

Monthly
Ecumenical
Letters from
Laboratories
Of
N - M - R
No. 14

UNIVERSITY OF CALIFORNIA

DEPARTMENT OF CHEMISTRY
BERKELEY 4, CALIFORNIA

October 29, 1959

Drs. A. A. Bothner-By and B. L. Shapiro
M.E.L.L.O.N.M.R.
Mellon Institute
4400 Fifth Avenue
Pittsburgh 13, Pennsylvania

Dear Drs. Bothner-By and Shapiro:

In MELLONMR No. 9 you included a letter on external referencing of samples. In an effort to further pursue this investigation, we have remeasured your sample tubes numbered 71-78 in this laboratory using a slightly different technique which is described below.

Our Hewlett Packard model 200J audio oscillator was modified in order to make possible much finer adjustments of the frequency. This was accomplished by ganging three Erie tubular condensers (1-8 μ fds.) and connecting these in parallel with the three tuning condensers in the oscillator. This made it possible to change the frequency by increments of approximately 0.005 cps. which is of the same order of magnitude as the stability of our oscillator.

In order to determine the frequency to this accuracy a Hewlett Packard electronic counter, model 524D, was employed. The period of the modulating signal was measured rather than its frequency. By so doing, a reading could be taken to six figures, only five of which were significant because of the instability of the oscillator. No errors were introduced by using a sine wave directly rather than converting it into a series of pulses; see MELLONMR No. 9. Moreover, a reading could be taken in milliseconds rather than having to let the counter count for ten second periods.

The sideband of the stronger signal was always superimposed on the weaker signal. The amplitude of the audio oscillator was adjusted so that when the sideband was almost superimposed on the weaker signal, the peak heights of the two signals were equal. After this had been accomplished, the signals were roughly superimposed using the oscilloscope. The modulating frequency was decreased by roughly 0.2 cps. The signals were then recorded, both in the directions of increasing and decreasing field, on a Brown recorder with a 1/4 second time constant using the slow sweep unit. A second person read the counter and recorded the period of the modulating signal. A

serial number was given to the pair of peaks so that the corresponding frequency could later be determined. The operator then increased the frequency by a small unknown amount, usually about 0.02 cps, and ran through the peaks again in both directions. Again, the period was read, recorded, and a serial number assigned to the pair of peaks. This routine was repeated until it was apparent to the operator that the superposition frequency had been passed. At this point the recording consisted of a series of pairs of peaks, each pair having a serial number assigned to it. The envelope of these peaks was nearly a smooth curve which went through a maximum. By taking this entire series of measurements, spuriously large or small signals due to drift or instantaneous changes in the homogeneity of the field could be disregarded. After the series of peaks had been recorded the operator decided if the conditions had remained constant enough during the run to make the results meaningful. At this point the entire run could be disregarded. However, if it was accepted at this point, it could no longer be thrown out. If the run was acceptable to the operator, without knowledge of the frequencies corresponding to the various peaks he designated one peak by serial number as being the best superposition. The corresponding frequency was then tabulated.

The two people making these runs switched off in the two positions. Six such determinations were made on each sample. All determinations were made at 60.0032 megacycles. The results and sample temperatures are tabulated on Enclosure (1).

From these measurements we have concluded, in agreement with you, that the capillary method of external referencing is quite suitable for high precision work. Although the differences between the measurements in the various laboratories are larger than the most probable error, they are quite small. It is difficult to imagine cases where this magnitude of systematic errors would cause trouble. Moreover, the random errors in both laboratories are sufficiently small to allow very precise self-consistent measurements to be made on a single instrument.

For very precise work, we recommend the procedure outlined here. Although it takes somewhat more time to complete a measurement by this method, small changes in the field homogeneity and errors introduced in frequency counting of a sine wave can be substantially minimized.

Sincerely,

Leon Petrakis

Leon Petrakis

Charles H. Sederholm

Charles H. Sederholm

Enclosure (1)

Tube Number	71	72	73	74	75	76	77	78	Ave. a,b
Temp.	30°C	29°C	28°C	29°C	30°C	30°C		30°C	
	237.58	237.72	237.73	237.64	237.70	237.65	broken	237.64	
	237.58	237.68	237.68	237.60	237.69	237.60		237.61	
	237.58	237.67	237.72	237.62	237.68	237.62		237.65	
	237.58	237.70	237.71	237.61	237.63	237.65		237.63	
	237.57	237.65	237.70	237.64	237.69	237.65		237.60	
	237.56	237.70	237.69	237.59	237.66	237.68		237.65	
	237.575	237.687	237.705	237.617	237.675	237.647		237.630	237.65
	±.002	±.007	±.005	±.006	±.007	±.008		±.005	±.01
	237.65 ± .02				237.65 ± .01				

a) $X2/3 = 158.43 \pm .01$.

b) At 60.0032 megacycles or 237.64 at 60 megacycles.

Leon Petrakis and Charles H. Sederholm

Department of Chemistry, University of California

Enclosure (1)

THE UPJOHN COMPANY

FINE PHARMACEUTICALS SINCE 1880

KALAMAZOO, MICHIGAN

RESEARCH DIVISION
301 HENRIETTA STREET

November 10, 1959

Dr. Aksel A. Bothner-by
Assistant Director of Research
Mellon Institute
4400 Fifth Avenue
Pittsburgh 13, Pennsylvania

Dear Dr. Bothner-by:

Recently we converted our Varian 4300-2 spectrometer from 40 to 60 mc. operation. Since others may be considering such a conversion, the results may be of general interest.

A. Effects on the spectra

For the increased frequency the resonant field strength has been increased from 9,400 to 14,100 gauss. This enhances chemical shifts and decreases second-order splitting. Enhancement of chemical shift is clearly of great value. The effect on the second-order splitting may be seen for the ethyl group as an example in Figure I¹. The field increase serves to diminish ω by one-third.

Ethanol, which is not highly coupled ($\omega^{40} = \text{ca. } 0.07$, $\omega^{60} = \text{ca. } 0.05$), is only slightly simplified, as shown in Figure II. Tetraethylsilane, which is more highly coupled ($\omega^{40} = -0.47$, $\omega^{60} = 0.31$), shows greater improvement (see Figure III). The 60 mc. spectrum fits the theoretical spectrum for $\omega = 0.31$, obtained by interpolation of Figure I, surprisingly well.

The improvement in the resolution of the spectra of steroids was quite dramatic. See Figure IV for example.

B. Sample requirement

The increase in frequency has lowered the concentration requirement on the sample by about one-half, and the improved receiver allows useful spectra to be recorded at a much higher gain. The result is that many steroids which were eliminated earlier by solubility requirements are now good subjects for NMR study. Sample concentration requirements for 40 mc. operation were given by Shoolery and Rogers². Data are recorded for 60 mc. spectra in Figure V.

The expert operation of the spectrometer by Mr. Forest MacKellar is gratefully acknowledged.

Very truly yours,

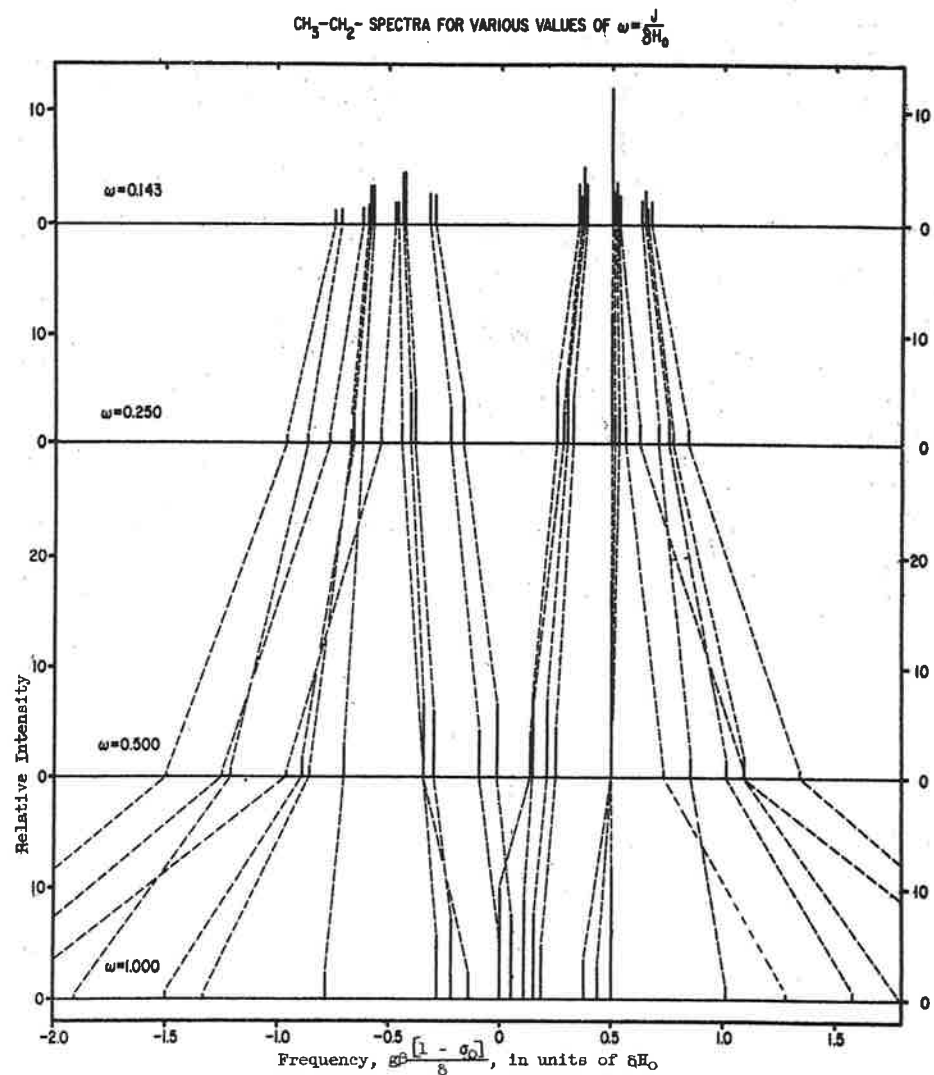
George Slomp
George Slomp
Department of Physical
and Analytical Chemistry

prv

¹B. R. McGarvey and G. Slomp, J. Chem. Phys. 50, 1533 (1959).

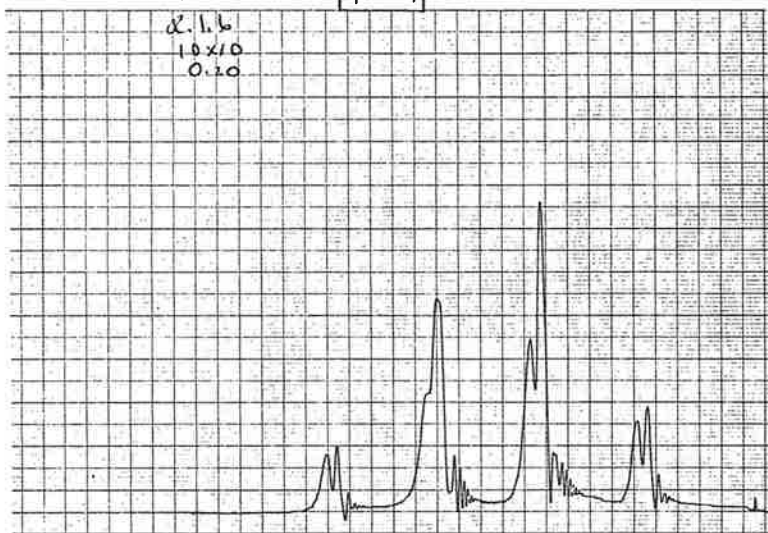
²J. N. Shoolery and M. T. Rogers, J. Am. Chem. Soc. 80, 5121 (1959).

Figure 1. - Calculated Proton Magnetic Resonance Spectra for Three-Hydrogen - Two-Hydrogen System.



7-950-431 40mc. MAY 1 1959

2.1.6
10x10
0.10



60 mc.

SEP 24 1959

90 down
10x5
1.00

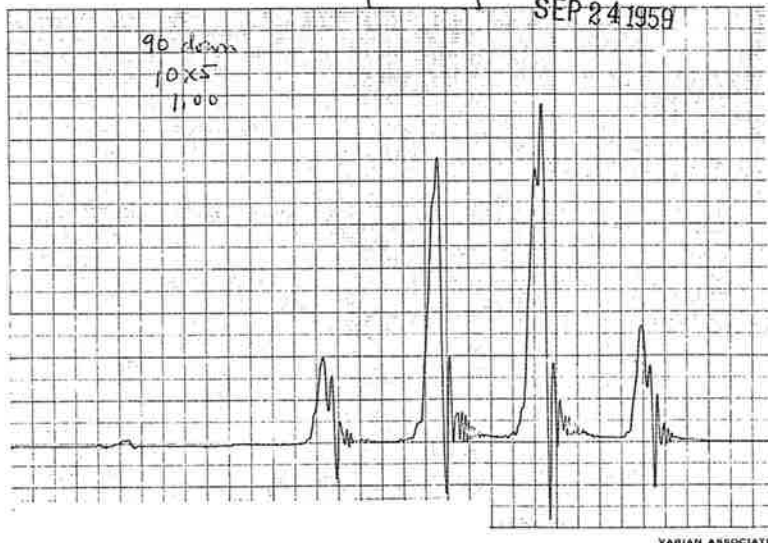


Fig. 2.-N.M.R. Spectra of Ethanol at 40 and 60 mc., Quartet Portion.

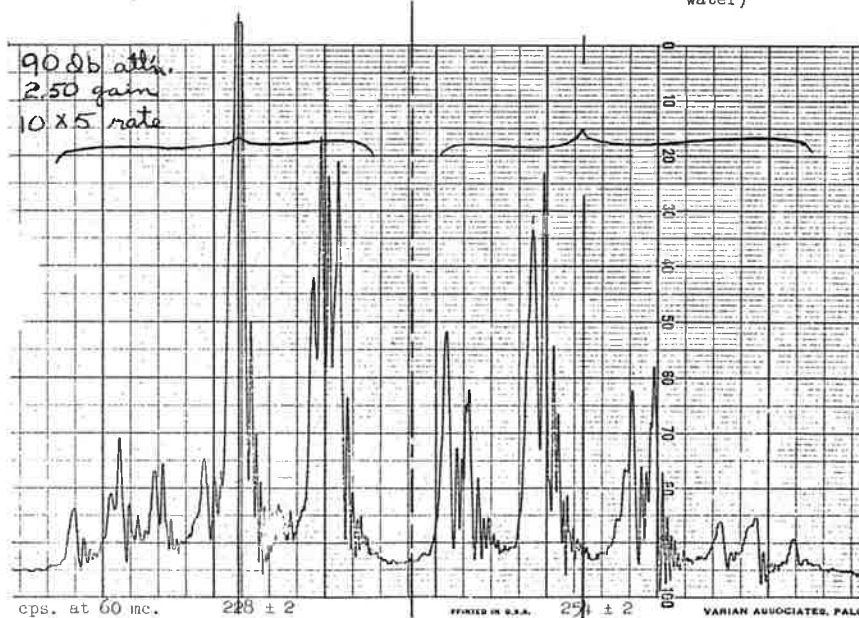
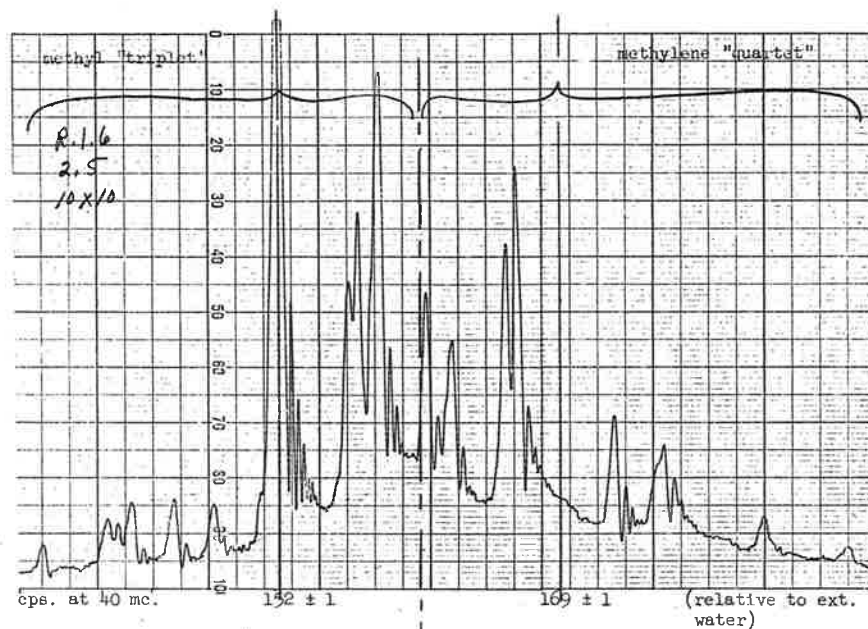
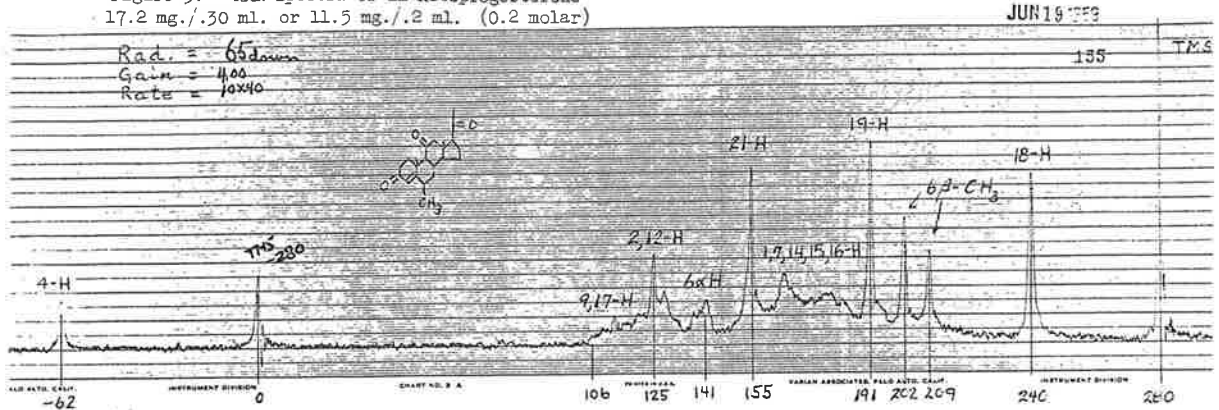
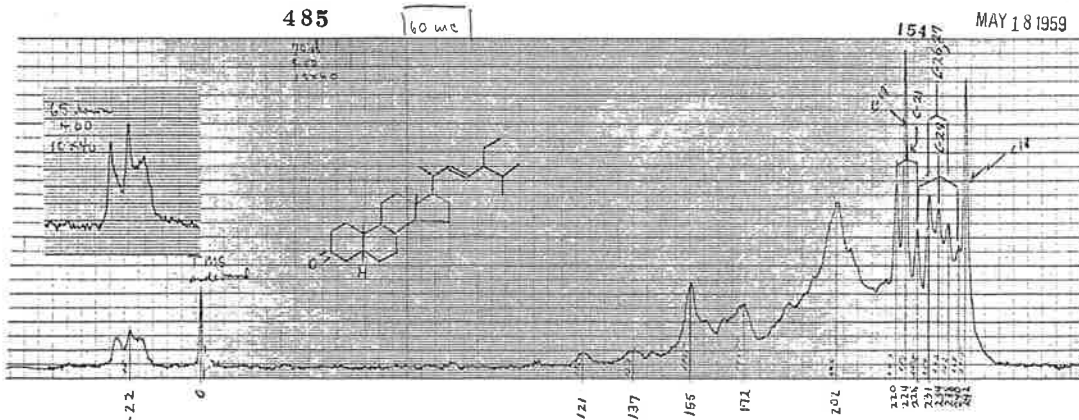
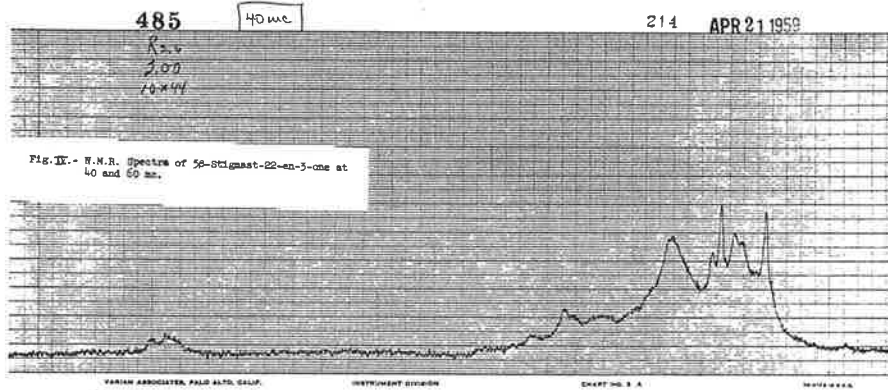
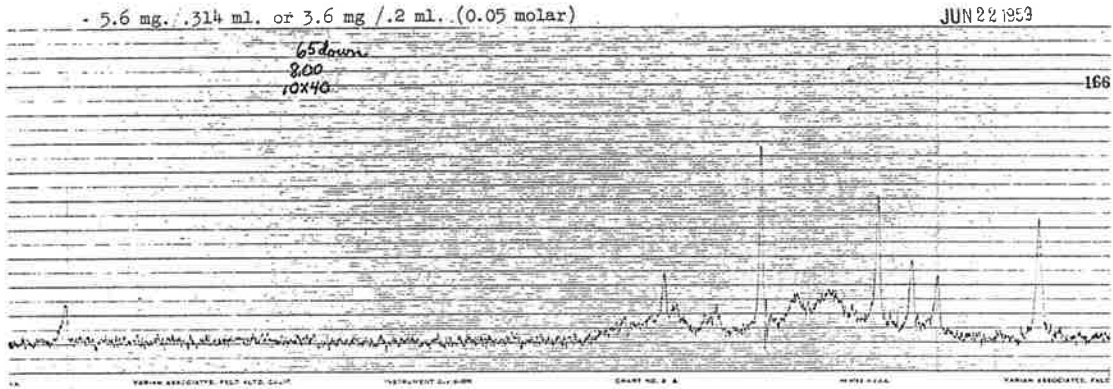


Figure 3. HMR Spectra of Tetraethylsilane at 40 and 60 mc.

Figure 5. - NMR Spectra of 11-Ketoprogesterone
 17.2 mg./30 ml. or 11.5 mg./2 ml. (0.2 molar)



- 5.6 mg./3.14 ml. or 3.6 mg./2 ml. (0.05 molar)



cps at 60 mc. (relative to water)

PURDUE UNIVERSITY
DEPARTMENT OF CHEMISTRY
LAFAYETTE, INDIANA

November 19, 1959

Proton Magnetic Resonance Spectrum of Aluminum Trimethyl Dimer

Sir:

It has been shown using X-ray diffraction data¹ that aluminum

(1) P. H. Lewis and (E. R.) Rundle, *J. Chem. Phys.*, 21, 986 (1953).

trimethyl exists in the solid state as a dimer with two methyl groups forming bridges between the aluminum atoms. The compound also appears to be predominantly dimeric in benzene solution² and in the gaseous state.³

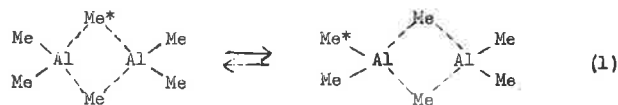
(2) K. S. Pitzer and H. S. Gutowsky, *J. Am. Chem. Soc.*, 68, 2204 (1946).

(3) A. W. Laubengayer and W. F. Gilliam, *Ibid.*, 63, 477 (1941).

It is therefore surprising that the room-temperature proton magnetic resonance spectrum⁴ of the liquid consists of a single peak rather than

(4) J. A. Pople, W. G. Schneider and H. J. Bernstein, "High-resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., New York, 1959, p. 296.

a pair of signals with relative intensities 1:2 corresponding to protons in bridging and in terminal methyl groups, respectively. This indicates either that all the protons are magnetically equivalent or that the two species are involved in a rapid exchange process which may be represented as:

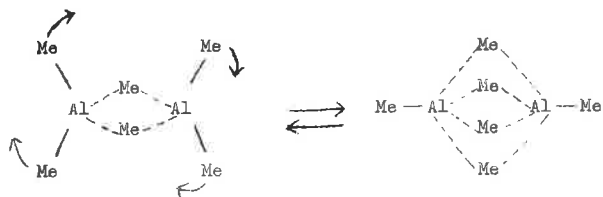


- 2 -

To decide between these possibilities we have examined the proton resonance spectrum at 56,445 mc of a liquid solution containing approximately 12 mole per cent of Al_2Me_6 in cyclopentane, between 25°C and -75°C. At the low temperature we observed the two signals expected for the bridge structure. We detected no further splitting of the smaller peak, showing that the protons in the bridging methyl groups remain magnetically equivalent at -75°C. Using the solvent resonance as an internal standard we found chemical shifts of +1.04 ppm and +2.17 ppm respectively for the protons of the bridging and the terminal methyl groups. As the temperature increases the peaks first broaden and eventually coalesce to a single, sharp peak at +1.79 ppm, precisely the weighted average of the low-temperature shifts. This behavior is characteristic of an exchange process.⁵

(5) Ref. 4, pp. 218 ff.

We are studying the detailed temperature-dependence of this spectrum in order to obtain the activation energy of reaction (1) as accurately as possible. The data already ~~available~~^{OBTAINED} indicate that this energy is between 6 and 14 kcal/mol. The heat of dissociation of the dimer is 20.2 kcal/mol at 100 to 150°C in the gaseous phase.³ We conclude that $AlMe_3$ monomer probably is not formed as an intermediate in (1) but that the exchange is an intramolecular process. Formation of the transition state may involve the breaking of one C---Al bond, or perhaps a deformation of the molecule in which no bonds are broken, leading to a structure having four bridging methyl groups at the corners of a square, i.e.



The 3d orbitals of the aluminum atom would then be expected to contribute to the bonding, involving four electron pairs in six-center molecular orbitals.

This work was made possible by grants from the Purdue Research Foundation, E. I. du Pont de Nemours and Company, and the National Science Foundation. We thank Professor Grant Urry and Mr. James Nuss for the sample of Al₂Me₆.

Norbert Muller
Donald E. Pritchard⁶

(6) Lubrizol Corporation Predoctoral Fellow.

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