

to us to be suspiciously similar to a poorly resolved spectrum of the biphenyl radical anion.<sup>10</sup>

(10) The spectrum given in ref 8 involves nine, or possibly 11, lines separated by 2.7 gauss (the spectrum was analyzed in terms of 13 lines). Biphenyl radical anion at high concentration yields a nine-line spectrum, with intensities similar to the central nine lines of the reported spectrum, and with a line separation of 2.7 gauss. It is possible that the central seven lines of this spectrum was previously identified as cyclopropane radical anion: K. W. Bowers and F. D. Greene, *J. Am. Chem. Soc.*, **85**, 2331 (1963); K. W. Bowers, G. J. Nolti, T. H. Lowry, and F. D. Greene, *Tetrahedron Letters*, 4063 (1966); see also F. Gerson, E. Heilbronner, and J. Heinzer, *ibid.*, 2095 (1966).

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### The Vacuum Ultraviolet Photolysis of Benzene<sup>1</sup>

Sir:

Two reports of the vapor phase photolysis of benzene at 1849 Å have appeared recently: one by Foote, Mallon, and Pitts,<sup>2</sup> and one by Shindo and Lipsky.<sup>3</sup>

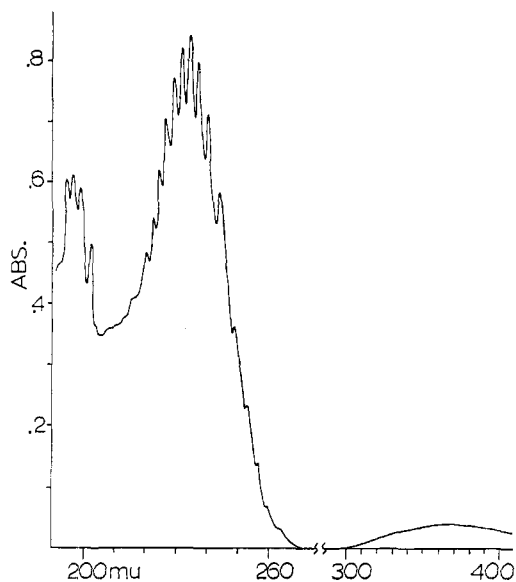


Figure 1. Vapor phase ultraviolet spectrum of fulvene produced by the photolysis of benzene.

Both groups report a single major product in addition to polymeric materials, and both groups suggest that this product is "benzvalene"<sup>4</sup> (I). In neither case was this product isolated, but the ultraviolet spectra<sup>5</sup> are nearly identical in the two reports<sup>2,3</sup> and there is little doubt that both groups have detected the same compound.

As part of a general investigation of vacuum ultraviolet photochemistry, we have examined the products formed from benzene on irradiation with light of 1600–2000 Å. We also find that a single major product is formed when benzene is photolyzed at pressures of 1–

(1) The authors gratefully acknowledge financial support from the National Science Foundation (GP-3496).

(2) J. K. Foote, M. H. Mallon, and J. N. Pitts, Jr., *J. Am. Chem. Soc.*, **88**, 3698 (1966).

(3) K. Shindo and S. Lipsky, *J. Chem. Phys.*, **45**, 2292 (1966).

(4) Tricyclo[2.1.1.0<sup>5,6</sup>]hex-2-ene.

(5) Lipsky<sup>3</sup> states that his published spectrum was obtained by subtracting absorption due to benzene. Pitts<sup>2</sup> does not report the method by which his spectrum was obtained.

100 mm, and we have succeeded in the isolation of this elusive compound by preparative gas chromatography. The separation was effected by a 0.25-in × 25 ft. Ucon 50-HB-100 column, 25% on 100–120 mesh Chromosorb W, operated at 45°. The effluent stream from the column was split with 10% going to a flame ionization detector, and 90% going to a collector trap. Traps were fitted with vacuum stopcocks and were kept in liquid nitrogen baths at all times during the collection sequence. The trapped material was vacuum-transferred from the traps directly into an absorption cell for determination of the ultraviolet spectrum. For infrared and nuclear magnetic resonance spectra, the sample was transferred onto frozen carbon tetrachloride. The compound is quite stable in the gas phase and in dilute solution (either in benzene or in carbon tetrachloride). Solutions of the compound are bright yellow in color.

The ultraviolet spectrum (vapor phase, Figure 1), although taken under higher resolution than the published spectra, shows the same absorption maxima and relative intensities.<sup>6</sup> The agreement between our spectrum and that published by Lipsky<sup>3</sup> is especially striking in the region 2560 to 2120 Å; both show a 17-member progression of fine structure bands with separations of about 500 cm<sup>-1</sup>. In addition, the gas chromatographic retention time is nearly the same as that reported by Pitts<sup>2</sup> on a Ucon-polar column (retention time relative to benzene is 0.90 on a Ucon 50-HB-100 column at 50°). This evidence leads us to believe that the photoproduct formed in our system is the same as that formed by photolysis at 1849 Å.<sup>2,3</sup>

The compound that we have isolated is *not* "benzvalene" (I) but has been demonstrated conclusively to be fulvene (II).<sup>7</sup> This product exhibits ultraviolet



and mass spectra and retention times identical with those of authentic fulvene prepared in the conventional way,<sup>8</sup> and the nuclear magnetic resonance and infrared spectra are the same as those reported<sup>9</sup> for fulvene.

Considerable attention was given to the possibility that fulvene might result from a rearrangement of "benzvalene" initially formed on photolysis. However, the photoproduct collected at 77°K in a flow system had the characteristic bright yellow color of fulvene, and analysis of samples taken immediately on melting the trapped product showed no evidence of rearrangement on the gas chromatography column. If such a rearrangement occurs it must be an exceedingly facile one.

The formation of fulvene from the irradiation of benzene at its first absorption band in the liquid phase has been reported by Bryce-Smith.<sup>10</sup> In the vapor phase,

(6) Spectra published by Pitts and Lipsky do not extend far enough to show the broad absorption band at about 365 mμ which is present in our spectrum.

(7) Pitts<sup>2</sup> mentions fulvene as a possible identity for his photoproduct.

(8) J. Thiec and J. Wiemann, *Bull. Soc. Chim. France*, 177 (1956); H. J. F. Angus and D. Bryce-Smith, *J. Chem. Soc.*, 1409 (1960).

(9) H. Schaltegger, M. Neuenschwander, and D. Meuche, *Helv. Chim. Acta*, **48**, 955 (1965).

(10) (a) J. Mc. Blair and D. Bryce-Smith, *Proc. Chem. Soc.*, 287 (1957); (b) H. J. F. Angus, J. M. Blair, and D. Bryce-Smith, *J. Chem. Soc.*, 2003 (1960).

however, benzene does not react significantly upon photolysis at the first absorption band (usually 2537-Å radiation).<sup>11</sup> Since fulvene is known not to revert to benzene,<sup>10b</sup> it seems unlikely that its formation is relevant to the known photoisomerization of alkyl-substituted benzenes.<sup>12</sup>

We are continuing our investigations to determine if the identities of the minor products of benzene photolysis may provide more useful information on the excited states produced by vacuum ultraviolet irradiation.

(11) J. N. Pitts, J. K. Foote, and J. K. S. Wan, *Photochem. Photobiol.*, **4**, 323 (1965).

(12) See K. E. Wilzbach and L. Kaplan, *J. Am. Chem. Soc.*, **87**, 4004 (1965), and references contained therein.

(13) NASA Trainee, 1965-1967.

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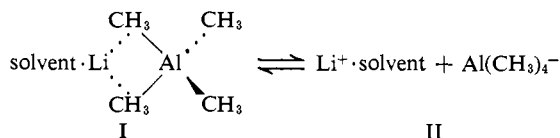
### <sup>27</sup>Al-<sup>1</sup>H Coupling and the Nature of LiAl(CH<sub>3</sub>)<sub>4</sub> Solutions

Sir:

The recent studies by Williams and Brown<sup>1</sup> on LiAl(CH<sub>3</sub>)<sub>4</sub> and the current wide interest in the nature of organometallic systems prompt us to report our findings on the pmr spectra of LiAl(CH<sub>3</sub>)<sub>4</sub> and LiB(CH<sub>3</sub>)<sub>4</sub> in a variety of solvents. Williams and Brown studied the <sup>7</sup>Li and <sup>1</sup>H nmr spectra of ether solutions of LiAl(CH<sub>3</sub>)<sub>4</sub>, both alone and in combination with other organometallic compounds, and have shown that the lithium ion exchanged rapidly in all cases, while exchange of methyl groups was only observed in the presence of Al(CH<sub>3</sub>)<sub>3</sub>.

They also observed that the proton resonance signal of LiAl(CH<sub>3</sub>)<sub>4</sub> was broadened, indicating that the <sup>27</sup>Al nucleus is weakly coupled to the methyl protons. In contrast to this, clear <sup>11</sup>B-<sup>1</sup>H coupling was resolved in an ether solution of LiB(CH<sub>3</sub>)<sub>4</sub>.

The observations on the aluminum system, *i.e.*, the nonexchange of methyl groups, the rapid exchange of the lithium ion, and the lack of <sup>27</sup>Al-<sup>1</sup>H coupling, were explained on the basis of the rapid equilibrium reaction



where I represents a contact ion pair and II represents a solvent-separated ion pair. The equilibrium reaction will certainly explain the absence of <sup>27</sup>Al-<sup>1</sup>H coupling since the exchange will cause the electric field gradient surrounding the <sup>27</sup>Al nucleus to fluctuate and prevent the observation of coupling due to quadrupole effects; therefore, the methyl groups need not undergo exchange to account for the observed spectrum.

There are several additional experimental facts which should be considered. In Table I the proton chemical shifts of LiAl(CH<sub>3</sub>)<sub>4</sub> in different solvents are given. It is clear from these data that there is only a negligible effect on chemical shift when one changes from cyclo-

(1) K. C. Williams and T. L. Brown, *J. Am. Chem. Soc.*, **88**, 4134 (1966).

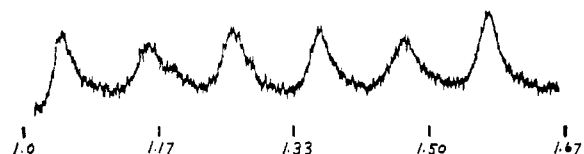


Figure 1. Spectrum (60-Mc) of LiAl(CH<sub>3</sub>)<sub>4</sub> in DME showing <sup>27</sup>Al-<sup>1</sup>H coupling.

pentane to diethyl ether, and one may conclude from this that LiAl(CH<sub>3</sub>)<sub>4</sub> is present predominately as contact ion pairs in diethyl ether. When the solvent is 1,2-dimethoxyethane (DME), the predominant species is the solvent-separated ion pair. This is evidenced by the increased chemical shift, the <sup>27</sup>Al-<sup>1</sup>H coupling, and by analogy with fluorenyllithium which has been shown to be completely separated.<sup>2</sup> In all other cases

Table I. Chemical Shifts, Coupling Constants, and Line Widths for LiAl(CH<sub>3</sub>)<sub>4</sub> and LiB(CH<sub>3</sub>)<sub>4</sub> in Several Solvents

Compound	Solvent	δ, ppm <sup>a</sup>	ν <sup>1/2</sup> , cps	J, cps
LiAl(CH <sub>3</sub> ) <sub>4</sub>	1,2-Dimethoxyethane	1.312	2.0 <sup>b</sup>	<sup>27</sup> Al- <sup>1</sup> H, 6.34
LiAl(CH <sub>3</sub> ) <sub>4</sub>	Ethylenediamine	1.192	1.8	...
LiAl(CH <sub>3</sub> ) <sub>4</sub>	Triethylamine	1.133	3.6	...
LiAl(CH <sub>3</sub> ) <sub>4</sub>	Diethyl ether <sup>c</sup>	1.11	3.8,	...
			1.7 <sup>d</sup>	
LiAl(CH <sub>3</sub> ) <sub>4</sub>	Cyclopentane	1.109	2.5	...
LiAl(CH <sub>3</sub> ) <sub>4</sub>	Benzene	0.590	1.8	...
LiB(CH <sub>3</sub> ) <sub>4</sub>	1,2-Dimethoxyethane	0.70	...	<sup>10</sup> B- <sup>1</sup> H, 1.88 <sup>11</sup> B- <sup>1</sup> H, 3.80
LiB(CH <sub>3</sub> ) <sub>4</sub>	Diethyl ether <sup>c</sup>	0.50	...	<sup>10</sup> B coupling not obsd <sup>11</sup> B- <sup>1</sup> H, 3.40
LiB(CH <sub>3</sub> ) <sub>4</sub>	Water <sup>e</sup>	...	...	<sup>10</sup> B- <sup>1</sup> H, 1.34 <sup>11</sup> B- <sup>1</sup> H, 3.90

<sup>a</sup> Chemical shifts are relative to tetramethylsilane and all are at higher field. <sup>b</sup> Over a temperature range of -40 to 44°. <sup>c</sup> Reference 1. <sup>d</sup> At 50 and at -50°, respectively. <sup>e</sup> Reference 3.

there is a mixture of the two species, with the amount of solvent-separated ion pair increasing as the ability of the solvent to coordinate Li<sup>+</sup> increases. The case of benzene is anomalous due to the magnetic anisotropy of this solvent.

Table I has been ordered with decreasing ability of the solvent to coordinate Li<sup>+</sup> and it should be noted that there is a corresponding decrease in the chemical shift. Furthermore, as is seen in Figure 1, <sup>27</sup>Al-<sup>1</sup>H coupling is clearly observed in DME, while this is not observed in any other solvent. Besides the fact that it is very unusual to observe clear <sup>27</sup>Al-<sup>1</sup>H coupling in organometallic systems, this coupling clearly indicates that the Al(CH<sub>3</sub>)<sub>4</sub><sup>-</sup> is in a stable symmetric field which would correspond to a nearly complete shift in the equilibrium to II. In all other cases this indicates an appreciable amount of I in the equilibrium mixture.

Strong support for this postulated equilibrium can be obtained by examination of the LiB(CH<sub>3</sub>)<sub>4</sub> system which is less inclined to form contact ion pairs of the type previously illustrated. In this instance B(CH<sub>3</sub>)<sub>4</sub><sup>-</sup> is free in both water<sup>3</sup> and in DME, as indicated by the <sup>10</sup>B- and <sup>11</sup>B-<sup>1</sup>H coupling observed.

(2) T. E. Hogan-Esch and J. Smid, *ibid.*, **88**, 307 (1966).

(3) A. G. Massey, E. W. Randall, and D. Shaw, *Spectrochim. Acta*, **20**, 379 (1964).