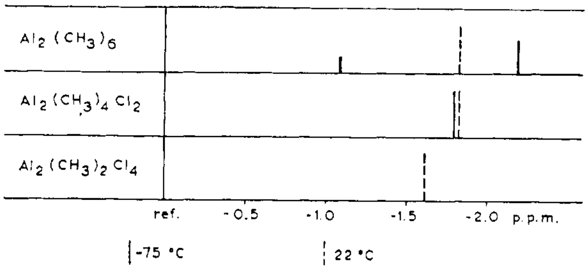

N.m.r. chemical shifts from C_5H_{10}

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	
	0.46	−1.60	[f]
	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 $Al_2(CH_3)_2Cl_4$.

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

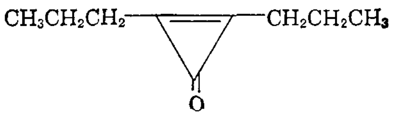
[8] L. M. Jackman, "Applications of NMR Spectroscopy in Organic Chemistry," Pergamon, New York, 1959, p. 52.

[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°).

[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).

the much more convenient reaction between diphenylacetylene, bromoform, and potassium *t*-butoxide. Although the stability of this ketone seemed to be due to aromaticity of the cyclopropenone system, there was the difficulty that the phenyl substituents might be markedly stabilizing an otherwise unstable ketone, as they do in the cyclopentadienone series. Accordingly we have now prepared a cyclopropenone with simple alkyl substituents, dipropylcyclopropenone, and have studied its stability.



Reaction of dipropylacetylene with dichlorocarbene, either from the decarboxylation of sodium trichloroacetate[3] or better (~ 5% yield) from the reaction between sodium methoxide and ethyl trichloroacetate,[4] yielded dipropylcyclopropenone after isolation by acid extraction (*vide infra*), b.p. 66° (0.3 mm.). *Anal.* Calcd. for $C_9H_{14}O$: C, 78.26; H, 10.15. Found: C, 77.99; H, 10.34. In the infrared the ketone had the strongest absorption at 1850 $cm.^{-1}$, as expected (the diphenyl ketone absorbs at 1865 $cm.^{-1}$, with a shoulder at 1850 $cm.^{-1}$), and in addition it had strong absorption at 1640 $cm.^{-1}$, as observed for the diphenyl ketone. The ultraviolet spectrum showed only end absorption ($\epsilon_{215\ m\mu} = 540$).[5] The n.m.r. spectrum[6] was as expected, showing the characteristic pattern of a propyl group with an electron-withdrawing substituent, with a (four proton) triplet centered at 240 (J, 7 c.p.s.), a (four proton) sextuplet at 293 (J, 7 c.p.s.), and a (six proton) triplet at 334 (J, 7 c.p.s.).

The dipropyl ketone is somewhat more basic than the diphenyl ketone, and with 12 *N* hydrochloric acid it is extracted completely from an equal volume of carbon tetrachloride, and 50% extracted with 6 *N* acid, while the diphenyl ketone is only 50% extracted with 12 *N* acid; the compounds are regenerated unchanged by addition of sodium bicarbonate. Dipropylcyclopropenone is moderately sensitive to oxygen, and indeed satisfactory analytical results could be obtained only when it was handled under nitrogen. However, in other respects it is remarkably stable. Thus after 15 min. at 190° under nitrogen the compound is only 75% destroyed, while the diphenyl ketone is destroyed completely after 5 min. under these conditions, and indeed is 75% destroyed after 15 min. at 160°. Perhaps more striking than this greater thermal stability of the dipropyl ketone is its greater stability toward base. Preliminary studies show that the diphenyl ketone is 90% cleaved after 3 min. at 31° in 0.1 *N* ethanolic sodium hydroxide, the product being stilbenecarboxylic acid, but the dipropyl ketone is recovered completely unchanged after one hour under the same conditions.

These results do not necessarily signify a greater stabilizing effect for the propyl substituents than for the phenyls, but on the contrary they more likely reflect greater stabilization by the phenyl groups of the transition states in the decompositions. It is particularly apparent that the developing anion in the basic ring-cleavage reaction would be strongly stabilized by phenyl groups. However, the properties of dipropylcyclopropenone support the idea that the high stability of these very strained compounds is due to special aromatic conjugation. The obvious extension of this work to other cyclopropenones of interest is currently under way.

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[3] W. M. Wagner, *Proc. Chem. Soc.*, 229 (1959).

[4] W. E. Parham and E. E. Schweizer, *J. Org. Chem.*, **24**, 1733 (1959).

[5] *Cf.* the similar interesting situation in the case of the dipropylcyclopropenium ion, R. Breslow and H. Höver, THIS JOURNAL, **82**, 2644 (1960).

[6] N.m.r. spectrum in CCl_4 solution at 60 megacycles. Shifts relative to an external benzene capillary.

STRUCTURE OF $B_{12}H_{12}^{-2}$ ION

Sir:

The recent isolation[1] of $K_2B_{12}H_{12}$ recalls the molecular orbital predictions of the stability of either the icosahedral[2,3] or the closely related cube-octahedral[4] $B_{12}H_{12}$ arrangements as the −2 ions. An X-ray diffraction study of $K_2B_{12}H_{12}$ has now shown that $B_{12}H_{12}^{-2}$ is very nearly icosahedral in the crystal.

The crystals are cubic in the space group T_h^3–Fm3, with $a = 10.61$ Å. (standard deviation, $\sigma = 0.01$ Å.), and with 4 molecules in the unit cell. With the origin at the center of the $B_{12}H_{12}^{-2}$ polyhedron (Fig. 1), the 8K atoms are in positions[5] 8(c): $\frac{1}{4}\ \frac{1}{4}\ \frac{1}{4}$, etc., and the 48 B are in positions 48(h): $0zy$, etc., with $y = 0.1359$ ($\sigma = 0.0004$) and $z = 0.0827$ ($\sigma = 0.0004$). The 48H atoms are also in positions 48(h) with $y = 0.220$ ($\sigma = 0.005$) and $z = 0.138$ ($\sigma = 0.005$). Weissenberg photographs of levels 1, 3 and 5 about the cube axis yield values of $R = \Sigma\ ||Fo| - |Fc||/\Sigma|Fo| = 0.099$ for the 43 observed reflections to which only B and H contribute. The 75 observed reflections from levels 0, 2, 4 and 6 yield $R = 0.061$ for the complete structure. Corresponding values of $r = \Sigma w(|F_0|^2 - |Fc|^2)^2/\Sigma w|F_0|^4$ are 0.067 for odd levels and 0.047 for even levels, after refinement by least squares procedures.

The space group requires at least T_h–m3 symmetry for the $B_{12}H_{12}^{-2}$ ion, but excludes the four-fold axes of the cube-octahedron. The 6 B–B bond distances along the edges of the cubic cell are 1.755 Å. ($\sigma = 0.007$ Å.), while the 24 B–B distances around the three-fold axes of the polyhedron are 1.780 Å ($\sigma = 0.007$ Å.) as if they are spread slightly by steric interaction between the corresponding H atoms and the K^+ ions. The deviations in the crystal of these two types of B–B distances from their mean distance of 1.77 Å. for a regular icosahedron are so small that it seems reasonable to believe that the isolated $B_{12}H_{12}^{-2}$ ion would indeed have the full icosahedral symmetry. Each K^+ ion is surrounded

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[1] A. R. Pitochelli and M. F. Hawthorne, THIS JOURNAL, to be published.

[2] H. C. Longuet-Higgins and M. de V. Roberts, *Proc. Roy. Soc.* (*London*), **A230**, 110 (1955).

[3] W. H. Eberhardt, B. L. Crawford, Jr., and W. N. Lipscomb, *J. Chem. Phys.*, **22**, 989 (1954).

[4] W. N. Lipscomb and D. Britton, *ibid.*, to be published.

[5] "International Tables for X-Ray Crystallography," Vol. I, The Kynoch Press, Birmingham, England, 1952, p. 311.