acta 49, 204 (1966)

"4H-Benzoc[4,5,cyclohepta[1,2-b]thiophene"

J.-M. Bastian, A. Ebnöther, E. Jucker, E. Rissi und A. P. Stoll  
Helv. Chim. Acta 49, 214 (1966)

"Reaktionen des Hexachlordibenzyls"

C. D. Weis  
Helv. Chim. Acta 49, 234 (1966)

"Photochemische Reaktionen. 32 Mitteilung [1]. UV-Bestrahlung von gesättigten und  $\beta, \gamma$ -ungesättigten, homo-

allylisch konjugierten Steroidaldenhyden"

J. Hill, J. Iriarte, K. Schaffner und O. Jeger  
Helv. Chim. Acta 49, 292 (1966)

"Die Konstitution von Verrucarín E"

E. Fetz und Ch. Tamm  
Helv. Chim. Acta. 49, 349 (1966)

"Über Reaktionen der Butan-1,2,3,4-Tetracarbonsäure"

H. Hopff und R. v. Rütte  
Helv. Chim. Acta 49, 329 (1966)

"Silicon-Fluorine Chemistry. IV. The Reaction of Silicon Difluoride with Aromatic Compounds"  
P. L. Timms, D. D. Stump, R. A. Kent, and J. L. Margrave  
J. Am. Chem. Soc. 88, 940 (1966)

"The Structure of Diazoketones. A Study of Hindered Internal Rotation"  
F. Kaplan and G. K. Meloy  
J. Am. Chem. Soc. 88, 950 (1966)

"Metal Ion Decomposition of Hydroperoxides. IV. Kinetics and Products of Copper Salt Catalyzed Decomposition of *t*-Butyl Hydroperoxide"  
W. H. Richardson  
J. Am. Chem. Soc. 88, 975 (1966)

"The Kinetics of Inversion of 2-Methylbutylmagnesium Bromide and Related Compounds"  
G. Fraenkel and D. T. Dix  
J. Am. Chem. Soc. 88, 979 (1966)

"Reduction of Alkylmercuric Hydroxides by Sodium Borohydride"  
F. G. Bordwell and M. L. Douglass  
J. Am. Chem. Soc. 88, 993 (1966)

"Preparation, Chemistry, and Photochemistry of Hexaalkyl-2,4-cyclohexadienones"  
H. Hart, P. M. Collins, and A. J. Waring  
J. Am. Chem. Soc. 88, 1005 (1966)

"Reactions of Carbodiimides. III. The Reactions of Carbodiimides with Peptide Acids"  
D. F. DeTar, R. Silverstein, and F. F. Rogers, Jr.  
J. Am. Chem. Soc. 88, 1024 (1966)

"A General, Stereospecific Synthetic Route to  $\Delta^2$ -Thiazolines"  
G. K. Helmkamp, D. J. Pettitt, J. R. Lowell, Jr., W. R. Mabey, and R. G. Wolcott  
J. Am. Chem. Soc. 88, 1030 (1966)

"The Reaction of 2,4,6-Triphenylpyrylium Ion with Phenylphosphine. 1-Hydroxy-1,2,4,6-tetraphenylphosphorabenzene"  
C. C. Price, T. Parasaran, and T. V. Lakshminarayan  
J. Am. Chem. Soc. 88, 1034 (1966)

"Nucleophilic Dequaternization of Condensed Azetidinium Salts"  
G. Podor  
J. Am. Chem. Soc. 88, 1040 (1966)

"The Periodate Oxidation of Indoles"  
L. J. Dolby and D. L. Booth  
J. Am. Chem. Soc. 88, 1049 (1966)

"A New Isomer of  $C_2B_3H_5$ , C,3-Dimethyl-1,2-dicarbaclavopentaborane(5)"  
R. N. Grimes  
J. Am. Chem. Soc. 88, 1070 (1966)

"The Oxidative Dealkylation of Mesityl with Activated Manganese Dioxide"  
E. McNelis  
J. Am. Chem. Soc. 88, 1074 (1966)

"Reactions of an Indolenine Salt as a Possible Model for Dehydrogenase Enzymes"  
K. A. Schellenberg, and G. W. McLean  
J. Am. Chem. Soc. 88, 1077 (1966)

"Stereospecific Oxidation of a 1,1-Disubstituted Hydrazine via Metal Ion Coordination. A New Approach to Isomeric Azo Compounds"  
P. S. Forcione, G. S. Sprague, and H. J. Troffkin  
J. Am. Chem. Soc. 88, 1079 (1966)

"The Aggregation of Acridine Orange in Aqueous Solution"  
D. J. Blears, S. S. Danyluk  
J. Am. Chem. Soc. 88, 1084 (1966)

"Proton Magnetic Resonance Studies of Water as a Hydrogen Donor"  
F. Takahashi and N. C. Li  
J. Am. Chem. Soc. 88, 1117 (1966)

"Nuclear Magnetic Resonance in Polycyclic Compounds. II. Long-Range  $H^1-H^1$  and  $H^1-P^{31}$  Coupling in Some Adamantane and Bicyclo[2.2.2]octane Derivatives"  
E. J. Boros, K. J. Coskran, R. W. King and J. G. Verkade  
J. Am. Chem. Soc. 88, 1140 (1966)

"Isotopically Labeled Tetraborane(10) and Pentaborane(11)"  
A. D. Norman and R. Schaeffer  
J. Am. Chem. Soc. 88, 1143 (1966)

"Oxygen-17 Nuclear Magnetic Resonance and Oxygen Exchange in Aqueous Solutions of Telluric Acid"  
Z. Luz and I. Pecht  
J. Am. Chem. Soc. 88, 1152 (1966)

"Studies in Magnetic Nonequivalence. Nuclear Magnetic Resonance Spectra of Some Three-Spin Systems"  
E. I. Snyder  
J. Am. Chem. Soc. 88, 1155 (1966)

"Studies in Magnetic Nonequivalence. The Conformation of Two 1-Substituted 1,2-Dibromoethanes"  
M. Buza and E. I. Snyder  
J. Am. Chem. Soc. 88, 1161 (1966)

"Studies in Magnetic Nonequivalence. A Model for Conformational Analysis of Acyclics from Spin-Coupling Constants"  
E. I. Snyder  
J. Am. Chem. Soc. 88, 1165 (1966)

"Geminal Proton Nonequivalences and Related Phenomena in some N-Substituted Amides"  
T. H. Siddall, III, and C. A. Prohaska  
J. Am. Chem. Soc. 88, 1172 (1966)

"Further Studies of Bond Insertion and Nonstereospecific Beckmann Rearrangements in 7-Alkyl-1-indanone Oximes"  
P. T. Lansbury and N. R. Mancuso  
J. Am. Chem. Soc. 88, 1205 (1966)

"Mechanisms of Photochemical Reactions in Solution. XXXVII. Solvent Effects in the Photolysis of Tetramethyloxetanone"  
P. J. Wagner, C. A. Stout, S. Searles, Jr. and G. S. Hammond  
J. Am. Chem. Soc. 88, 1242 (1966)

"Acid-Catalyzed Isomerization in the Peptide Part of Ergot Alkaloids"  
H. Ott, A. Hofmann and A. J. Frey  
J. Am. Chem. Soc. 88, 1251 (1966)

"Free-Radical Elimination Reactions. The Reaction of Phenyl Radicals with *t*-Butyl Sulfide and Phenyl *t*-Butyl Sulfide"  
J. A. Kampmeier, R. P. Greer, A. J. Meskin and R. M. D'Silva  
J. Am. Chem. Soc. 88, 1257 (1966)

"Nuclear Magnetic Resonance Investigation of  $-C^{13}$  Phenylmethylolithiums"  
R. Waack, M. A. Doran, E. B. Baker and G. A. Olah  
J. Am. Chem. Soc. 88, 1272 (1966)

"Highly Strained Bicyclic Systems. XI. Synthesis of 2-Bicyclo[2.1.1]hexanol and Tricyclo[2.2.0.0<sup>2,6</sup>]hexane-1-carboxylic Acid"  
J. Meinwald and J. K. Crandall  
J. Am. Chem. Soc. 88, 1292 (1966)

"Direct Observation of  $Mn^{55}$  NMR in Antiferromagnetic  $CsMnF_3$ "  
V. Minkiewicz and A. Nakamura  
Phys. Rev. 143, 361 (1966)

"Reduktion von 3-Methylen-norbornanon-(2)"  
H. Krieger, K. Manninen und J. Paasivirta  
Suomen Kemistilehti 39, 8 (1966)

"Three and Four Bond Phosphorus-Proton Couplings in Isomeric  
Tolylphosphonates and Tolyphosphine Oxides"  
C. E. Griffin, R. B. Davison and M. Gordon  
Tetrahedron 22, 561 (1966)

"Nuclear-Spin, Hyperfine-Structure, and Magnetic-Moment  
Investigations on  $^{61}Cu$ ,  $^{62}Cu$ , and  $^{64}Cu$ "  
B. M. Dods-worth and H. A. Shugart  
Phys. Rev. 142, 638 (1966)

"Reaction of Di-, and Trialkyl Phosphites with Isatins"  
A. Mustafa, M. M. Sidky and F. M. Soliman  
Tetrahedron 22, 393 (1966)

"Reaction of Trivalent Phosphorus Compounds with  $\alpha,\beta$ -Unsatu-  
rated Ketones. Reaction of Amino, Alkyl and Aryl Phosphines  
with trans-Dibenzoyl ethylene  $^{31}P$  Nuclear Magnetic Resonance"  
F. R. Mirez, O. P. Madan and C. P. Smith  
Tetrahedron 22, 567 (1966)

"Kernresonanzuntersuchungen an diffundierenden Punktdefekten  
in  $AgBr$ "  
J. Kluge  
Phys. Stat. Sol. 13, 401 (1966)

"Preparation of Dicyclopropylcarbinyl Phosphorochloridate  
and its Use in Phosphorylation Reactions"  
A. M. Schoffstaff and H. Tiechelmann  
Tetrahedron 22, 399 (1966)

"Derivates of 1,1,4,4-Tetramethylcyclohexane. Low Temperature  
NMR Studies"  
W. Reusch and D. F. Anderson  
Tetrahedron 22, 583 (1966)

"Proton Resonance Spectra and Tacticity of Poly-2-vinyl-  
pyridine"  
G. Geuskens, J. C. Lubikulu and C. David  
Polymer 7, 63 (1966)

"Reaction of Olefins with Acetylacetone in the Presence of  
Thallic Acetate"  
K. Ichikawa, S. Uemura and T. Sugita  
Tetrahedron 22, 407 (1966)

"Oxidation of Steroidal Ketones—VI. Mechanism of Reaction  
and Proof of Structure of Ring a Contracted Acid"  
E. Caspi, S. K. Malhotra, Y. Shimizu, K. Maheshwari and  
M. J. Gasic  
Tetrahedron 22, 595 (1966)

"Nuclear Magnetic Resonance in the System: Polymer in Monomer  
Matrix"  
Ya. G. Urman, I. Ya. Slonim and A. D. Yermolayev  
Polymer Sci (USSR) (English Transl) 6, 2336 (1964)

"The Reaction of Ammonium Polysulphide with Benzylidene  
Chloride and Some Derivatives Thereof"  
K. Aghoramurthy  
Tetrahedron 22, 415 (1966)

"Proton Magnetic Resonance Studies of Cyclic Compounds—IV.  
The Influence of Alkyl Substituents on the Chemical Shifts  
of the Ring Protons in Cyclohexane Compounds"  
H. Booth  
Tetrahedron 22, 615 (1966)

"Nuclear Magnetic Resonance Spin-Spin Relaxation"  
S. Clough and I. R. McDonald  
Proc. Phys. Soc. (London) 86, 833 (1965)

"Aromatic Polyfluoro Compounds—XXVIII. Further Reactions of  
the Pentafluorophenyl Anion"  
D. D. Callander, P. L. Goe and J. C. Tatlow  
Tetrahedron 22, 419 (1966)

"Nuclear Magnetic Resonance Spectra and Stereochemistry of  
4-Substituted Flavans"  
B. J. Bolger, A. Hirwe, K. G. Marathe, E. M. Philbin and  
M. A. Vickars  
Tetrahedron 22, 621 (1966)

"The Nuclear Magnetic Resonance Spectrum of a Cobyrinic  
Acid Derivative"  
R. Bonnett and D. G. Redman  
Proc. Roy Soc. (London) Ser. A 288, 342 (1965)

"Fluorocyclopentanes—V. Lithium Aluminium Hydride Reduction  
of Octafluoro-, 1,2-Dichlorohexafluoro-, and 1-Chlorohepta-  
fluoro-Cyclopentene and 1H,2-Chloro-Octafluorocyclohexene"  
W. J. Feast, D. R. A. Perry and R. Stephens  
Tetrahedron 22, 433 (1966)

"Stereochemical Studies—XXXVI. An Approach to Conformational  
Analysis of Medium Ring Compounds. Unsaturated Ten-Member-  
ed Ring Derivatives"  
J. Sicher, M. Svoboda, J. Zavada and R. B. Turner and P. Goebel  
Tetrahedron 22, 659 (1966)

"The Reaction of Acetone with Hydrogen Sulfide"  
H. M. Van Dort and W. J. Mijs  
Rec. Trav. Chim. 85, 15 (1966)

"Bromination of 2-Pyrazolines and 3,4,5-Trimethylpyrazole.  
New Syntheses of the 3H-Pyrazole System"  
G. L. Closs and H. Heyn  
Tetrahedron 22, 463 (1966)

"The Structure of Lamertianic Acid. A New Diterpenic Acid"  
W. G. Dauben and V. F. German  
Tetrahedron 22, 679 (1966)

"Proton Magnetic Resonance Spectra of Protonated Methoxy-  
benzenes; C-Protonation Versus O-Protonation"  
D. M. Brouwer, E. L. Mackor and C. MacLean  
Rec. Trav. Chim. 85, 109 (1966)

"Photochemical Reactions of Diphenylketene in Solution"  
H. Nozaki, M. Kakano and K. Kondo  
Tetrahedron 22, 477 (1966)

"The Constituents of Cacalia Decomposita A. Gray. Structures  
of Maturin, Maturinin, Maturone and Maturinone"  
J. Correa and J. Romo  
Tetrahedron 22, 685 (1966)

"Modulation of NMR Signal Under Conditions of Strong  
Saturation"  
A. A. Samokhin  
Soviet Phys. Solid State (English Transl.) 7, 2353 (1966)

"Trityl Hydroxypentachloroantimonate"  
W. M. Pasika  
Tetrahedron 22, 557 (1966)

"Constituents of Gaillardia Species—III. The Structure of  
Gaillardilin, A New Pseudoguaianolide"  
W. Herz, S. Rajappa, M. V. Lakshmikantham and J. J. Schmid  
Tetrahedron 22, 693 (1966)

"Laws Governing Additions to Polyacetylenes. VI. Orientation in the Addition of Hydrogen, Bromine, and Hydrogen Bromide to 1, 5-Alkadiynyltrimethylsilanes"  
M. P. Forost, O. A. Muzovskaya, and A. A. Petrov  
J. Gen. Chem. USSR (English Transl) 35, 708 (1965)

"Synthesis of Acetylenic Tertiary Phosphine Sulfides"  
G. M. Gogolyubov and A. A. Petrov  
J. Gen. Chem. USSR (English Transl) 35, 705 (1965)

"Reactions of Metal Derivatives of Compounds Containing Mobile Hydrogen with  $\alpha$ -Halo Epoxides. V. Structure of Products of the Reaction of Sodiaoacetoacetic Ester with 1-Bromo-2,3-Epoxy-3-Methylbutane, 1-Bromo-2,3-Epoxybutane, 3-Bromo-1,2-Epoxybutane, and Epibromohydrin"  
T. I. Temnikova, B. A. Ershov and A. I. Arditi  
J. Gen. Chem. USSR (English transl.) 35, 792 (1965)

"Complexes of Aromatic Hydrocarbons with Metal Halides and Hydrogen Halides. II. Proton Magnetic Resonance Spectra of Complexes of Methylbenzenes with Aluminum Bromide and Hydrogen Bromide"  
V. A. Koptug, A. I. Rezvukhin, V. G. Shubin and D. B. Korchagina  
J. Gen. Chem. USSR. (English Transl.) 35, 867 (1965)

"Pentafluorophenyl-phosphorus chemistry—I. Tris(pentafluorophenyl)phosphine sulphide and tris(pentafluorophenyl)dichlorophosphorane"  
H. J. Emeleus and J. M. Miller  
J. Inorg. Nucl. Chem. 28, 662 (1966)

"The Reaction of the Trimetaphosphate Ion with the Fluoride Ion in Aqueous Solution"  
R. E. Mesmer  
J. Inorg. Nucl. Chem. 28, 691 (1966)

"Synthesis and Characterization of 1- and 2-Monoglycerides of Anteiso Fatty Acids"  
B. Serdarevich and K. K. Carroll  
J. Lipid Res. 7, 277 (1966)

"The Synthesis of Substituted Tricyclo[6.2.2.0<sup>2,7</sup>]dodecanes from 2-Cyclohexenone"  
N. J. Leonard and W. J. Musliner  
J. Org. Chem. 31, 639 (1966)

"The Chemistry of Carbanions. XI. Michael Reactions with 2-Methylcyclopentanone and 2-Methylcyclohexanone"  
H. O. House, W. L. Roelofs, and B. M. Trost  
J. Org. Chem. 31, 646 (1966)

"Acid-Catalyzed Rearrangements of Some Bicyclic  $\alpha,\beta$ -hydroxy- $\alpha,\beta$ -enones"  
S. Swaminathan, R. K. Natarajan, S. R. machandran and S. K. Sankarappa  
J. Org. Chem. 31, 656 (1966)

"Synthesis of 4-Substituted 1,1-Dimethyl-trans-2-decalones via Conjugate Addition of Grignard Reagents"  
J. A. Marshall and N. H. Andersen  
J. Org. Chem. 31, 667 (1966)

"Structure of Hysterin, a New Sesquiterpene Lactone"  
A. Romo de Vivar, E. A. Bratoeff, and T. Rios  
J. Org. Chem. 31, 673 (1966)

"Synthesis of Simple Hydrazones of Carbonyl Compounds by an Exchange Reaction"  
G. R. Newkome and D. L. Fishel  
J. Org. Chem. 31, 677 (1966)

"The Structure of Ambrosiol. A New Sesquiterpene Lactone from Ambrosia psilostachya"  
T. J. Mabry, W. Renold, H. E. Miller and H. B. Kagan  
J. Org. Chem. 31, 681 (1966)

Terpenes. III. The Nuclear Magnetic Resonance Spectra and Absolute Configuration of the Thujylamines"  
H. E. Smith, J. C. D. Brand, E. H. Massey  
J. Org. Chem. 31, 690 (1966)

"Stereochemical Studies. II. Conformational Analysis of  $\Delta^2$ -3-Keto Steroids"  
M. Gorodetsky, A. Yagev, and Y. Mazur  
J. Org. Chem. 31, 699 (1966)

Synthesis and Stereochemistry of Hydrophenanthrenes. IV. 1,2,3,4,4a $\alpha$ ,4b $\beta$ ,5,6,7,9,10,10a $\beta$ -Dodecahydro-4,7-dioxo-2 $\alpha$ -phenanthrenecarboxylic Acid"  
Z. G. Hajos, D. R. Parrish, and M. W. Goldberg  
J. Org. Chem. 31, 713 (1966)

"Reactions of  $\alpha,\beta$ -Unsaturated Acid Chlorides with Tertiary Amines"  
G. B. Payne  
J. Org. Chem. 31, 718 (1966)

"The Reaction of Imidoyl Isothiocyanates with Enamines. A New Synthesis of 1,2-Disubstituted Pyrimidine Derivatives"  
H. M. Blatter and H. Lukaszewski  
J. Org. Chem. 31, 722 (1966)

"Reactions of  $\alpha$ -Haloalkaneboronic Esters"  
D. S. Matteson and G. D. Schauberg  
J. Org. Chem. 31, 726 (1966)

"On Steroidal Sapogenins. X. Structural Influences of the A Ring on 11 $\alpha$ -p-Toluenesulfonyloxy Steroidal Sapogenin Acetolyses"  
K. Takeda, H. T. nida, and K. Horiki  
J. Org. Chem. 31, 734 (1966)

"Difunctional Tetrafluorobenzene Compounds from Fluoro-aromatic Organolithium Intermediates"  
C. Tamborski and E. J. Soloski  
J. Org. Chem. 31, 746 (1966)

"The Acylation of 1,3,5-Triphenylbenzene. The Solvent Effect"  
G. E. Lewis  
J. Org. Chem. 31, 749 (1966)

"Stereochemical Course of the Free-Radical Addition of Hydrogen Bromide to 1-Chloro-4-t-butylcyclohexene"  
P. D. Read and P. S. Skell  
J. Org. Chem. 31, 753 (1966)

"Stereochemistry of the Free-Radical Addition of Methyl Mercaptan to 1-Chloro-4-t-butylcyclohexene"  
P. D. Read and P. S. Skell  
J. Org. Chem. 31, 759 (1966)

"7-Azabenzonorbornadiene"  
L. A. Carpino and D. E. Barr  
J. Org. Chem. 31, 764 (1966)

"Tetrachlorocyclopentadienyldiene and Thermal Rearrangements of Its Cyclopropyl Adducts"  
E. T. McBee, J. A. Bosoms and C. J. Morton  
J. Org. Chem. 31, 768 (1966)

"Synthesis of Some Alkylidenecyclopropanes from Allenes"  
W. Rahman and H. G. Kuivila  
J. Org. Chem. 31, 772 (1966)

"The Chemistry of Allene. I. Factors Governing the Orientation of Free-Radical Addition"  
E.-A. I. Heiba  
J. Org. Chem. 31, 776 (1966)

"The Synthesis and Thermal and Photolytic Decomposition of 1,2-Dihydro-2,4,6-triphenyl-s-triazine"  
H. L. Nyquist  
J. Org. Chem. 31, 784 (1966)

"New Metabolites of Gibberella Fujikuroi—X. Gibberellin  
A<sub>10</sub>"

J. R. Hanson  
Tetrahedron 22, 701 (1966)

"Aldgarose, A Cyclic Carbonate Sugar of Natural Origin"

M. P. Kunstmann, L. A. Mitscher and N. Bohonos  
Tetrahedron Letters 839 (1966)

"Orientation of Ribonucleoside Derivatives by Proton Magnetic  
Resonance Spectroscopy"

H. P. M. Fromageot, B. E. Griffin, C. B. Reese, J. E. Sulston  
and D. R. Trentham  
Tetrahedron 22, 705 (1966)

"Cleavage of Steroidal Epoxides with Organoaluminum Cyanides"

W. Nagata, M. Yoshioka and T. Okumura  
Tetrahedron Letters 847 (1966)

"The Reactions of Dialkyl Hydrogen Phosphites with Alkyl Vinyl  
Ethers"

T. Nishiwaki  
Tetrahedron 22, 711 (1966)

"Studies on Alkaloids from Thalictrum Species. III. Oxydation  
of Thalicarpine and Thalmelatine"

N. M. Mollov and H. E. Dutschewska  
Tetrahedron Letters 853 (1966)

"Dehydrogenation Studies with Tetrachloro- -Benzoquinone.  
Structure of a Novel Dehydrogenation-Addition Product of  
Abietic Acid"

T. R. Kasturi, E. Raghavan, Sukh Dev and D. K. Banerjee  
Tetrahedron 22, 745 (1966)

"Ring Inversion of Some 1,3-Dioxanes"

J. E. Anderson and J. C. D. Brand  
Trans. Faraday Soc. 62, 39 (1966)

"Acyl Rearrangement and the Structures of Some Esters Related  
to Pyridoxine"

W. Korytnyk and B. Paul  
Tetrahedron Letters 777 (1966)

"High Resolution Nuclear Magnetic Resonance Spectroscopy"

J. W. Emsley, J. Feeney, and L. H. Sutcliffe  
Pergamon Press, Oxford, New York. Vol. 1 (1966)

"FMR - Spektroskopie Ungesättigter Ringsysteme III. Die  
Spektren Cyclischer Diene und Triene"

H. Günther und H. H. Hinrichs  
Tetrahedron Letters 787 (1966)

"A New Method for the Synthesis of  $\Delta^1$ -Butenolides"

W. W. Epstein and A. C. Sonntag  
Tetrahedron Letters 791 (1966)

"Photochemical Reactions in the Presence of Tetrafluoro-  
hydrazine the Synthesis of  $\alpha$ -Difluoroamino Ethers"

M. J. Cziesla, K. F. Mueller, and O. Jones  
Tetrahedron Letters 813 (1966)

"Phenacylidenedimethylsulfurane (I)"

A. W. Johnson and R. T. Amel  
Tetrahedron Letters 819 (1966)

"Long-range Shielding Effects of the Oximido Group in 4-tert-  
Butylcyclohexanone Oxime"

W. F. Trager and A. C. Huitric  
Tetrahedron Letters 825 (1966)