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

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.

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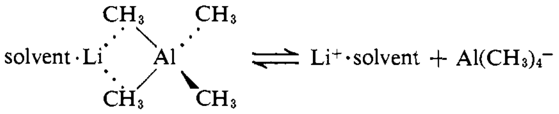
^{27}Al–^{1}H Coupling and the Nature of LiAl(CH$_3$)$_4$ Solutions

Sir:

The recent studies by Williams and Brown[1] on LiAl(CH$_3$)$_4$ and the current wide interest in the nature of organometallic systems prompt us to report our findings on the pmr spectra of LiAl(CH$_3$)$_4$ and LiB(CH$_3$)$_4$ in a variety of solvents. Williams and Brown studied the ^{7}Li and ^{1}H nmr spectra of ether solutions of LiAl(CH$_3$)$_4$, 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$_3$)$_3$.

They also observed that the proton resonance signal of LiAl(CH$_3$)$_4$ was broadened, indicating that the ^{27}Al nucleus is weakly coupled to the methyl protons. In contrast to this, clear ^{11}B–^{1}H coupling was resolved in an ether solution of LiB(CH$_3$)$_4$.

The observations on the aluminum system, *i.e.*, the nonexchange of methyl groups, the rapid exchange of the lithium ion, and the lack of ^{27}Al–^{1}H coupling, were explained on the basis of the rapid equilibrium reaction



I II

where I represents a contact ion pair and II represents a solvent-separated ion pair. The equilibrium reaction will certainly explain the absence of ^{27}Al–^{1}H coupling since the exchange will cause the electric field gradient surrounding the ^{27}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$_3$)$_4$ 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 cyclopentane to diethyl ether, and one may conclude from this that LiAl(CH$_3$)$_4$ 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 ^{27}Al–^{1}H coupling, and by analogy with fluorenyllithium which has been shown to be completely separated.[2] In all other cases 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$^+$ increases. The case of benzene is anomalous due to the magnetic anisotropy of this solvent.

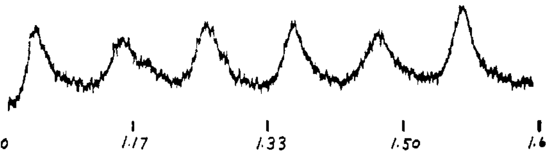


Figure 1. Spectrum (60-Mc) of LiAl(CH$_3$)$_4$ in DME showing ^{27}Al–^{1}H coupling.

Table I. Chemical Shifts, Coupling Constants, and Line Widths for LiAl(CH$_3$)$_4$ and LiB(CH$_3$)$_4$ in Several Solvents

Compound	Solvent	δ, ppm[a]	$\nu_{1/2}$, cps	J, cps
LiAl(CH$_3$)$_4$	1,2-Dimethoxyethane	1.312	2.0[b]	^{27}Al–^{1}H, 6.34
LiAl(CH$_3$)$_4$	Ethylenediamine	1.192	1.8	. . .
LiAl(CH$_3$)$_4$	Triethylamine	1.133	3.6	. . .
LiAl(CH$_3$)$_4$	Diethyl ether[c]	1.11	3.8, 1.7[d]	. . .
LiAl(CH$_3$)$_4$	Cyclopentane	1.109	2.5	. . .
LiAl(CH$_3$)$_4$	Benzene	0.590	1.8	. . .
LiB(CH$_3$)$_4$	1,2-Dimethoxyethane	0.70	. . .	^{10}B–^{1}H, 1.88 ^{11}B–^{1}H, 3.80
LiB(CH$_3$)$_4$	Diethyl ether[c]	0.50	. . .	^{10}B coupling not obsd ^{11}B–^{1}H, 3.40
LiB(CH$_3$)$_4$	Water[e]	. . .	. . .	^{10}B–^{1}H, 1.34 ^{11}B–^{1}H, 3.90

[a] Chemical shifts are relative to tetramethylsilane and all are at higher field. [b] Over a temperature range of −40 to 44°. [c] Reference 1. [d] At 50 and at −50°, respectively. [e] Reference 3.

Table I has been ordered with decreasing ability of the solvent to coordinate Li$^+$ and it should be noted that there is a corresponding decrease in the chemical shift. Furthermore, as is seen in Figure 1, ^{27}Al–^{1}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 ^{27}Al–^{1}H coupling in organometallic systems, this coupling clearly indicates that the Al(CH$_3$)$_4^-$ 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$_3$)$_4$ system which is less inclined to form contact ion pairs of the type previously illustrated. In this instance B(CH$_3$)$_4^-$ is free in both water[3] and in DME, as indicated by the ^{10}B- and ^{11}B–^{1}H coupling observed.

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

(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).

^{11}B–^{1}H coupling has also been observed in a diethyl ether solution of $LiB(CH_3)_4$ at elevated temperatures.[1] One can estimate that appreciable concentrations of the solvent-separated ion pairs are present when ^{10}B–^{1}H or ^{27}Al–^{1}H coupling can be observed, but estimates of actual concentrations are not possible. Observation of ^{11}B–^{1}H coupling is less meaningful because of the magnitude of the ^{11}B quadrupole (3.55×10^{-2} e $\times$ 10^{-24} cm^2) in comparison with that of ^{27}Al (0.149 e $\times$ 10^{-24} cm^2) and ^{10}B (0.111 e $\times$ 10^{-24} cm^2).

Studies on the infrared spectra of these systems[4] have also been undertaken and the preliminary results tend to support the postulated change in equilibrium with the change in solvent. The infrared spectrum of a diethyl ether solution is very similar to that obtained from a mull of the solid, while these are quite different from the spectrum obtained in DME. The spectrum in DME is considerably simplified in keeping with a change from C_{2v} to T_d symmetry.

All samples were prepared under an argon atmosphere and a high vacuum system. The $Al_2(CH_3)_6$ was obtained from the Ethyl Corp. The $LiCH_3$ was prepared from Li metal and $Hg(CH_3)_2$ while the $B(CH_3)_3$ was prepared by a Grignard reaction. $LiAl(CH_3)_4$ was prepared from $Al(CH_3)_3 + LiCH_3$ in DME. $LiB(CH_3)_4$ was prepared from $B(CH_3)_3$ with $LiAl(CH_3)_4$ in DME. All volatile compounds were purified by vacuum distillation and their nmr spectra used as a criterion for purity. The nmr spectra were obtained on a Varian Associates A-60-A spectrometer and were calibrated by the audio side-band technique *vs.* cyclopentane as internal standard. The chemical shifts were then related to tetramethylsilane by $\delta_{TMS} = \delta_{C_5H_{10}} - 1.516$. The infrared spectra were obtained on a Perkin-Elmer 621 infrared spectrometer.

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[4] These preliminary results are in general agreement with those of K. Mach, *J. Organometal. Chem.* (Amsterdam), **2**, 410 (1964).

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Photoreduction of *p*-Aminobenzophenone. Effect of Tertiary Amines[1]

Sir:

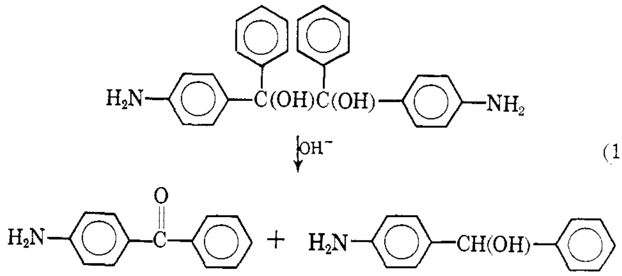
While *p*-aminobenzophenone (PAB) does not undergo photoreduction appreciably by alcohols,[2] it is reported to be photoreactive in cyclohexane.[3] It has been suggested that this reaction may not lead to the pinacol.[4] In alcohol solutions the first excited triplet of *p*-aminobenzophenone may be of the "charge-transfer" type and chemically unreactive.[3] In cyclohexane the lowest lying triplet of PAB may be n → π^*, and for this reason reactive in abstraction of hydrogen.[3] We wish to report that systems containing tertiary aliphatic amines may combine low polarity with heteroatom activation and lead to photoreduction of PAB with efficiency similar to that of benzophenone, quantum yields ~0.5, and with formation of the pinacol.

Solutions were irradiated in Pyrex under argon, with a Bausch and Lomb 38-86-01 grating monochromator, Osram SP-200 lamp, at 313 and at 334 mμ or with unfiltered light from a GE H-85-A3 lamp. Analyses for residual ketone were made from absorbancies at and near λ_{max}. Quantum yields were determined on the monochromator with a ferrioxalate[5] or benzophenone–benzhydrol[6] actinometer. Results of some photoreductions of PAB and of benzophenone are given in Table I.

Comparison of the photoreduction of the two ketones is difficult because the two reactions are differently affected by concentration of ketone and light intensity. Also, the quantum yield for photoreduction of benzophenone by alcohols may be decreased by formation of a light-absorbing intermediate.[7] Such an intermediate is either not formed in photoreduction of PAB or its effect may not be observed because of the high absorption coefficient of the ketone, ϵ ~18,000.

The results confirm that PAB is not photoreduced appreciably in 2-propanol[2] (expt 1) and show that it is also not photoreduced in *n*-butylamine (expt 2), which is very effective in photoreducing benzophenone.[8] The polarity and hydrogen bonding are sufficiently weak in diisopropylamine to result in appreciable but slow photoreduction, ϕ ~0.04 (expt 3). A solution (0.02 *M*) of PAB in this amine was photoreduced and the pinacol was isolated in 65% yield, mp 179–180° from methylene chloride–petroleum ether. *Anal.* Calcd for $C_{26}H_{24}N_2O_2$: C, 78.75; H, 6.10; N, 7.07. Found: C, 78.57; H, 6.10; N, 7.28 (Schwarzkopf).

The pinacol was further characterized by (i) appropriate spectral comparison with *p*-aminobenzhydrol, mp 116–117°, and (ii) by base-catalyzed decomposition (eq 1) to a quantitative yield of 1 mole of PAB, determined spectrophotometrically.



(1)

The base-catalyzed decomposition of photolysates was then used to determine the yields of pinacol in the several solvents, with the following results: benzophenone in 2-propanol, 100% pinacol; PAB in cyclohexane, 90%; PAB in triethylamine, 50%; PAB in diisopropylamine, 100%. Formation of mixed coupling products, which may but need not occur, will lower yields of pinacol below 100%.

Photoreduction of PAB was observed in cyclohexane (expt 4), ϕ ~0.07, less than that reported,[3] 0.2. The

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[1] We are pleased to acknowledge generous support by a predoctoral fellowship under Title IV, NDEA, and by the U. S. Atomic Energy Commission (AT(30-1)2499) and the National Science Foundation (GP1833).

[2] (a) J. N. Pitts, Jr., H. W. Johnson, and T. Kutawa, *J. Phys. Chem.*, **66**, 2456 (1962); (b) A. Beckett and G. Porter, *Trans. Faraday Soc.*, **59**, 2051 (1963).

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[7] J. N. Pitts, Jr., R. L. Letsinger, R. P. Taylor, J. M. Patterson, G. Recktenwald, and R. B. Martin, *ibid.*, **81**, 1068 (1959).

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