

^{11}B - ^1H coupling has also been observed in a diethyl ether solution of $\text{LiB}(\text{CH}_3)_4$ at elevated temperatures.¹ One can estimate that appreciable concentrations of the solvent-separated ion pairs are present when ^{10}B - ^1H or ^{27}Al - ^1H coupling can be observed, but estimates of actual concentrations are not possible. Observation of ^{11}B - ^1H coupling is less meaningful because of the magnitude of the ^{11}B quadrupole ($3.55 \times 10^{-2} e \times 10^{-24} \text{ cm}^2$) in comparison with that of ^{27}Al ($0.149 e \times 10^{-24} \text{ cm}^2$) and ^{10}B ($0.111 e \times 10^{-24} \text{ cm}^2$).

Studies on the infrared spectra of these systems⁴ 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 $\text{Al}_2(\text{CH}_3)_6$ was obtained from the Ethyl Corp. The LiCH_3 was prepared from Li metal and $\text{Hg}(\text{CH}_3)_2$ while the $\text{B}(\text{CH}_3)_3$ was prepared by a Grignard reaction. $\text{LiAl}(\text{CH}_3)_4$ was prepared from $\text{Al}(\text{CH}_3)_3 + \text{LiCH}_3$ in DME. $\text{LiB}(\text{CH}_3)_4$ was prepared from $\text{B}(\text{CH}_3)_3$ with $\text{LiAl}(\text{CH}_3)_4$ 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 $\delta_{\text{TMS}} = \delta_{\text{C}_5\text{H}_{10}} - 1.516$. The infrared spectra were obtained on a Perkin-Elmer 621 infrared spectrometer.

(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 Amines¹

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 $n \rightarrow \pi^*$, and for this reason reactive in abstraction of hydrogen.³ We wish to report that systems containing tertiary aliphatic amines

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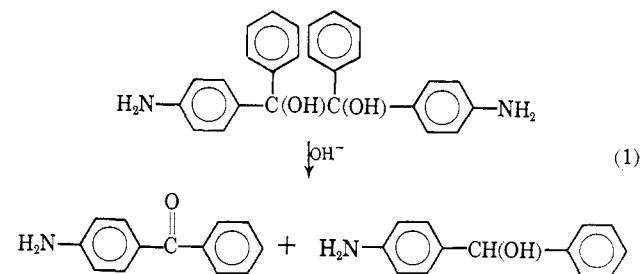
may combine low polarity with heteroatom activation and lead to photoreduction of PAB with efficiency similar to that of benzophenone, quantum yields ~ 0.5 , and with formation of the pinacol.

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 $m\mu$ 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 ferrioxalate⁵ or benzophenone-benzhydrol⁶ 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, $\epsilon \sim 18,000$.

The results confirm that PAB is not photoreduced appreciably in 2-propanol² (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, $\phi \sim 0.04$ (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 $\text{C}_{26}\text{H}_{24}\text{N}_2\text{O}_2$: 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.



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), $\phi \sim 0.07$, less than that reported,³ 0.2. The

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