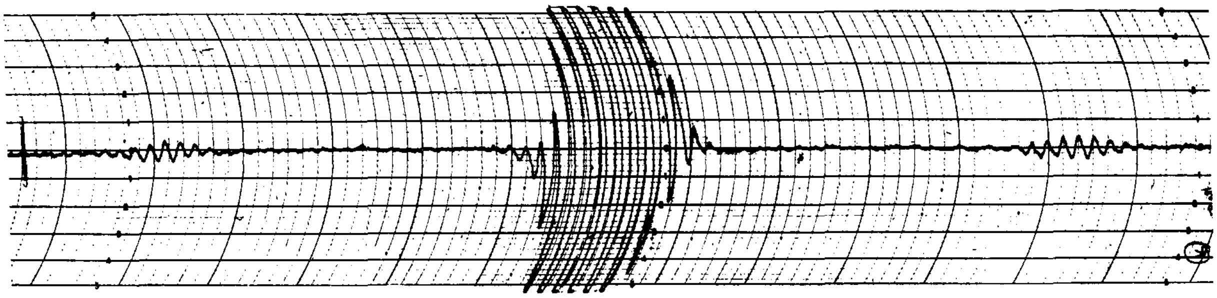


Fig. 1.—dX''/dH *vs.* H for potassium ketyl of hexamethylacetone in THF.

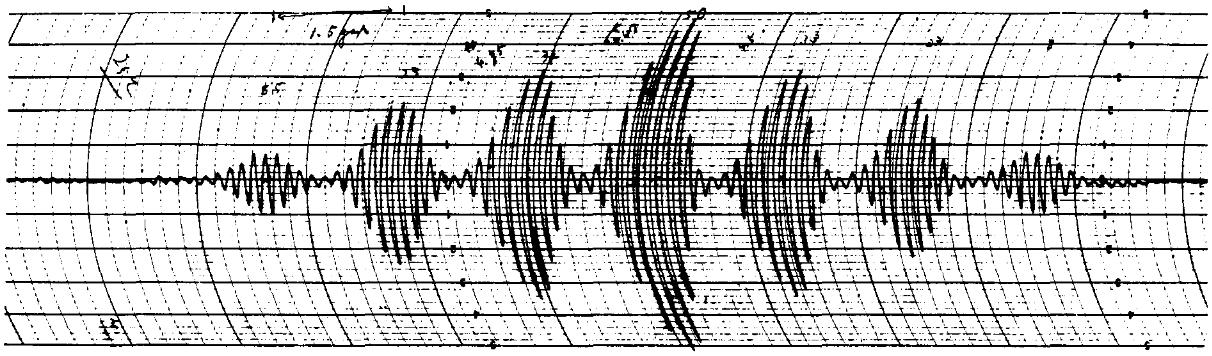
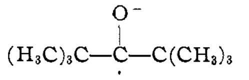
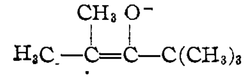


Fig. 2.—dX''/dH *vs.* H for sodium ketyl of hexamethylacetone in THF.

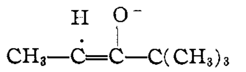
and suggest structure I as the major ingredient in the ground state of each of the ketyls.



$(H_3C)_3C-\overset{O^-}{\underset{\cdot}{C}}-C(CH_3)_3$ (I)



$H_3C-\underset{\cdot}{\overset{CH_3}{C}}=\overset{O^-}{C}-C(CH_3)_3$ (II)



$CH_3-\overset{H}{\dot{C}}=\overset{O^-}{C}-C(CH_3)_3$ (III)

Splittings by the methyl carbons and by the unique proton in pentamethylacetone could be accounted for by admixture of conjugated structures such as II and III. (In view of the recent proliferation in names of conjugations we don't know which kind we are reporting.) Admixture of two or three per cent. of each of structure II and of about 0.5 per cent. of structure III could account for the observed splittings.

The absence of splittings by the quaternary carbons is not easily explained. Spin polarization of the σ bond between them and the central carbon might be expected to produce observable splittings. Probably other structures which produce spin density of opposite sign to that produced by I must be included.

When sodium or lithium is used as reducing agent, the splittings by protons and C^{13} in the ketyls are almost identical with those described in the preceding paragraphs. In addition, splittings by two equivalent alkali metal nuclei per paramagnetic molecule are found. The sodium compound in tetrahydrofuran yields seven evenly spaced lines at interval 1.58 oe. with intensities 1:2:3:4:3:2:1 (Fig. 2). The spectrum of the lithium ketyl is somewhat more complex because of the presence of the isotopes Li^6 and Li^7. The complexes with sodium and lithium are under further investigation.

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RECEIVED JULY 11, 1960

N.M.R. SPECTRA AND STRUCTURE OF ALUMINUM METHYL CHLORIDES

Sir:

Recently Brownstein, *et al.*,[1] have published n.m.r. data on $Al_2(CH_3)_6$, $Al_2(CH_3)_4Cl_2$ and $Al_2(CH_3)_2Cl_4$. The interpretation of their results for $Al_2(CH_3)_4Cl_2$ and $Al_2(CH_3)_2Cl_4$ is based on the methyl bridge model for these two molecules deduced from Raman Spectra by Van der Kelen and Herman.[2] However, for $Al_2(CH_3)_4Cl_2$ a chlorine bridge structure was deduced from electron diffraction measurements by Brockway and Davidson,[3] from the infrared spectrum by Schomburg,[4] and from infrared and Raman work.[5,6] The vibrational spectrum of $Al_2(CH_3)_2Cl_4$ gives evidence of a centrosymmetrical structure[6] but subsequent Raman work did not yet allow of a definite choice between the chlorine bridge model (C_{2h} symmetry) and the methyl bridge model (D_{2h} symmetry).

The n.m.r. spectra of Brownstein, *et al.*, were

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[1] S. Brownstein, B. C. Smith, G. Ehrlich and A. W. Laubengayer, THIS JOURNAL, **82**, 1000 (1960).

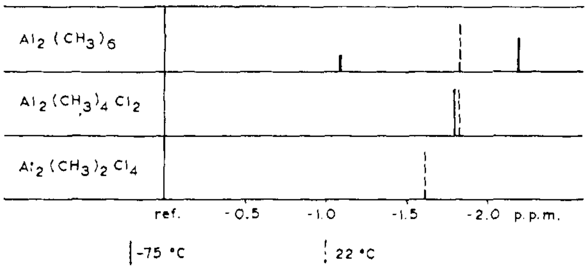
[2] G. P. Van der Kelen and M. A. Herman, *Bull. Soc. Chim. Belges*, **65**, 350 (1956).

[3] L. O. Brockway and N. R. Davidson, THIS JOURNAL, **63**, 3287 (1941)

[4] G. Schomburg, "Infrarot spektroskopische Untersuchungen an aluminum-organischen Verbindungen," Diss., Aachen, 1956.

[5] M. P. Groenewege, *Z. physik Chemie, Neue Folge*, **18**, 147 (1958).

[6] M. P. Groenewege, *Revue Universelle des Mines* (*Liege*), 9 Série, **15**, 461 (1959).



N.m.r. chemical shifts from C_5H_{10}

taken in cyclohexane solution so that no low temperature high-resolution data could be obtained, the melting point of the solutions being 0°. We therefore repeated these measurements in cyclopentane solution as was done for $Al_2(CH_3)_6$ by Muller and Pritchard.[7]

The spectra were taken by means of a Varian V 4300-B high-resolution n.m.r. spectrometer operating at a frequency of 40 mhz. The measurements were made in three different concentrations to eliminate concentration effects. The chemical shifts in p.p.m. relative to cyclopentane are presented in the table. The negative values correspond to resonance at a higher field than the reference protons. The precision is ± 0.03 p.p.m. The results of references 1 and 7 have been included in the table for comparison. Brownstein's chemical shifts, based on cyclohexane, have been reduced to cyclopentane by adding −0.07 p.p.m., this being the difference in chemical shift between cyclopentane and cyclohexane.[8]

TABLE I

N.M.R. CHEMICAL SHIFTS RELATIVE TO C_5H_{10} IN P.P.M. ±0.03

Compound	Concentration[a]	22°	−75°
$Al_2(CH_3)_6$	1.80	−1.81	−1.10[b] −2.20[c]
	0.52	−1.85	
	0.21	−1.83	−1.05[b] −2.20[c]
		−1.79[d]	−1.04[d] −2.17[d]
		−1.82[e]	
$Al_2(CH_3)_4Cl_2$	1.20	−1.83	−1.85
	0.60	−1.87	
	0.24	−1.85	−1.80
		−1.82[e]	
$Al_2(CH_3)_2Cl_4$	0.93	−1.60	[f]
	0.46	−1.60	
	0.19	−1.62	
		−1.52[e]	

[a] Concentration in mole/l. of monomer. [b] Bridge CH_3 groups. [c] Outer CH_3 groups. [d] Ref. 7. [e] Ref. 1. [f] Solubility too low.

It can be seen from the table that the effect of dilution in cyclopentane solution is within the experimental error.

The room temperature peak of $Al_2(CH_3)_6$ occurs at the weighted average of the two low temperature peaks. The effect of temperature is negligible in the case of $Al_2(CH_3)_4Cl_2$. The low-temperature spectrum of $Al_2(CH_3)_2Cl_4$ could not be observed because of the low solubility in cyclopentane at temperatures below 0°.

The compounds were prepared from Al and CH_3Cl[5]) according to Söll's procedure.

Several conclusions can be drawn:

$Al_2(CH_3)_6$: Our observations and conclusions are in good agreement with those of Muller and Pritchard[7] and Brownstein, *et al.*[1] The bridge CH_3 group protons are less shielded than those of the outer CH_3 groups. At room temperature a rapid exchange of bridge and outer CH_3 groups makes the two resonances coalesce into a single peak.

$Al_2(CH_3)_4Cl_2$: The unsplit low temperature resonance can be explained readily in terms of the chlorine bridge model exhibiting four equivalent outer CH_3 groups. The shift over about 0.35 p.p.m. to a lower field (see figure) with respect to the outer CH_3 group protons in $Al_2(CH_3)_6$ is seen as a consequence of the substitution of CH_3 by Cl. It is in good agreement with our unpublished results for $Ti(CH_3)_2Cl_2$ and $TiCH_3Cl_3$ where the proton resonance shifts over 0.30 p.p.m. to a lower field on substitution of CH_3 by Cl.

The low temperature spectrum observed does not support the methyl bridge model adhered to in references 1 and 2. The bridge and outer CH_3 groups of this model would have to exchange rapidly even at −75°.[9] Moreover, the substitution of two CH_3-groups by Cl atoms in $Al_2(CH_3)_6$ is expected to shift the weight average resonance to a lower field.

$Al_2(CH_3)_2Cl_4$: The low temperature spectrum is expected to be almost identical with the room temperature spectrum. There is little reason to expect any splitting by unequivalent positions in this molecule. The effect of temperature on the resonance of $Al_2(CH_3)_4Cl_2$ was seen to be very small. The shift to a lower field over about 0.25 p.p.m. with respect to $Al_2(CH_3)_4Cl_2$ and over about 0.60 p.p.m. with respect to the outer CH_3 groups of $Al_2(CH_3)_6$ suggests that there are outer CH_3 groups in this molecule as well. Finally it is improbable that the bridge CH_3 group protons of $Al_2(CH_3)_6$ would shift over about 0.5 p.p.m. to a higher field if four CH_3 groups should be replaced by Cl atoms.

Consequently, our N.m.r. data are thought to support the chlorine bridge hypothesis in both $Al_2(CH_3)_4Cl_2$ and $Al_2(CH_3)_2Cl_4$.

---

(7) N. Muller and D. E. Pritchard, THIS JOURNAL, **82**, 248 (1960).

(8) L. M. Jackman, "Applications of NMR Spectroscopy in Organic Chemistry," Pergamon, New York, 1959, p. 52.

(9) The half width of the peak is invariably 1 hertz, even down to −85°, which is in marked contrast with $Al_2(CH_3)_6$ where the broadening sets in a little below room temperature (the half width increases from 1 to 7 hertz between 22 and −36°).

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RECEIVED JUNE 29, 1960

DIPROPYLCYCLOPROPENONE

Sir:

Some time ago we reported[1] the synthesis of diphenylcyclopropenone, utilizing the reaction between phenylketene acetal and phenyl chlorocarbene, and only shortly thereafter Volpin and his coworkers described[2] an independent synthesis using

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(1) R. Breslow, R. Haynie and J. Mirra, THIS JOURNAL, **81**, 247 (1959).

(2) M. Volpin, Yu. Koreshkov and D. Kursanov, *Izvest. Akad. Nauk SSSR*, 560 (1959).