

Printed ✓
Mailed:
February 26, 1963

Monthly
Encumenical
Letters from
Laboratories
Of
N - M - R

No. 53

(done Lit)

LuValle Preparation of the Useful NMR Solvents Tetrafluorodichloroacetone Deutero-hydrate and Hexafluoroacetone Deutero-hydrate.	1
Brownstein Syn-anti Isomerism in Methazonic Acid	2
Heeschen A Self-Adjusting Magnetic Field Controller for the A-60	5
Colebrook Apparatus, Technique and Some Applications of H-H Spin-Decoupling	8
Greizerstein, McCallum A Use of NMR for Inorganic Structural Proof	9
Kullnig, Nachod Long-Range H-H Coupling in 2-Butyl-2-ethyl-5-methyl-3,4-hexadienal	9
Smith, W. B. Structure of the 2:1 Acetone:Cyclopentadiene Condensation Product	10
Berlin Structure Proof of Three Bicyclic Phosphonates	11
Ourisson, Lehn, Riess Méthylphosphonates d'alcoyle et de méthyle; An Offer to Help with Triterpene Structure Elucidation; A Problem of Ethics	12
Shapiro A Reply to Dr. Ourisson's 'Problem of Ethics'	13
Reddy Concerning Methyl Substitution Effects on the C^{13} Shifts in Ethylenic Systems	14
Smith, G. V., Kriloff Vinyllic Proton Coupling Constants in Cycloalkenes	15
Dischler Pyrrole Coupling Constants; Compilation of Calculated A_{2B_2} Spectra	16
Koski B_{11} NMR Studies of Nuclear Quadrupole Interactions in Trimethoxyboroxine and N-Trimethyl Borazole	17
Anet Temperature Studies of (Deuterated) Cyclooctane(s)	18
Günther, Mini, Castellano Unusual Deshielding of Some Aromatic Protons in Phenyl Substituted s-Triazines	19
Martin, Uebel Shifts and Couplings (Including Signs) in a Diazirine	20
Kaeszi, Flitcroft Proton Magnetic Resonance Studies on Stannane and the Methylstannanes	20

DEADLINE FOR NEXT ISSUE
March 25, 1963

由各核磁共振實驗室內每月搜集之非正式私人函件。
本刊內容專為讀者之用，未得個別通訊者許可，不得擅自
引用。任何引用之資料必需列為“私人通訊”。



February 1, 1963

Dr. B. L. Shapiro
Mellon Institute
Pittsburgh, Pennsylvania

Dear Barry:

During the past year, we have had considerable trouble finding solvents which would permit high resolution studies of polymethine dyes, both cyanines and merocyanines. These dyes are so insoluble in most solvents that it was impossible to perform the desired investigations. We have synthesized two solvents which permit one to obtain at least 0.1M solutions of polymethine dyes. The solvents may be of use to other people; we are therefore including details of their preparation.

Tetrafluorodichloroacetone Deutero-hydrate: $(CF_2Cl_2CO \cdot (D_2O)_{2.5}$

Ice cold D_2O was added dropwise to the ketone, the temperature being held below $25^\circ C$. The lower-boiling materials were stripped off at atmospheric pressure and the residue was distilled at $106.5-107.5^\circ C$. The final product is quite viscous.

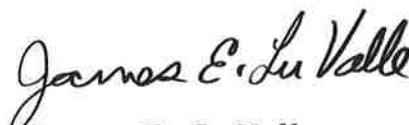
Hexafluoroacetone Deutero-hydrate: $(CF_3)_2CO \cdot D_2O$

The gaseous ketone was very slowly bubbled through deuterium oxide, the temperature being held between 5° to $10^\circ C$, until no further weight pick up was noted. The low-boiling materials were stripped off and the residue retained as a product. This compound melts at room temperature.

The halogenated acetones were obtained from the General Chemical Division of the Allied Chemical Company.

The acetones alone are not able to dissolve the dyes. The deutero-hydrates are the good solvents. We plan to prepare the hydrates and study the bonding by looking at both the proton and fluorine resonance.

Sincerely yours,


James E. LuValle

January 21, 1963

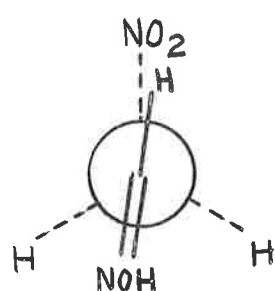
Dr. B. L. Shapiro,
Mellon Institute,
440 Fifth Avenue,
Pittsburgh 13, Penn.,
U.S.A.

Dear Barry,

While studying the reactions of aliphatic nitro anions we came across some unusual proton resonance results which might be of interest to MELLONMR readers. Methazonic acid, O_2NCH_2CHNOH , may be prepared by reaction of nitromethane with base, acidification and recrystallization from an appropriate organic solvent. The proton resonance spectrum of a freshly prepared acetone solution has a single peak at 8.90 p.p.m. to low field of acetone due to the oxime proton, a triplet centered at 5.08 p.p.m. due to the $-CH$ and a doublet at 3.35 due to the $-CH_2$ with $J=4.6$ cycles/sec. With time a second similar group of peaks appear at 8.78, 5.56, and 3.17 with $J=6.0$ cycles. At equilibrium? (two weeks later) the high field doublet and low field triplet i.e. the syn isomer are more intense (1.29:1.00). These results may be explained by syn-anti isomerism about the carbon-nitrogen bond of the oxime. From previous work on aldoximes one may assign the initially observed peaks to the anti form.

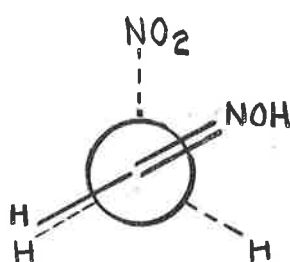
Since the average coupling constants are different for the two isomers it is likely that there is free rotation about the carbon-carbon bond with different populations in the various conformations for each isomer. Assuming that the proton rather than the oxime group will eclipse the substituent on the second carbon atom the conformations for both isomers are shown, along with the proton dihedral angles and coupling

constants taken from Karplus' calculations.

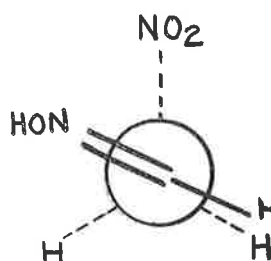


A 120°

$$J = 2.2 \text{ cycles/sec}$$



B 0° AND 120°



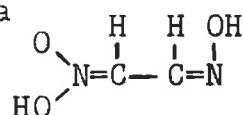
C 0° AND 120°

$$J = \frac{8.0 + 2.2}{2} = 5.1 \text{ cycles/sec}$$

Conformations B and C are mirror images with a calculated coupling constant of 5.1 cycles/sec. The approximations of exact eclipsing of substituents and no effect of syn-anti isomerism on coupling constants for the individual conformations certainly introduce some error. However it is likely that the syn isomer is largely in conformations B and C, while the anti isomer is approximately 25% in conformation A. This is consistent with molecular models which show considerable hindrance to conformations B and C of the anti form. Presumably these conformations are stabilized by hydrogen bonding between the oxime and nitro groups, but steric repulsion is great enough in the anti form that some of conformation A is present.

When methazonic acid is dissolved in water no peak is observed which can be attributed to the oxime proton, which presumably exchanges rapidly with the solvent. Two triplets at 2.46 p.p.m. to low field of water, $J=4.8$ cycles and 2.90 p.p.m., $J=6.1$ cycles, are observed along with two pair of doublets at 0.67 p.p.m., $J=4.9$ cycles, and 0.48 p.p.m., $J=5.9$ cycles. All of these peaks are observed as soon as the methazonic acid is dissolved and its proton resonance spectrum obtained. The intensity ratio in aqueous solution is 2.53:1.00 favoring the low field triplet and high field doublet, i.e. the syn isomer.

The reaction of nitromethane with base in water or methanol yields, after a short time, the methazonate ion. The proton resonance spectrum consists of eight peaks whose spacing and intensity is consistent with two AB pairs. The numbers are $\delta A = 3.19$ p.p.m. to low field of water, $\delta B = 1.19$ p.p.m., $\delta C = 2.83$ p.p.m., $\delta D = 2.33$ p.p.m., $JAB = 9.1$ cycles, $JCD = 8.7$ cycles. This assignment is confirmed by studies of deuterium exchange in aqueous solution which also yields the exchange rates $D > B > C > A$. We may conclude that syn and anti-isomers are present of general formula



where one or both hydrogens on oxygen are ionized or exchanging rapidly with the solvent. To be consistent with methazonic acid protons A and B are assigned to the syn isomer and C and D to the anti isomer. The initial ratio is 1.41:1.00 in favor of the anti isomer while at equilibrium the syn isomer is favored by 2.02:1.00.

Yours truly,

Syd Brownstein

S. Brownstein

SB/md

A SELF-ADJUSTING MAGNETIC FIELD CONTROLLER FOR THE A-60

J. P. Heeschen
The Dow Chemical Company
Midland, Michigan

A self-adjusting magnetic field controller has been built for a Varian Model A-60 Analytical High Resolution NMR Spectrometer. The design is a direct adaptation to this instrument of a magnetic field controller described by E. B. Baker and L. W. Burd.

¹E. B. Baker and L. W. Burd, Rev. Sci. Instr., February, 1963.

This controller was designed by Parke Brown and built by Rex Thorpe.

In this system, deviation from the desired operation (~ 5.0 kc sideband, as measured by the FREQUENCY meter) causes a corrective change in the field determining circuit (a variable resistor in series with the FIELD adjustment) via a recording potentiometer.

A schematic diagram of the circuit is shown in Figure 1. Components within the dashed line are mounted inside the cabinet of a Brown ELECTRONIK self-adjusting potentiometer. The remaining components are A-60 parts, as labelled, and a toggle switch to stop Brown recorder operation when desired.

Current through the 1 K resistor in series with the FREQUENCY meter develops ~ 5 MV drop at 5 kc (meter half-scale). This is compared with a reference voltage and the difference recorded by the Brown recorder (0-5 millivolts full scale).

The Brown recorder motor also drives a variable resistor (10 turns for full-scale recorder deflection) in series with the FIELD resistor of the A-60. The resulting field change returns the sideband frequency nearly to the starting value. The FIELD control is adjusted occasionally to return the Brown recorder to mid-scale.

Operation of the controller is made necessarily slow to give maximum gain without oscillation. In addition to using a slow recorder motor (12 seconds full scale), the gain of the Brown amplifier is reduced to a point just below oscillation of the controller.

Typical operation of the system is tabulated below. Net long-term gain is $\sim 10^4$ - thus a magnetic field drift corresponding to 1000 cps would cause a recorded absorption line shift of only 0.1 cps. Gain of the A-60 without automatic field adjustment is ~ 300 (as measured for a sideband frequency change of 240 cps). The automatic field adjustment, then, furnishes control gain of ~ 30 -50.

This system has been very useful for controlling drift of field or RF frequency over periods of a few minutes and longer. It does not correct for unstable operation of the sample positioning and sweep circuits. Maintaining a nearly constant side-band frequency should prevent small shifting of line positions and, especially, base-line drift during integration. Such control has been necessary at times for the A-60 in our laboratory.

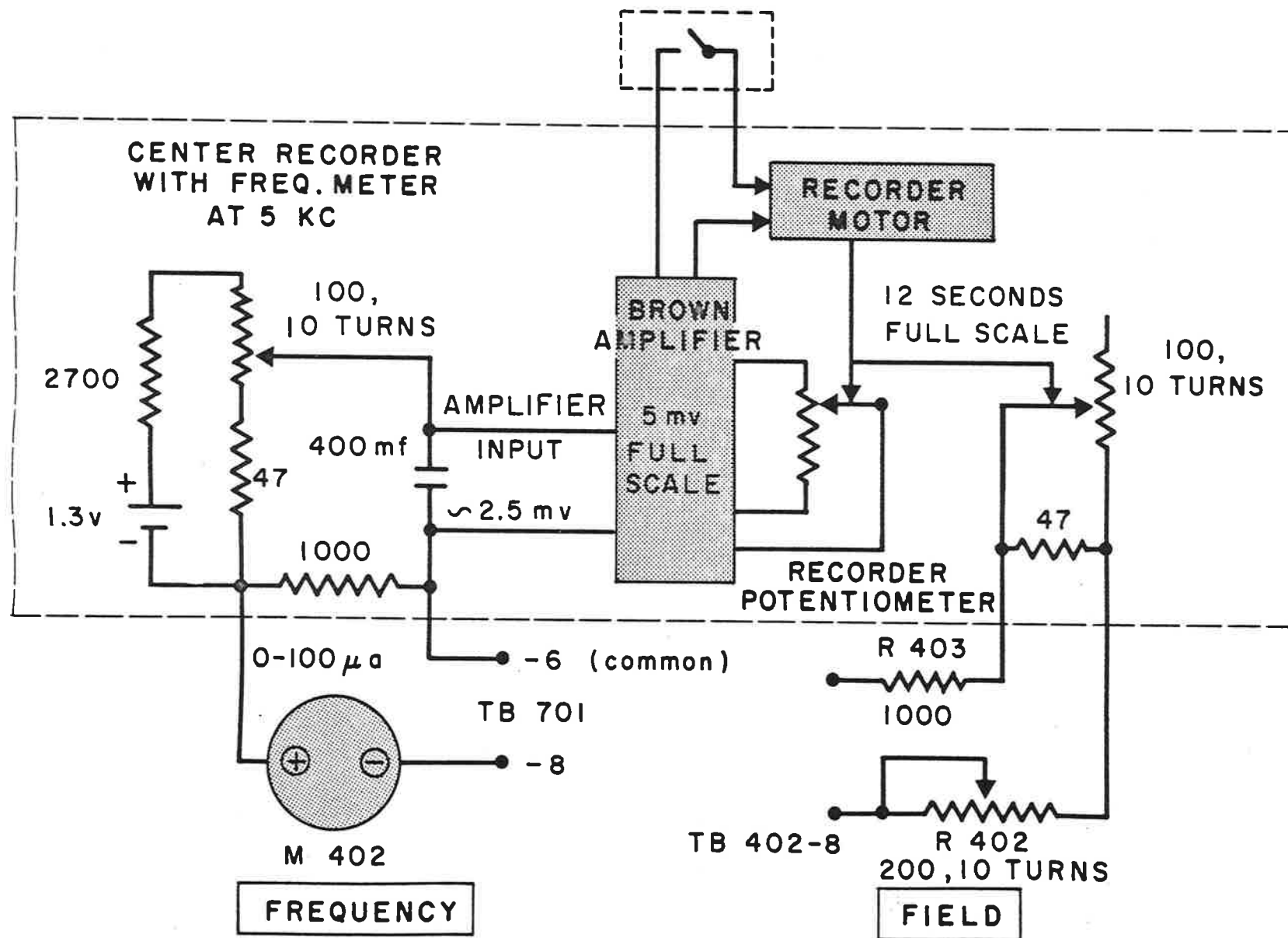
Typical A-60 operation with and without automatic magnetic field adjustment.

<u>Field Controller</u>	<u>FREQ. meter</u>	<u>Sideband Frequency ($\pm 5-10$)</u>	<u>Recorded line position (cps)</u>	<u>Brown position</u>	<u>Gain</u>
[OFF	5.0	5040̄	0	50.2	290
OFF	5.2	5272̄	+0.90̄	50.2	
[ON	5.0	5040̄	+0.15̄	48.2	
[ON	5.0	5040	0	55.0	10,000
[ON	5.0	"6260"★	+0.12	44.3	
(observe 5060)					

★ Total increase of 1220 cps in five steps of ca 240 cps each. The sequence, (field controller off-change FIELD control and measure sideband frequency-field controller on), was repeated five times to calibrate the net change in Brown recorder reading.

FIGURE I

SELF-ADJUSTING FIELD CONTROL FOR A-60



THE UNIVERSITY OF ROCHESTER
COLLEGE OF ARTS AND SCIENCE
RIVER CAMPUS STATION
ROCHESTER 20, NEW YORK

January 30, 1963

DEPARTMENT OF CHEMISTRY

Dr. B. L. Shapiro,
Mellon Institute,
4400 Fifth Avenue,
Pittsburgh 13, Pennsylvania.

Dear Dr. Shapiro,

As I am at present doing most of the NMR work in this department Dr. Wilson has suggested that I take over his subscription to *MILLONER*. For a first contribution I would like to outline some of the work we are doing on spin-spin decoupling.

We have become interested in spin decoupling as a means of simplifying the interpretation of the spectra of complex molecules. Our detector is a slightly modified Freeman type ¹ incorporating a 600 c/s tuned circuit which may be switched out as required. To avoid the problem of the two sideband spectra overlapping and perhaps obscuring the region of interest we use two audio oscillators, one operating at the fixed frequency of 600 c/s and providing the sidebands used for recording and the other providing the strong sidebands used for decoupling. The use of a multiple of the line frequency enables us to check for drift in our fixed oscillator by monitoring the 600 c/s - 60 c/s Lissajous figure on an oscilloscope, there being no need to disconnect the frequency counter from the variable frequency oscillator at any stage. The V-4300 B spectrometer is operated in the HR Phase Detector-1 setting. A small adjustment to the R-F Reference Phase control must be made when moving from one sideband spectrum to the other.

Spin decoupling has been successfully applied in the course of some work on natural products related to totarol being carried out with Dr. R. D. Combie of the University of Auckland, New Zealand. These compounds have five methyl groups, two of which are present in an isopropyl group. The other methyls, being situated on tertiary carbon atoms, show no fine structure. In certain cases there was an ambiguity in sorting out the isopropyl methyl doublet from the other methyl peaks when the methyl line spacings were compared with those in the isopropyl methine multiplet. This ambiguity was readily resolved by irradiating the methine proton at the appropriate frequencies and noting which two methyl peaks collapsed to a single line. Mention of one such example will appear shortly in a paper on the chemistry of the podocarpaceae in *Tetrahedron*.

We have also used the technique in work on some natural products of unknown constitution. In the spectrum of one such compound under investigation by Dr. S. A. Davis of the University of Auckland the fine structure due to several independent spin systems overlapped to such an extent that the separate systems could not be identified. Spin decoupling was used to determine the chemical shifts of the protons involved in coupling, the correct frequencies being found by guesswork plus a certain amount of trial and error. From relative areas it was

possible to estimate the number of protons in each spin system. This work will be reported in detail when some further chemical work has been completed.

In our recent investigation into the structure of actinamine ², a hydrolysis product of the antibiotic actinospectacin, we were faced with the analysis of an AB₂X₂ system for the A and B chemical shifts and J_{AB}. Strong irradiation of the X protons simplified the problem to the analysis of an AB₂ system. The accuracy obtainable proved adequate for the solution of the structural problem.

¹ R. Freeman, *Mol. Phys.*, **2**, 435 (1960).

² L. D. Colebrook & R. H. Gourlay, *Proc. Natl. Acad. Sci. (U.S.)*, **48**, 1693 (1962).

Yours sincerely,

L. D. Colebrook

L. D. Colebrook.

A Use of NMR for Inorganic Structural Proof

Nuclear magnetic resonance proved a convenient means of determining the ratio of coordinated NH_3 to NH_4^+ in a series of zinc salts.

The resonance position of the NH_4^+ ion was determined from solutions of ammonium chloride in dimethylsulfoxide. The position is substantially invariant over a reasonable concentration range of 5-10% by weight. The NH_3 resonance was determined from a solution of $\text{Zn}(\text{NH}_3)_2\text{Cl}_2$. It was verified that exchange of protons between charged and uncharged nitrogen was rapid by adding ammonium chloride to solutions of the zinc diammine chloride. Only a single sharp resonance was observed at a position between those of the charged and uncharged nitrogen protons.

The empirical formula of a compound obtained during the course of this work corresponded to the structure $\text{Zn}(\text{NH}_3)_2\text{Cl}_2 \cdot \text{NH}_4\text{Cl}$. Assuming rapid exchange between 6 uncharged nitrogen and 4 charged nitrogen sites with equal residence times in each, an average resonance position of 292 cps is expected. A dimethylsulfoxide solution of the compound showed a single sharp resonance band at 295 cps. This observation confirms the ratio for a 1:1 double salt of zinc diammine chloride and ammonium chloride.

Observed Resonance Positions (Dimethylsulfoxide Solutions)

NH_4Cl (5%)	453 cps at 60 mc.
(10%)	453
$\text{Zn}(\text{NH}_3)_2\text{Cl}_2$	184
$\text{Zn}(\text{NH}_3)_2\text{Cl}_2 + \text{NH}_4\text{Cl}$	269
$\text{Zn}(\text{NH}_3)_2\text{Cl}_2 \cdot \text{NH}_4\text{Cl}$	295
$\text{Zn}(\text{NH}_3)_2\text{Cl}_2 \cdot \text{NH}_4\text{Cl} + \text{NH}_4\text{Cl}$	335

Dr. Walter Greizerstein and Dr. Keith S. McCallum

STERLING-WINTHROP RESEARCH INSTITUTE A DIVISION OF STERLING DRUG INC. RENSSELAER, NEW YORK

February 4, 1963

Dr. B. L. Shapiro
Mellon Institute
4400 Fifth Avenue
Pittsburgh 13, Pennsylvania

Dear Dr. Shapiro:

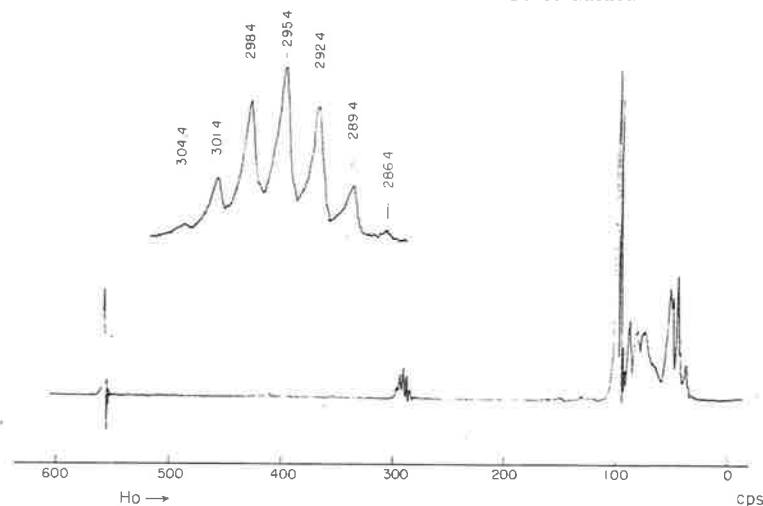
As it is fashionable to report on long-range coupling, we are pleased to submit a particularly pretty set which we observed in the NMR spectrum of 2-butyl-2-ethyl-5-methyl-3,4-hexadienal shown in the accompanying figure. The J value for the spin coupling between the allenic proton and the terminal methyl groups (5 bonds) is 3 c.p.s.

The details of this work, covering also another allene, will be reported in greater detail in J. Phys. Chem.

With best regards

Sincerely yours,

R. K. Kullberg
R. K. Kullberg
F. C. Nachod
F. C. Nachod





February 5, 1963

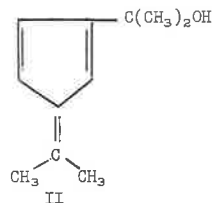
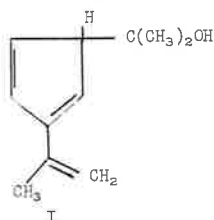
Dr. Bernard L. Shapiro
Mellon Institute
4400 Fifth Avenue
Pittsburgh 13, Pa.

Dear Dr. Shapiro:

I wish to report a case where the use of n.m.r. helped resolve a rather knotty problem in the determination of the structure of an organic molecule.

The structure of the product formed when cyclopentadiene condenses with two moles of acetone has never been clearly elucidated in the literature. The material is formed as a by-product during the formation of dimethylfulvene, and since we had occasion to prepare rather large amounts of the latter we also set out to look at the structure of the by-product.

Chemical degradation, infrared spectrum, and mechanistic intuition suggested structure I as most likely. The n.m.r., however, is not consistent with I.



The areas for the two sets of methyl groups are equal and twice as large as the total area for the ring-Hs. Furthermore, the latter are split into two bands with areas in the ratio of 2:1. Most reasonably the structure corresponds to II, which can be readily rationalized as a rearranged product of I (the reaction is carried out in the presence of a strong base).

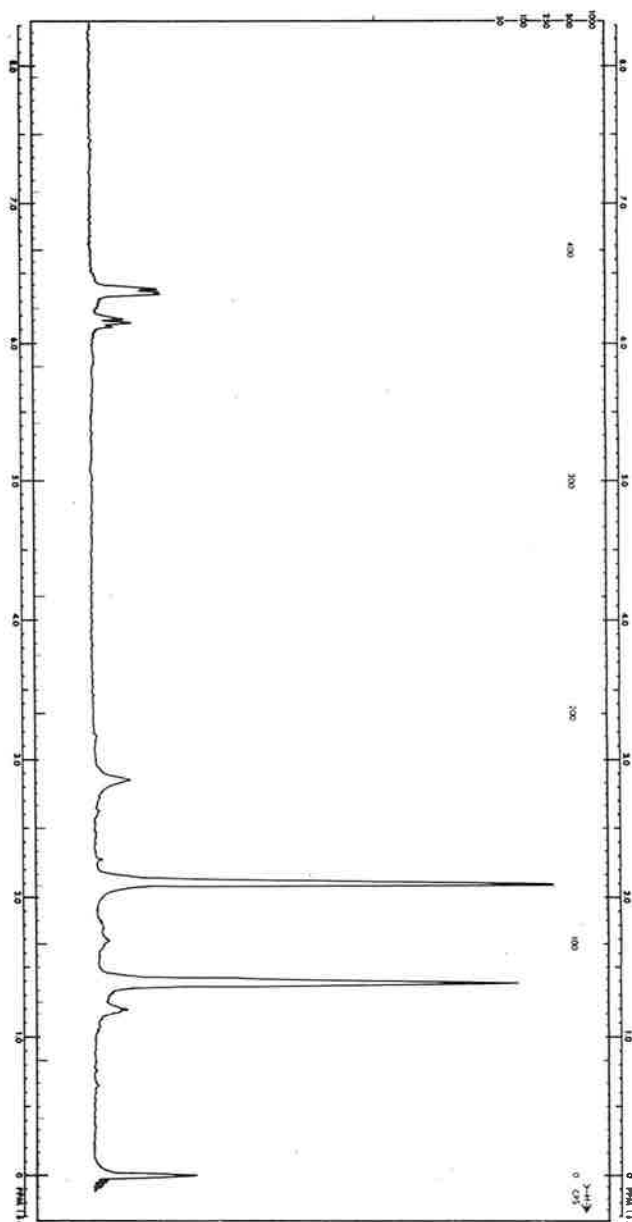
Simple molecular orbital calculations of the charge distribution in the dimethylfulvenyl anion and delocalization energies of I and II suggest that I is the kinetically first formed product which subsequently rearranges to the thermodynamically more stable II.

Yours sincerely,

William B. Smith

William B. Smith
Professor of Chemistry

The n.m.r. spectrum of the condensation product of dimethylfulvene with acetone determined at 60 mc. (10% solution in carbon tetrachloride with tetramethylsilane as the internal standard). The weak bands in the 1-2 ppm. region were due to trace impurities in the sample.





OKLAHOMA STATE UNIVERSITY • STILLWATER

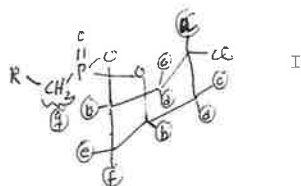
Department of Chemistry
 Faculty 2-6211 Lab 5-1513

February 7, 1963

Dr. B. L. Shapiro
 Mellon Institute
 4400 Fifth Avenue
 Pittsburgh 13, Pennsylvania

Dear Dr. Shapiro:

Although we just started with Mellonmr, we trust we can enter this to be applied toward the first required contribution. We have recently completed the structure proof of three bicyclic phosphonates. Specifically, the stereochemistry of 3-benzyl-7-chloro-2,4-dioxo-3-phosphabicyclo[3.3.1]nonane,3-oxide[I] was substantiated in part by NMR analysis on the A-60.



R=C₆H₅

The methylene protons [g] were observed as a doublet at 6.83 [J=22 cps] with the model compound, dimethyl benzylphosphonate displaying a doublet at 6.75 τ [J=21.7 cps].

Proton "a" was revealed as the predicted nine line spectra, although it was not well resolved at 60 Mc but was cleanly observed at 100 Mc. Where R=1-naphthyl, the nine lines were plainly visible at 60 Mc. The peak center in R=C₆H₅ was at 5.3 τ [J_{aa}=12.1 cps; J_{ae}=5.1 cps]. Tertiary protons "b" occurred as a doublet centered at 5.22 τ [J=17.5 cps]. Protons "c" "d" "e" and "f" were somewhat observed at 60 Mc and required

Dr. B. L. Shapiro
 February 7, 1963
 Page 2

the resolution of the 100 Mc instrument. That conformational homogeneity is present in R=C₆H₅ is implied by the nine lines displayed by proton "a". Recently, the spectrum of trans-4-t-butylnitrocyclohexane. [A. C. Huitric and W. F. Trager, J. Org. Chem., 27, 1926 [1962]] was reported at 50 Mc. In this system, believed to be conformationally homogeneous, the axial proton geminal to the nitro group also displayed a nine line spectra. We plan to publish our results soon.

Very truly yours,

K. D. Berlin
 Assistant Professor

KDB:kp

Monthly
 Encuminal
 Letters from
 Laboratories
 Of
 N - M - R

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".

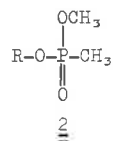
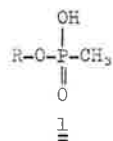
Strasbourg, le February 6, 1963
2, rue Goethe

Dr Bernard L. Shapiro
Mellon Institute
4400 Fifth Avenue
PITTSBURGH 13, Penn.

Méthylphosphonates d'alcoyle et de méthyle

Cher Dr Shapiro,

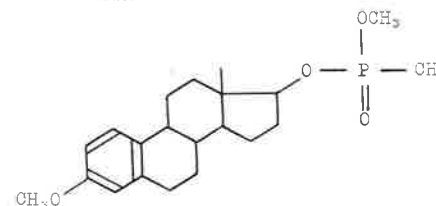
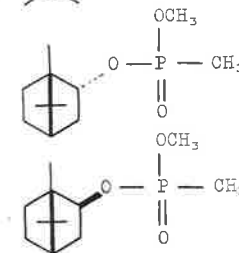
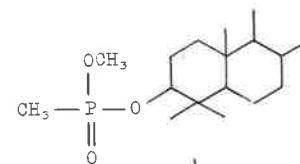
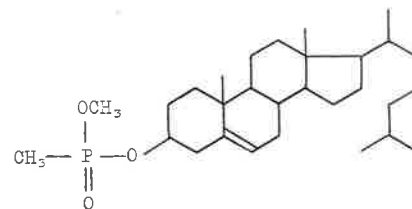
1) Les méthylphosphonates de divers alcools 1 donnent, avec le diazométhane, des esters méthyliques 2.



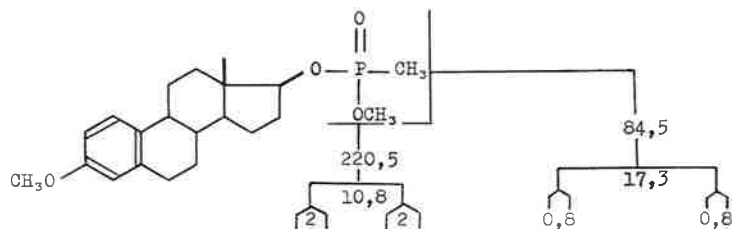
Dans ces derniers produits, le méthyle lié à l'oxygène résonne à env. 220cps du TMS (à 60Mc). Il donne un doublet ($J = 10,7 - 11\text{cps}$) par couplage avec P^{31} . En outre, dans les cas où R est asymétrique et encombré au voisinage du groupe étudié, on observe un dédoublement secondaire $\Delta\delta$ de 0 à 2,6cps, suivant le degré d'encombrement. Le Tableau I montre quelques exemples parmi ceux que nous avons rencontrés. Nous attribuons cet effet à une rotation gênée.

Le méthyle lié au phosphore résonne vers 85cps. Il donne un doublet ($J = 17 - 18\text{cps}$) par couplage avec P^{31} . En outre, un dédoublement secondaire $\Delta\delta$ de 0,8cps apparaît dans le spectre du produit 3. Ce dédoublement est absent quand le cycle A n'est pas aromatique.

Tableau I



$\delta(\text{cps})$	$J(\text{cps})$	$\Delta\delta(\text{cps})$
221,5	11	0
223	10,8	1,7
220,5	10,7	0,6
216,5	10,7	2,3
220,5	10,8	2



Nous ne savons pas interpréter ce second phénomène.

2) Nous poursuivons l'étude systématique des spectres de RMN des Triterpènes. Nous pourrions peut-être aider ceux de vos lecteurs qui disposeraient de Triterpènes de structure inconnue, dans les séries du lupane et du dammarane (publiées), et dans les autres séries classiques (à l'étude).

3) We have a problem of ethics : Quotation from MellonMR is loathed, except as 'Private Communication'. How would you refer to one of your own letters, if it were the only available evidence of priority (and if you wished to claim that priority) ?

Yours sincerely,

For Paul Allen -

Guy Ourisson

MELLON INSTITUTE

4-400 FIFTH AVENUE
PITTSBURGH 13, PA.

18 February 1963

Professor G. Ourisson
Université de Strasbourg
Institut de Chimie
2, rue Goethe
Strasbourg, France

Dear Professor Ourisson:

Thank you for your MELLONMR contribution of February 6. In reply to your "problem of ethics", I am afraid that I have very little help to offer. Quotation of MELLONMR by name is, of course, not permitted. I can therefore see no way to use MELLONMR as an evidence of priority, other than the rather devious and probably impracticable method of having some friend of yours quote these results for you in a paper of his as a "Private Communication". I am sure that if you have a need for a priority claim which will itself not appear in public print that we can arrange to provide the appropriate person(s) with evidence supporting your claim. We would, of course, be receptive to any solutions to your problem which you might have in mind.

Yours sincerely,

B. L. Shapiro
Bernard L. Shapiro

lws



E. I. DU PONT DE NEMOURS & COMPANY

EXPLOSIVES DEPARTMENT
EASTERN LABORATORY
POST OFFICE BOX 8
GIBBSTOWN, N. J.

February 8, 1963

Dr. B. L. Shapiro
Mellon Institute
4400 Fifth Avenue
Pittsburg 13, Pa.

Dear Dr. Shapiro:

I thought I had better catchup, before receiving a reminder from you which is due any time now, by sending my first contribution since I left Emory eight months ago.

I would like to make some comments and supporting remarks on Friedel and Retcofsky's observations (MELLON-M-R No. 52) concerning the methyl substitution effects on the C^{13} chemical shifts in ethylenic systems. They have observed in $>C=CH$ systems, when the proton is replaced by a methyl group the $\beta-C^{13}$ resonance shifts to higher field while the $\alpha-C^{13}$ resonance shifts to lower field. Some time ago we studied the methyl substitution effects on the proton chemical shifts in ethylene, substituted ethylenes, and some heterocyclic systems with ethylenic bonds^{1,2,3}. We have found that in ethylenic systems when a proton is replaced by a methyl group the β -protons shift to higher field to the extent of 0.30 to 0.42 ppm while the α -proton shifts to lower field by about 0.45 ppm. We have attributed the β -proton shifts towards upfield as due to negative charge on the β -carbon atom arising as a result of electron release by the methyl group either by hyperconjugative or inductive mechanism (it does not make any difference what the mechanism is since the result observed by NMR is the same in any case). Recently

- 2 -

we have also estimated the C-C bond anisotropy effects on the proton shifts in methanes⁴. Applying this value for the C-C bond anisotropy which is about -0.8 to -1.0 ppm in methanes and ethanes, I calculated the anisotropy effect of C-C bond on the α -proton in propylene as about -0.5 ppm. This anisotropy is of the same order as the observed low-field shift of the α -proton in these systems. In addition to this anisotropy it is plausible to think that by inductive or hyperconjugative mechanism the methyl group releases electrons and this charge will polarize the π -bond. As a result the α -carbon atom has a small net positive charge. The magnitude of this charge is very hard to estimate (at least for me). Applying the results of Fraenkel et al.⁵ and those of Spiess and Schneider⁶ who obtained a shift of +160 ppm for C^{13} for a unit negative charge localized on the carbon and a shift of only +10 ppm for the hydrogen on the same carbon (it is the ratio of these shifts which is important in this connection) to the proton shifts we have observed, I have calculated an expected shift of +4.8 to +6.8 ppm for β -carbon and about -7.2 ppm for α -carbon. These values are in excellent agreement with the experimental values obtained by Friedel and Retcofsky (MELLON-M-R No. 52).

Actually we wanted to measure the C^{13} shifts in all the systems we have studied and see if this kind of correspondence exists. But we did not have necessary equipment to do C^{13} work. Now that Friedel and Retcofsky have done it, this clears my doubt about our proton studies.

Hope this will rescue me from being dropped from your mailing list.

Sincerely,
G. S. Reddy
G. S. Reddy

References:

1. G.S. Reddy and J.H. Goldstein, J. Am. Chem. Soc. 83, 2045 (1961)
2. G.S. Reddy and J.H. Goldstein, J. Am. Chem. Soc. 83, 5020 (1961)
3. G.S. Reddy, R.T. Hobgood, and J.H. Goldstein, J. Am. Chem. Soc. 84, 336 (1962)
4. G.S. Reddy and J.H. Goldstein, J. Chem. Phys. In press.
5. G. Fraenkel, R.E. Carter, A. McLachlan, and J.H. Richards, J. Am. Chem. Soc. 82, 5846 (1960)
6. H. Spiesecke and W.G. Schneider, Tetrahedron Letters, No. 14, 468 (1961)

ILLINOIS INSTITUTE OF TECHNOLOGY
TECHNOLOGY CENTER
CHICAGO 16

Department of Chemistry

February 13, 1963

Dr. B. L. Shapiro
Mellon Institute
4400 Fifth Avenue
Pittsburgh, Pennsylvania

Dear Dr. Shapiro:

With the help of FREQUINT IV computer program, we have been interpreting the olefinic splitting patterns of some unsubstituted cycloolefins. Among others the J's for the vinylic protons appear in the pattern, and we are confident of their values.

They are, for cyclopentene; 5.1 cps
cyclohexene; 8.8
cycloheptene; 10.8
cis-cyclooctene; 10.3
cis-cyclodecene; 10.8
trans-cyclodecene; 15.1.


The spectra were obtained on an A60 console using a DF60 power supply and magnet (all Varian Associates); no solvent was used; and the upper limit of error seems to be ± 0.2 cps.

These are six spin systems and when the appropriate number of J's are given to the computer, 53 lines are obtained. Thirty-eight of these are due to long range coupling between the four allylic protons, but fortunately this second order effect mainly causes just line-broadening of the 15 lines from first order considerations.

We greatly appreciate Dr. Bothner-By furnishing FREQUINT IV, which we changed for use on a 7090. Thanks are given to the Computer Centers of both the Illinois Institute of Technology and the Armour Research Foundation of the Illinois Institute of Technology for co-operation and help.

We are looking forward to being on the mailing list of MELLONMR.

Sincerely,


Gerard V. Smith
and Harvey Kriloff

GVS:mc

INSTITUT FÜR ELEKTROWERKSTOFFE

GEMEINNÜTZIGES FORSCHUNGsinstitut DER Fraunhofer-Gesellschaft

INSTITUTSDIREKTOR:
PROF. DR. R. MECKE

Dr. Bernard L. Shapiro
Mellon Institute
4400 Fifth Avenue
Pittsburgh 13, Pennsylvania

U.S.A.

FERNRUF NR. 5514

FREIBURG I. BR.
ECKERSTRASSE 4

February 12th, 1963

Dear Dr. Shapiro,

We are very sorry for the delay in sending you the following two comments:

1) Hoffmann and Gronowitz have pointed out¹⁾ that in substituted pyrroles the sum of the coupling constants J_{25} and J_{34} deviates from our own value found for pyrrole²⁾. Since the appearance of our paper²⁾ we have reinvestigated³⁾ the spectrum, using the additional information from C¹³ satellites. We obtained $J_{25}=2.1$ and $J_{34} = 3.7$ cps. These values are close to the average values given for substituted pyrroles¹⁾.

2) In the course of our investigations on A_2B_2 spectra²⁾³⁾ we have calculated a big number of theoretical spectra, 192 of which have been plotted. In this collection we have used 32 different sets of coupling constants (listed below) and 6 different chemical shifts (∞, 100, 60, 20, 10 and 2 cps). The plots allow for graphical interpolation and for the immediate assignment of lines in a corresponding experimental spectrum. The collection may be used in addition to the A_2B_2 -spectra given by Corio⁴⁾ and Wiberg⁵⁾, which are limited to the following cases: $L=O$ ($J_{AB}=J_{A'B'}$); or two identical J_{AB} .

We have available a limited number of copies (blueprints) and we should be glad to send single sheets or the whole set to those, who are interested. As an example I enclose page 30, containing the spectra typical for symmetrically ortho-disubstituted benzenes. There is a remarkable crossing over of lines h and i and of f and j. (notation explained in²⁾). Lines m and n are very weak mixed transitions, the distance of which from ν_A is given in cps, their intensities in powers of ten.

Thank you very much for sending us the most valuable Mellon-newsletters,

Sincerely yours

Bernhard Dischler

1) MELLON-M-R No. 51 (January 1963)

2) B. Dischler u. G. Englert, Z.Naturforschg. 16a, 1180 (1961)

3) B. Dischler, Dissertation, Universität Freiburg, 1962

4) P.L. Corio, Chem.Rev. 60, 363 (1960)

5) K.B. Wiberg u. J. Nist, Benjamin, New York, 1962

Zusammenstellung der in der A_2B_2 -Spektrenkollektion benutzten

Kopplungsparameter.

Blatt Nr.	J_{12} Hz	J_{34} Hz	J_{13} Hz	J_{14} Hz	K Hz	M Hz	N Hz	L Hz	Bemerkung
1	beliebig		4,0	4,0	beliebig		8,0	8,0	Gruppenkopplung
2	6,0	0,5	7,0	1,0	6,5	5,5	9,0	6,0	
3	6,0	0,5	4,0	3,0	6,5	5,5	7,0	1,0	
4	6,0	0,5	-3,0	-1,0	6,5	5,5	-7,0	1,0	
5	6,0	0,5	4,0	1,0	6,5	5,5	5,0	3,0	
6	6,0	0,5	4,0	-1,0	6,5	5,5	3,0	5,0	
7	6,0	0,5	1,0	-4,0	6,5	5,5	-7,0	5,0	
8	6,0	0,5	1,0	-1,0	6,5	5,5	0	2,0	
9	3,5	2,5	7,0	1,0	6,0	1,0	9,0	6,0	
10	3,5	-2,5	7,0	1,0	1,0	6,0	3,0	6,0	
11	3,5	2,5	4,0	3,0	6,0	1,0	7,0	1,0	o-Benzolderivate p-Benzolderivate 4-Pyridine
12	3,5	-2,5	4,0	3,0	1,0	6,0	7,0	1,0	
13	3,5	2,5	-3,0	-4,0	6,0	1,0	-7,0	1,0	
14	3,5	-2,5	-3,0	-4,0	1,0	6,0	-7,0	1,0	
15	3,5	2,5	4,0	1,0	6,0	1,0	5,0	3,0	
16	3,5	-2,5	4,0	1,0	1,0	6,0	5,0	3,0	
17	3,5	2,5	4,0	-1,0	0,0	1,0	3,0	5,0	
18	3,5	-2,5	4,0	-1,0	1,0	6,0	3,0	5,0	
19	3,5	2,5	1,0	-4,0	6,0	1,0	-3,0	5,0	
20	3,5	-2,5	1,0	-4,0	1,0	6,0	-3,0	3,0	
21	3,5	2,5	1,0	-1,0	6,0	1,0	0	2,0	
22	3,5	-2,5	1,0	-1,0	1,0	6,0	0	2,0	
23	3,5	0,5	7,0	1,0	4,0	3,0	6,0	6,0	
24	3,5	0,5	4,0	3,0	4,0	3,0	7,0	1,0	
25	3,5	0,5	1,0	-1,0	4,0	3,0	3,0	5,0	
26	0,5	0,5	7,0	1,0	1,0	0	8,0	6,0	
27	0,5	-0,5	7,0	1,0	0	1,0	8,0	6,0	
28	0,5	0,5	4,0	3,0	1,0	0	7,0	1,0	
29	0,5	-0,5	4,0	3,0	0	1,0	7,0	1,0	
30	7,5	0,5	8,0	1,6	3,0	7,0	9,6	6,4	
31	2,7	2,3	8,5	0,3	5,0	0,4	8,8	8,2	
32	2,5	0,5	8,5	1,5	3,0	2,0	10,0	7,0	

UNIVERSITY OF CALIFORNIA

DEPARTMENT OF CHEMISTRY
LOS ANGELES 24, CALIFORNIA

February 14, 1963

Dr. Bernard L. Shapiro
Mellon Institute
4400 Fifth Avenue
Pittsburgh 13, Pa.

Dear Dr. Shapiro:

Mr. J. S. Hartman and I have been studying the n.m.r. spectra of various systems to obtain energy barriers to inversion or to restricted rotation. In order to simplify spectra as much as possible, we have made deuterated compounds and examined the proton spectra with double irradiation at the deuterium frequency. An interesting example is that of cyclooctane, which gives a single line at room temperature and a broad three-peaked band (see Fig.) at -135° (vinyl chloride solution). On the other hand massively deuterated cyclooctane (mainly $C_8D_{15}H$), which also gives a single sharp line (on double irradiation) at room temperature, showed two distinct, well separated lines at -135° . The chemical shift between the two types of protons is 18.8 c.p.s. A study of the coalescence of the two lines and of the band-width after coalescence gave an activation energy of 7.7 kcal./mole with $\Delta S^\ddagger = 4$ e.u. at $T_c (-111.5^\circ)$ and showed that a single process was taking place. These results are quite different to those obtained by Harris and Sheppard and by Meiboom from line-width measurements of cyclooctane.

We intend to carry out similar measurements on other systems and in particular on deuterated cyclohexane.

Yours sincerely,

F. A. L. Anet

F. A. L. Anet

FALA:de

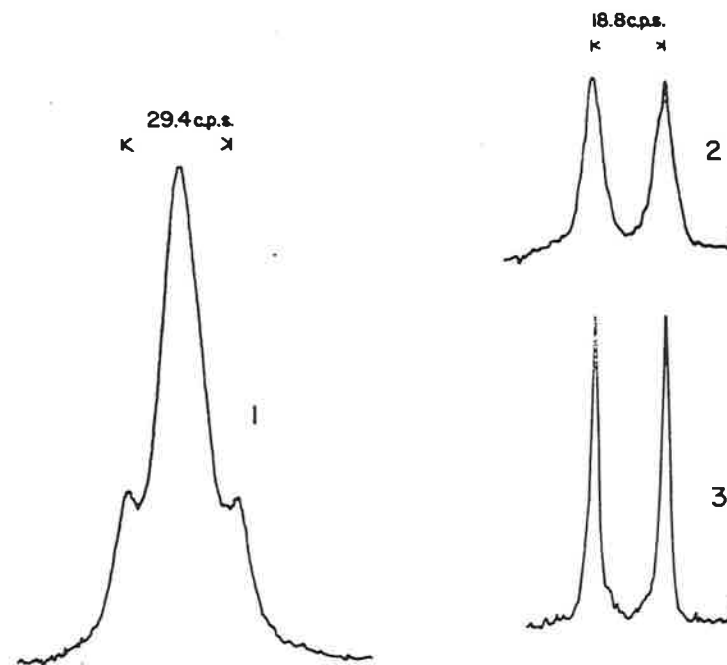


FIG. 1. — CYCLO-OCTANE at -135°
(1) C_8H_{16} , (2) $C_8D_{15}H$, (3) $C_8D_{15}H$, D decoupled

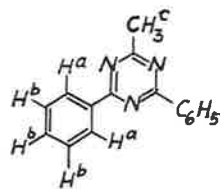
MELLON INSTITUTE

4400 FIFTH AVENUE
PITTSBURGH 13, PA.

February 20, 1963

Dear Barry,

Recently we observed some unusual deshielding of aromatic protons in phenylsubstituted s-triazines. Fig. 1 shows the spectra of methyl-diphenyl-s-triazine. The ratio of the peak areas is 4 : 6 : 3 ($H^a : H^b : H^c$), indicating the following assignment:



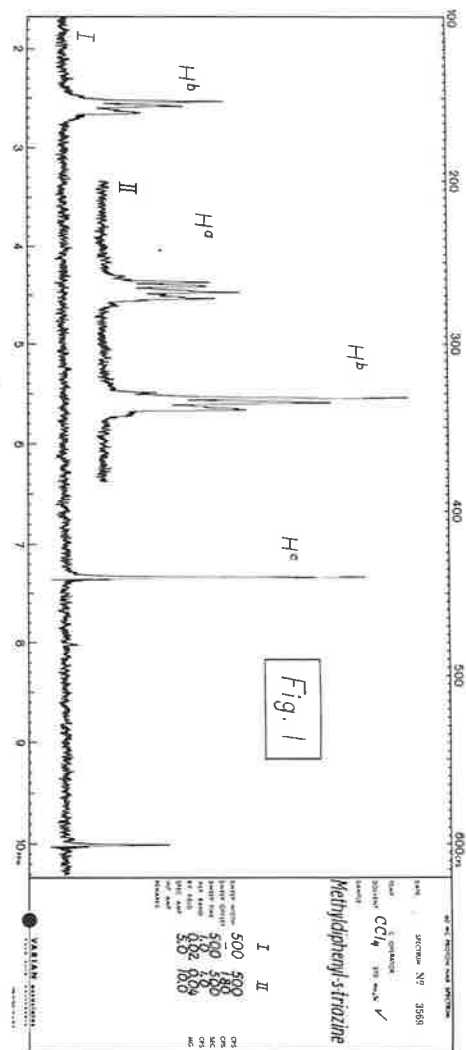
A complete analysis of the shown spectra and further investigation of other substituted triazines is at present under way.

Very truly yours,

H. Günther
H. Günther

V. Mini
V. Mini

S. Castellano
S. Castellano



UNIVERSITY OF ILLINOIS

Department of
CHEMISTRY AND CHEMICAL ENGINEERING
URBANA

UNIVERSITY OF CALIFORNIA

LOS ANGELES 24, CALIFORNIA

February 21, 1963

The William Albert Nevers Laboratory

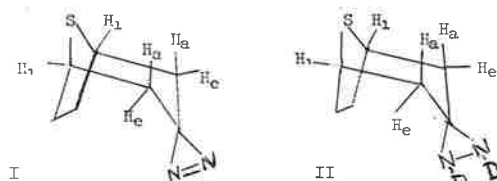
February 18, 1963

Dr. B. L. Shapiro
Mellon Institute
4400 Fifth Avenue
Pittsburgh 13, Pennsylvania

Dr. B. L. Shapiro
Mellon Institute
4400 Fifth Avenue
Pittsburgh 13, Pennsylvania

Dear Barry:

Dear Barry:



The spectrum of the pictured diazirine, I, is of interest because of the large chemical shift difference between H_a and H_e (1.56 p.p.m., in CCl_4). The portion of the spectrum attributed to H_a and H_e approximates the AM portion of an AMX spectrum with $J_{a,e} = -15.1$ c.p.s., $J_{1,a} = +2.9$ c.p.s., and $J_{1,e} = +4.0$ c.p.s. Chemical shifts (on the τ scale) correspond to 9.31 for H_e , 7.75 for H_a , and 6.38 for H_1 . The protons on the ethylene bridge fall in a narrow band, partially obscuring the H_a multiplet. Coupling between H_1 and the ethylene bridge hydrogens is less than 5 c.p.s. Cross-ring coupling constants are negligibly small.

Assignments for H_a and H_e were made on the reasonable assumption that the six-membered ring exists mainly in the chair form, a conformation which places H_e above the plane of the three-membered ring. In this model H_1 is within 5° of a *gauche* relationship to H_a and H_e , in keeping with the near equality of $J_{1,a}$ and $J_{1,e}$. This small difference in these constants is in the direction expected if H_e is responsible for the signal at 9.31. Confirmation of this assignment is available from a comparison of the spectrum of I and II. H_e is at ~ 0.8 p.p.m. lower field in the saturated analog II than in I. This is the direction of shift predicted for this proton either from qualitative bond anisotropy considerations based on analogy to the carbonyl double bond or ring-current predictions based on observations of effects in carbocyclic analogs of the three-membered diazirine ring.

Relative signs of J's were determined by a method similar to that of Freeman [Mol. Phys., 4, 385 (1961)] through spin-decoupling studies by the Johnson procedure [MELLONMR, No. 43, 1962]. The sign of $J_{a,e}$ was taken as negative by analogy with recently published findings of others in systems allowing a comparison of C^{13} -H and geminal H-H coupling constants.

Yours,

J. C. Martin, J. J. Uebel

JCM:lgf

The attached spectra were obtained in connection with proton magnetic resonance studies on stannane and the methylstannanes. A paper has been accepted for publication in J. Am. Chem. Soc. and is to appear sometime in May, however, the figures will not be published there. We are planning to submit them separately to the A.P.I. project 44 collection, but it is likely that six months or more would elapse before these spectra become available through the normal channels. Because of these reasons we think it might be useful to circulate the spectra in MELLONMR, however, we also invite you to exercise an editorial decision on this in case in the eyes of an objective third party this would lead to unnecessary duplication. We understand there are cost factors to be considered, so we will leave the final decision up to you.

Sincerely yours,

Herbert Kaesz and
Neville Flitcroft

Herbert Kaesz and
Neville Flitcroft

(Herb -- A non-editorial comment by the non-editor: I think that this is indeed a very good kind of contribution, both for the timing aspects of it and because these spectra will not actually appear in the formal publication. If there were not to be the time lag you mention, then I would agree with you that it would be unnecessary duplication. In general, let me repeat for you and everyone else's benefit -- we exercise no editorial function, but will simply print anything (within any kind of reason!) submitted. We leave it to the conscience of each contributor whether or not he is being prolix or submitting material which the same readers would see otherwise in the very near future, etc.

BLS)

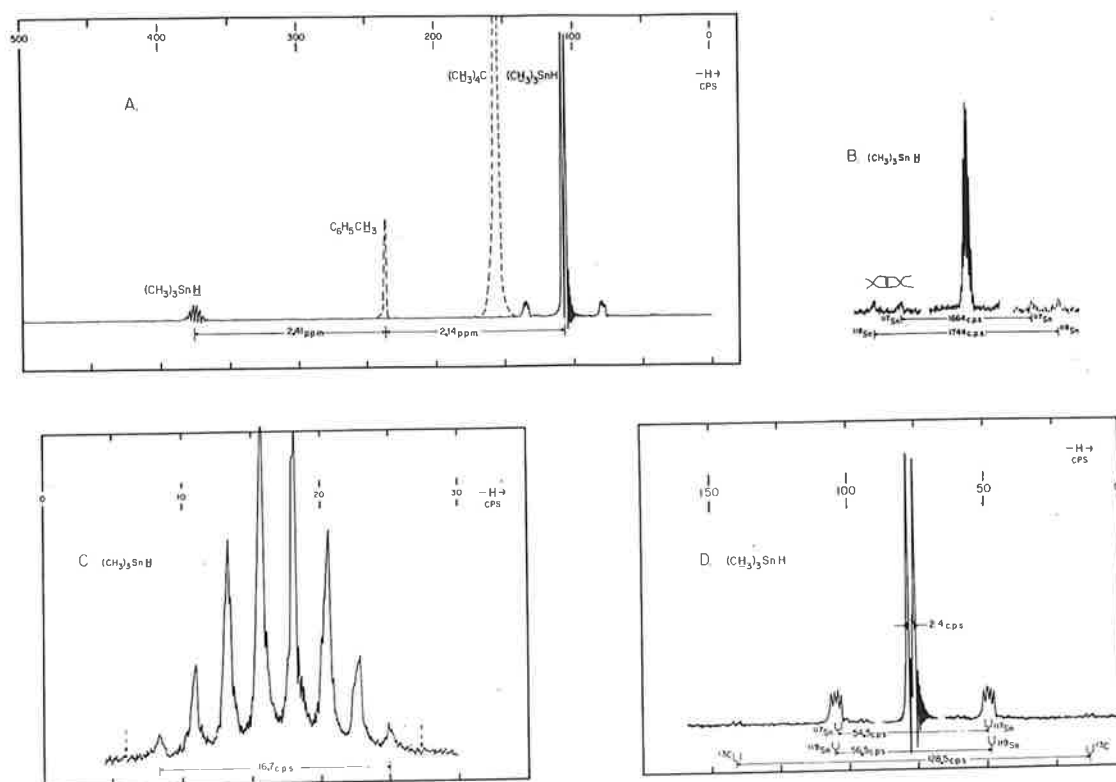


FIGURE 1. Proton magnetic resonance for $(\text{CH}_3)_3\text{SnH}$, 60 mc. A. Main features of proton resonances with relative position of solvent (neopentane) and internal standard (methyl protons of toluene); B. Tin-bonded proton resonance with ^{119}Sn and ^{117}Sn satellites; C. Enlarged scan of tin-bonded proton resonance; D. Enlarged scan of methyl resonance with ^{119}Sn , ^{117}Sn and ^{13}C satellites.

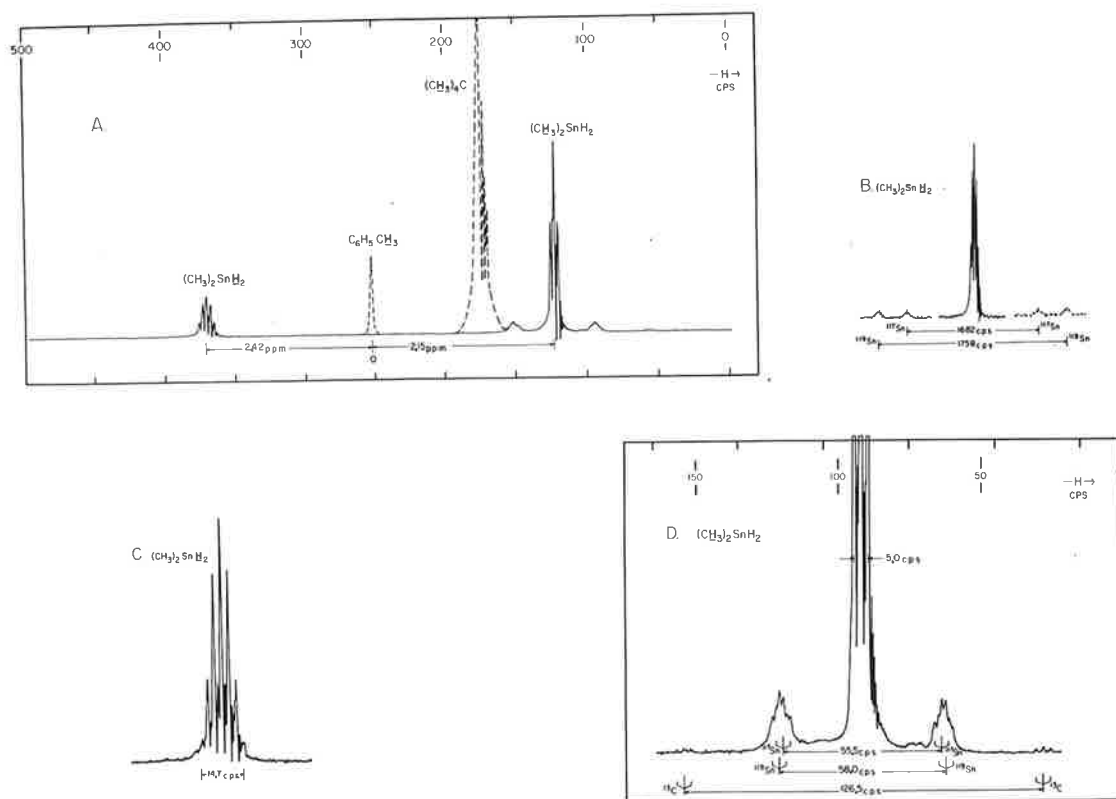


FIGURE 2. Proton magnetic resonance for $(\text{CH}_3)_2\text{SnH}_2$, 60 mc. A. Main features of proton resonances with relative position of solvent (neopentane) and internal standard (methyl protons of toluene); B. Tin-bonded proton resonance with ^{119}Sn and ^{117}Sn satellites; C. Enlarged scan of tin-bonded proton resonance; D. Enlarged scan of methyl resonance with ^{119}Sn , ^{117}Sn and ^{13}C satellites.

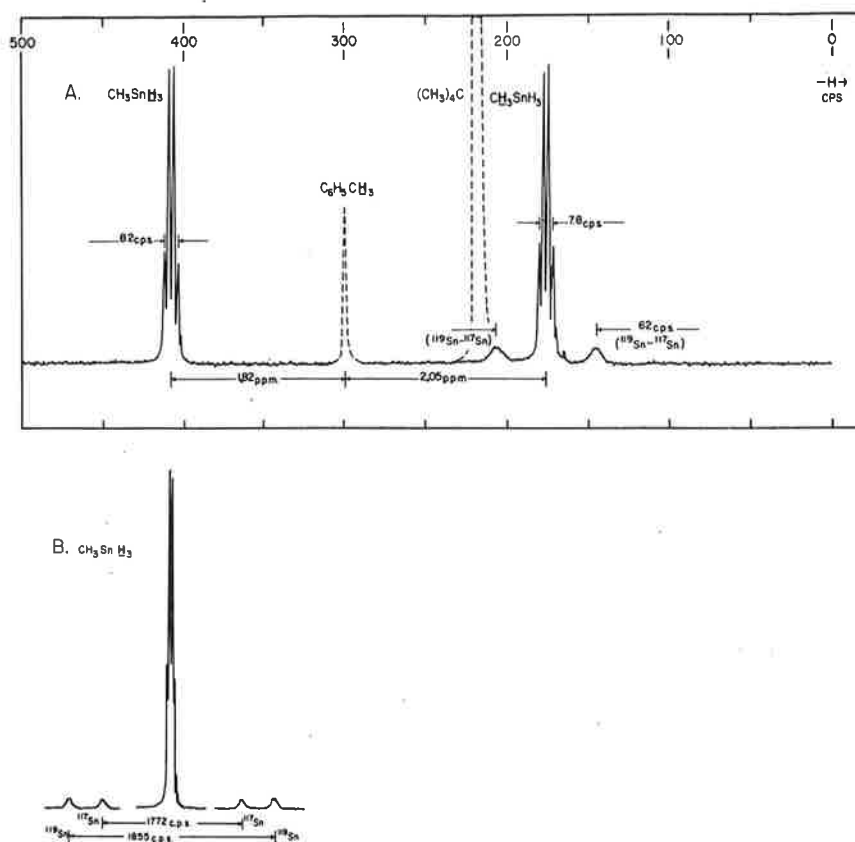


FIGURE 3. Proton magnetic resonance for CH_3SnH_3 , 60 mc. A. Main features of proton resonances with relative position of solvent (neopentane) and internal standard (methyl protons of toluene); B. Tin-bonded proton resonance with ^{119}Sn and ^{117}Sn satellites.

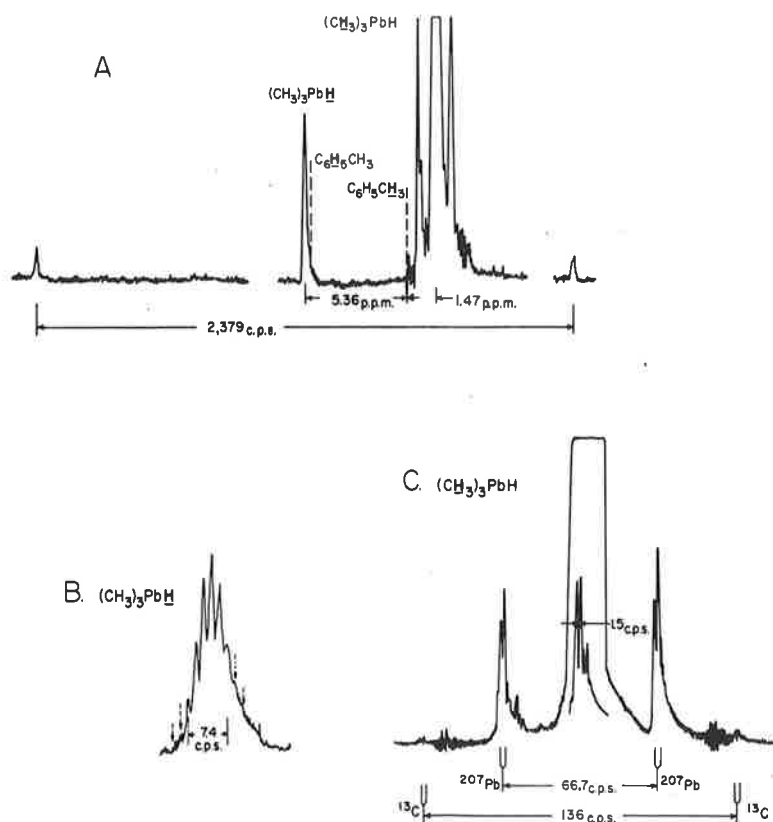


FIGURE 4. Proton magnetic resonance for $(\text{CH}_3)_3\text{PbH}$, 40 mc, -50°C . A. Main features of proton resonances with relative position of internal standard (toluene); B. Enlarged scan of lead-bonded proton resonance; C. Enlarged scan of methyl resonance with ^{207}Pb and ^{13}C satellites.

"The Structure of Dibromodiethyl Ketone"
C. Rappe and L. Schotte
Acta Chem. Scand. 16, 2060 (1962)

"Isothiocyanates XLVI. Glucocappasalin, a New Naturally Occurring Thioglucoside"
A. Kjær and H. Thomsen
Acta Chem. Scand. 16, 2065 (1962)

"The Biosynthesis of Leucine. I. The Accumulation of β -Hydroxyisocaproate by Leucine Auxotrophs of *Salmonella typhimurium* and *Neurospora crassa*"
C. Jungwirth, S. R. Gross, P. Margolin and H. E. Umbarger
Biochem. 2, 1 (1963)

"Variation of Coupling Constants in some Indoline Derivatives"
F. A. L. Anet and J. M. Muchowski
Chem. & Ind. 81 (1963)

"Configuration of Flavan-4-ols"
C. P. Lilly, D. Kehoe, E. M. Philbin, M. A. Vickars and T. S. Wheeler
Chem. & Ind. 84 (1963)

"The Conformational Equilibrium Constant of the Sulphydryl Grouping"
E. L. Eliel and B. P. Thill
Chem. & Ind. 88 (1963)

"Reactions of some 1,1-Dibromo-2-Alkenylcyclopropanes with Methylolithium: An Intramolecular Addition of a Carbene to a Double Bond"
L. Skattebøl
Chem. & Ind. 2146 (1962)

"On Steroids. LXX. Cyclopropane Ring Formation on Deamination of 18-Amine Steroids"
J. Hora V. Cerny and F. Sorm
Coll. Czechoslov. Chem. Commun. 27, 2771 (1962)

"Sur l'octaline-9,10 et quelques-uns de ses derives"
M. Mousseron, M. Mousseron-Canet, G. Philippe et J. Wylde
Compt. Rend. 256, 51 (1963)

"Isomerisation des derives alcoyles du vinyl-2-dihydro-2,3 furanne en produits cyclopropaniques"
J. Wiemann, N. Thoai et F. Weisbuch
Compt. Rend. 256, 178 (1963)

"The NMR Spectra of Substituted *s*-Trithianes and the Addition of Hydrogen Sulfide to 1,3-Diphenyl-2-Propanone and Related Ketones"
B. E. Edwards
Diss. Abstr. 23, 1924 (1962)

"Steric Effects on ^{13}C Nuclear Magnetic Resonance Spectra of Substituted Benzenes"
P. C. Lauterbur
Diss. Abstr. 23, 1944 (1962)

"Preparation of Diphosphorus Tetrachloride"
A. A. Sandoval and H. C. Moser
Inorg. Chem. 2, 27 (1963)

"Tris-(ethanolamineborane) Borate and Ethanolamineborane"
J. C. Kelly and J. O. Edwards
Inorg. Chem. 2, 39 (1963)

"Chelates of β -Diketones. V. Preparation and Properties of Chelates Containing Sterically Hindered Ligands"
S. Hammond, D. C. Nonhebel, and C.-H. S. Wu
Inorg. Chem. 2, 73 (1963)

"Nuclear Magnetic Resonance Studies on the Existence of Perchlorate Complexes of Transition Metal Ions in Aqueous Perchloric Acid"
P. Klanberg, J. P. Hunt, and H. W. Dodgen
Inorg. Chem. 2, 139 (1963)

"The Preparation of Difluoroamino Sulfur Pentafluoride"
A. L. Logothetis, C. N. Sausen, and R. J. Shozda
Inorg. Chem. 2, 173 (1963)

"Chemistry of Ethylenimines. X. Reactions with Phosphorus Nitrilochloride Trimer"
Y. Kobayashi, L. A. Chasin and L. B. Clapp
Inorg. Chem. 2, 212 (1963)

"Evidence for the Open Chain Structure of Ethane 1,2-Diamine-borane"
H. C. Kelly and J. O. Edwards
Inorg. Chem. 2, 226 (1963)

"The Inorganic Chemistry of Carbon Difluoride"
W. Mahler
Inorg. Chem. 2, 230 (1963)

"Constituents of Helenium Species. XIII. The Structure of Helenalin and Mexicanin A"
W. Herz, A. Romo de Vivar, J. Romo and N. Viswanathan
J. Am. Chem. Soc. 85, 19 (1963)

"The Conjugate Acids of 2,5-Dimethylpyrrole"
E. B. Whipple, Y. Chiang and R. L. Hinman
J. Am. Chem. Soc. 85, 26 (1963)

"A General Synthesis of the Troponoid System Based on Solvolysis of 1,4-Dihydrobenzyl Tosylates"
O. L. Chapman and P. Fitton
J. Am. Chem. Soc. 85, 41 (1963)

"The Configuration of the Double Bond in Naturally-occurring Alkenyl Ethers"
H. R. Warner and W. E. M. Lands
J. Am. Chem. Soc. 85, 60 (1963)

"Stereospecific Total Synthesis of Two 5-Amino-5,6-dideoxy-DL-hexonic Acids, A Novel Class of Aminosugar Related Compounds"
B. Belleau and Y.-K. Au-Young
J. Am. Chem. Soc. 85, 64 (1963)

"Sommelet-Hauser Rearrangement of Allylbenzyltrimethylammonium Bromide and Cyclopropylcarbinylbenzyltrimethylammonium Bromide. Evidence for Carbanion Stabilization by the Cyclopropane Ring"
C. L. Bumgardner
J. Am. Chem. Soc. 85, 73 (1963)

"The Action of Elementary Fluorine upon Organic Compounds. XXVI. The Direct Fluorination of Some Perfluoroalkyl-s-triazines"
B. Hynes, B. C. Bishop, P. Bandyopadhyay and L. A. Bigelow
J. Am. Chem. Soc. 85, 83 (1963)

"Carbenes from Alkyl Halides and Organolithium Compounds. V. Formation of Alkylcyclopropanes by Ring Closure of Alkenyl Substituted Carbenoid Intermediates"
L. Gloss and L. E. Gloss
Am. Chem. Soc. 85, 99 (1963)

"The Chemistry of Bluensomycin. I. The Structure of Bluensidine"
B. Bannister and A. D. Argoudelis
Am. Chem. Soc. 85, 119 (1963)

"Organometallic Chemistry of the Transition Metals. I. Metal Complexes of a Bicyclo[2,2,2]octatriene Derivative"
B. King
J. Am. Chem. Soc. 84, 2705 (1962)

"Proton Magnetic Resonance of Amino Acids, Peptides and their Metal Complexes"
C. Li, R. L. Scruggs and E. D. Becker
J. Am. Chem. Soc. 84, 4650 (1962)

"Synthesis and Properties of Alkylpyrroles"
P. S. Skell and G. P. Bean
J. Am. Chem. Soc. 84, 4655 (1962)

"Kinetics of Proton Transfer in Methanol and the Mechanism of the Abnormal Conductance of the Hydrogen Ion"
E. Grunwald, C. F. Jumper and S. Meiboom
J. Am. Chem. Soc. 84, 4664 (1962)

"Proton Exchange Rates and Hydrogen-Bonding for Water in Organic Solvents"
J. R. Holmes, D. Kivelson, and W. C. Drinkard
J. Am. Chem. Soc. 84, 4677 (1962)

"The Carbonylation of Organoboranes. I. The Carbonylation of Trialkylboranes. A Novel Synthesis of Trialkylcarbinols"
M. E. D. Hillman
J. Am. Chem. Soc. 84, 4715 (1962)

"2-Bora- and 2-Thia-1,3-diazazulenes"
H. E. Holmquist and R. E. Benson
J. Am. Chem. Soc. 84, 4720 (1962)

"Aromatic Silicon Systems. II. The Silacyclopentadienide Anion"
R. A. Benkeser, R. F. Crossman and G. M. Stanton
J. Am. Chem. Soc. 84, 4727 (1962)

"A Preparation of Primary Perfluoroalkylamines"
R. K. Pearson and R. D. Dresdner
J. Am. Chem. Soc. 84, 4743 (1962)

"Small Charged Rings. II. The Synthesis of Aziridinium Salts"
N. J. Leonard and K. Jann
J. Am. Chem. Soc. 84, 4806 (1962)

"The Mechanism of Decarboxylation of Glycidic Acids"
V. J. Shiner, Jr., and B. Martin
J. Am. Chem. Soc. 84, 4824 (1962)

"Cyclopropanes. XIII. The Absolute Configuration of 1-Methyl-2,2-diphenylcyclopropane"
H. M. Walborsky and C. G. Pitt
J. Am. Chem. Soc. 84, 4831 (1962)

"Proximity Effects. XXVI. Synthesis and Stereochemistry of Bicyclo[5.1.0]octanols"
A. C. Cope, S. Moon and G. H. Park
J. Am. Chem. Soc. 84, 4843 (1962)

"Proximity Effects. XXVIII. The Solvolysis of 5,5-Diphenylcyclooctyl p-Toluenesulfonate"
A. C. Cope, P. E. Burton and M. L. Caspar
J. Am. Chem. Soc. 84, 4855 (1962)

"Proximity Effects. XXX. Stereochemistry of Bicyclo[3.2.1]octan-8-ols and Bicyclo[4.2.0]octan-2- and 3-ols"
A. C. Cope, S. Moon, C. H. Park and G. L. Woo
J. Am. Chem. Soc. 84, 4865 (1962)

"Structure of the 7-Norbornadienyl Carbonium Ion"
P. R. Story and M. Saunders
J. Am. Chem. Soc. 84, 4876 (1962)

"General Methods of Synthesis of Indole Alkaloids. II. A Flavopercirine Synthesis"
E. Wenkert and B. Wickberg
J. Am. Chem. Soc. 84, 4914 (1962)

"Reactions of Amines. X. 1-t-Butyl-3-Phenylaziridinone"
H. E. Baumgarten
J. Am. Chem. Soc. 84, 4975 (1962)

"C(19)-Substituted Steroids. IV. Studies of Long Range Shielding by the Carbonyl Group with Nuclear Magnetic Double Resonance and Nuclear Magnetic Triple Resonance at 100 MC."
N. Bhacca, M. E. Wolff, and R. Kwok
J. Am. Chem. Soc. 84, 4976 (1962)

"Capture of a Favorskii Intermediate by Furan"
A. W. Fort
J. Am. Chem. Soc. 84, 4979 (1962)

"High Resolution Nuclear Magnetic Resonance Spectra of Various Polyisoprenes"
M. A. Golub, S. A. Fuqua and N. S. Bhacca
J. Am. Chem. Soc. 84, 4981 (1962)

"A Non-Carbenoid Ring Expansion of a Benzenoid System"
L. A. Paquette
J. Am. Chem. Soc. 84, 4987 (1962)

"An Enamine Synthesis of β -Amino- β -Lactams (4-Amino-2-Azetidinones)"
M. Perelman and S. A. Mizsak
J. Am. Chem. Soc. 84, 4988 (1962)

"NMR Spectra of Some Fluorine Compounds"
S. K. Alley, Jr., and R. L. Scott
J. Chem. Eng. Data 9, 117 (1963)

"Phosphorus-31 Nuclear Magnetic Resonance Spectra of Phosphorus Compounds"
K. Moedritzer, L. Maier and L. C. D. Groenweghe
J. Chem. & Eng. Data 7, 307 (1962)

"Structural Interpretation of Asymmetrically Broadened NMR Fine-Structure Lines"
D. F. Holcomb and B. Pedersen
J. Chem. Phys. 38, 54 (1963)

"NMR in Hydrate Crystals: Structural Information from Broadened Fine-Structure Lines"
B. Pedersen and D. F. Holcomb
J. Chem. Phys. 38, 61 (1963)

"Nuclear Spin Relaxation in Liquid CH_2Cl_2 "
R. J. C. Brown, H. S. Gutowsky and K. Shimomura
J. Chem. Phys. 38, 76 (1963)

"Pressure Dependence of the NMR Chemical Shifts in Cesium and Rubidium Halides"
R. Baron
J. Chem. Phys. 38, 173 (1963)

"Proton Magnetic Resonance Studies in Sodium-Ammonia Solutions"
T. R. Hughes, Jr.
J. Chem. Phys. 38, 202 (1963)

"Proton Magnetic Resonance Study of the Structure of Two Tutton's Salts"
R. Chidambaram and C. R. Rao
J. Chem. Phys. 38, 210 (1963)

"NMR Spectrum of 1,1-Difluoroethylene in the Gas Phase"
G. W. Flynn and J. D. Baldeschwieler
J. Chem. Phys. 38, 226 (1963)

"Anomalous Ring Proton Shifts in Triphenyl Derivatives of Group IV Elements"
S. Cawley and S. S. Danyluk
J. Chem. Phys. 38, 285 (1963)

"Diterpenoid Bitter Principles. Part V. The Constitution of Palmarin and its Congeners"
S. K. Balasubramanian, D. H. R. Barton and L. M. Jackman
J. Chem. Soc. 4816 (1962)

"The Protonation of Tricarboylcyclo-octatetraeneiron and Some Related Compounds"
A. Davison, W. McFarlane, L. Pratt and G. Wilkinson
J. Chem. Soc. 4821 (1962)

"The Infrared and Nuclear Magnetic Resonance Spectra of a Cyclic Perfluoroazo-compound"
E. A. V. Ebsworth and G. L. Hurst
J. Chem. Soc. 4840 (1962)

"Hydrido-complexes of Platinum(II)"
J. Chatt and B. L. Shaw
J. Chem. Soc. 5075 (1962)

"Biphenylenes. Part VIII. Synthesis and Reactions of 2-Hydroxybiphenylene and of Biphenylene-2,3-quinone"
J. M. Blatchly, J. F. W. McOmie and S. D. Thatté
J. Chem. Soc. 5090 (1962)

"The Structure and Properties of Certain Polycyclic Indolo- and Quinolino-derivatives. Part XV. Derivatives of 1-Phenyl-4-piperidone and its Phosphorus and Arsenic Analogues"
M. J. Gallagher and F. G. Mann
J. Chem. Soc. 5110 (1962)

"Proton Magnetic Resonance Spectra of Grignard Reagents and Related Metal Alkyls"
D. F. Evans and J. P. Maher
J. Chem. Soc. 5125 (1962)

"Adducts from Quinones and Diazoalkanes. Part I. 3-Hydroxy-thymoquinone and Diazomethane"
F. M. Dean, P. G. Jones and P. Sidisunthorn
J. Chem. Soc. 5186 (1962)

"Heterocyclic Compounds of Nitrogen. Part V. The Preparation of 1,3-Diacetyl- and 3-Acetyl-1-methyl-3-phenyloxindole"
J. M. Bruce
J. Chem. Soc. 5302 (1962)

"On the Cyclic Trimerization of Acetylenes"
V. O. Reikhsfel'd, K. L. Makovetskii, and L. L. Erokhina
J. Gen. Chem. USSR 32, 646 (1962)

"The Nuclear Magnetic Resonance Spectra of Enyne and Dienyne Hydrocarbons and Their Silicon-, tin-, and Lead-Containing Analogues"
A. A. Petrov and V. B. Lebedev
J. Gen. Chem. USSR 32, 653 (1962)

"On the Hydrogen Bond Between the Molecules of Acetylenic Aldehydes and Ketones"
A. A. Petrov, V. B. Lebedev, and I. G. Savich
J. Gen. Chem. USSR 32, 655 (1962)

"One Proof of the Hypothesis of the Static π - Conjugation Effect Based on a Mechanistic Concept of Characteristic Frequency. Reply to E. N. Prilezhaena"
M. I. Batuev
J. Gen. Chem. USSR 32, 666 (1962)

"Studies in the Field of Conjugated Systems. CLIII. Bromination of Vinylallylacetylene and its Homologs"
A. A. Petrov and Yu. I. Porfir'eva
J. Gen. Chem. USSR 32, 748 (1962)

"Organo Silylethylenediamine Compounds. II. The Nuclear Magnetic Resonance Spectra of Silylamines"
D. Kummer and J. D. Baldeschwieler
J. Phys. Chem. 67, 98 (1963)

"Nuclear Magnetic Resonance Spectra of Some Alkyl Vinyl Ethers and Methyl Vinyl Sulfide"
R. T. Hobgood, Jr., G. S. Reddy and J. R. Goldstein
J. Phys. Chem. 67, 110 (1963)

"Carbon-13 Splittings in Fluorine Nuclear Magnetic Resonance Spectra"

N. Muller and D. T. Carr
J. Phys. Chem. 67, 112 (1963)

"High Resolution NMR Spectra of Polypropylene"

S. Satoh, R. Chujo, T. Ozeki and E. Nagai
J. Poly. Sci. 62, S101 (1962)

"On Determination of the Tacticity of Polyvinyl Chloride from High Resolution NMR Spectra"

W. C. Tincher
J. Poly. Sci. 62, S148 (1962)

"Proton Magnetic Resonance Investigation of Enzyme-Coenzyme Complexes"

O. Jardetzky, N. G. Wade, and J. J. Fischer
Nature 197, 183 (1963)

"Nuclear Relaxation as a Probe of Electron Spin Correlation"

P. A. Wolff
Phys. Rev. 129, 84 (1963)

"Analysis of Nuclear Magnetic Resonance Line Shapes by Lattice Harmonics"

D. E. O'Reilly and T. Tsang
Phys. Rev. 128, 2639 (1962)

"The Effect of Temperature, Conversion and Solvent on the Stereospecificity of the Free Radical Polymerization of Methyl Methacrylate"

T. G. Fox and H. W. Schnecko
Polymer 3, 575 (1962)

"Proton Magnetic Resonance Spectra of 2,3,4-Tri-O-acetyl-1,6-anhydro-D-hexopyranoses: a Long-range Coupling"

L. D. Hall and L. Hough
Proc. Chem. Soc. 382 (1962)

"The Diamagnetic Shielding of Nuclei in Metals"

J. E. Hebborn
Proc. Phys. Soc. 80, 1237 (1962)

"A Nuclear Magnetic Resonance Investigation of Polypropylene"

M. P. McDonald and I. M. Ward
Proc. Phys. Soc. 80, 1249 (1962)

"The Broadening of Magnetic Resonance Lines due to Field Inhomogeneities in Powdered Samples"

W. M. Lomer
Proc. Phys. Soc. 80, 1380 (1962)

"Spin Diffusion and Nuclear Magnetic Resonance in Rotating Solids"

S. Clough and K. W. Gray
Proc. Phys. Soc. 80, 1382 (1962)

"A Total Synthesis of Griseofulvin and Its Optical Antipode"

D. Taub, C. H. Kuo, H. L. Slates and N. L. Wendler
Tetrahedron 19, 1 (1963)

"Synthesis and Stereochemistry of 16-Substituted Pregnenes and Isoprenenes"

P. Grabbe and L. M. Guerrero and J. Romo and F. Sanchez-Viesca
Tetrahedron 19, 25 (1963)

The Synthesis, Rearrangement and Certain Reactions of 1-(3,4-Dihydroxybenzyl)-1,2,3,4-Tetrahydro- β -Carboline and its 9-Methyl Analogue"

J. Harley-Mason and W. R. Waterfield
Tetrahedron 19, 65 (1963)

"The Stereochemistry and Conformations of 1,2,3,4,4a,9,9a,10-Octahydroacridine"

H. Booth
Tetrahedron 19, 91 (1963)

"Magnetic Shielding of Acetylenic Protons in Substituted Phenylacetylenes"

C. D. Cook and S. S. Danyluk
Tetrahedron 19, 177 (1963)

"Nuclear Magnetic Resonance and Infra-Red Spectra and Structure of the $(C_4H_4Ag)^+$ Ion, and of the Dimer C_8H_8 "

M. Avram, H. P. Fritz, R. Keller, Ch. Mateescu, J. F. W. McOmie, N. Sheppard and C. D. Nenitzescu
Tetrahedron 19, 187 (1963)

"Chemistry of the Podocarpaceae-VII. Podototar and the Constituents of the Heartwood of Podocarpus Halli Kirk"

R. C. Cambie, W. R. J. Simpson and L. D. Colebrook
Tetrahedron 19, 209 (1963)

"The Alkaloids of American Lotus, Nelumbo Lutea"

S. M. Kupchan, B. Dasgupta, E. Fujita and M. L. King
Tetrahedron 19, 227 (1963)

"Indirekte Spin-Spin-Kopplung zwischen Protonen und C^{13} "

H. Dreeskamp and E. Sackmann
Z. Physik. Chem. 34, 273 (1962)

"C-H-Kopplungskonstanten und Hybridisierung des C-Atoms fluorsubstituierter Methane"

E. Sackmann
Chem. 34, 283 (1962)