${}^{11}B-{}^{1}H$ coupling has also been observed in a diethyl ether solution of LiB(CH₃)₄ at elevated temperatures.¹ One can estimate that appreciable concentrations of the solvent-separated ion pairs are present when ¹⁰B-¹H or ²⁷Al-¹H coupling can be observed, but estimates of actual concentrations are not possible. Observation of ¹¹B-¹H coupling is less meaningful because of the magnitude of the ¹¹B quadrupole (3.55 \times 10⁻² e \times 10^{-24} cm²) in comparison with that of ²⁷Al (0.149 e \times $10^{-24} \,\mathrm{cm}^2$) and ${}^{10}\mathrm{B} (0.111 \,\mathrm{e} \times 10^{-24} \,\mathrm{cm}^2)$.

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 $Al_2(CH_3)_6$ was obtained from the Ethyl Corp. The LiCH₃ 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(CH₃)₃ + LiCH₃ in DME. LiB(CH₃)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.

(4) These preliminary results are in general agreement with those of K. Mach, J. Organometal. Chem. (Amsterdam), 2, 410 (1964).
 (5) Ethyl Corporation Fellow, 1966–1967.

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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

(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).

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(3) G. Porter and P. Suppan, *ibid.*, **61**, 1664 (1965).
(4) E. J. Baum, J. K. S. Wan, and J. N. Pitts, Jr., J. Am. Chem. Soc., 88, 2657 (1966).

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 μ 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 $C_{26}H_{24}N_2O_2$: 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.



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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Table I. Photoreduction of p-Aminobenzophenone (PAB) and Benzophenone

		PAB		Benzophenone	
Expt	Solvent	Μ	ϕ	M	φ
1	1-Propanol	1×10^{-3}	<0.001 ^{b,c}	5×10^{-4} 1 × 10^{-1}	1.35 ^a 1.9 ^a
2	<i>n</i> -Butylamine	1×10^{-2}	<0.001°	2×10^{-1}	$\sim 0.9^d$
3	Diisopropylamine	6×10^{-2}	$\sim 0.02^{b}$	2×10^{-1}	$\sim 0.3^d$
	L · · ·	1×10^{-3}	0.038		
4	Cyclohexane	1×10^{-3}	0.075		0.50
5	1 M 2-propanol in cyclohexane	1×10^{-3}	$\sim 0.01^{b}$		
6	Triethylamine	2×10^{-2}	0.23^{b}	2×10^{-1}	$\sim 0.2^{d}$,
		1×10^{-2}	0.29^{b}		
		1×10^{-3}	0.38		
7	1 M triethylamine in cyclohexane	1×10^{-3}	0.57 ^b		
8	0.05 M triethylenediamine in cyclohexane	1×10^{-3}	0.25		

^a Reference 9, light intensity 6×10^{13} quanta cm⁻² sec⁻¹, 2537 A. ^b This work, $10^{15}-10^{16}$ quanta cm⁻² sec⁻¹, 313 m μ or 334 m μ . ^c This work, unfiltered light, GE H-85-A3 source. ^d Reference 8, irradiation as in footnote c. ^e Reference 3.

capacity of 1 *M* 2-propanol to decrease the quantum yield of photoreduction in cyclohexane, or possibly of cyclohexane to increase that due to 2-propanol (expt 5), may indicate a yield of the $n \rightarrow \pi^*$ triplet in this medium which is intermediate between the negligible value in 2-propanol and the higher value in cyclohexane.

Photoreduction of PAB in triethylamine was efficient. The quantum yield is similar to that of benzophenone in this solvent, but an unusual effect of concentration of ketone is observed (expt 6). Benzophenone may show higher quantum yield with rising initial concentration of ketone⁹ (expt 1), but PAB in triethylamine showed quantum yields falling from 0.38 at 10^{-3} M to 0.23 at 2 \times 10^{-2} M (expt 6). A plot of $1/\phi$ against initial concentration of PAB is linear, indicating that PAB may be a quencher for its own photoreduction, with $k_{\rm q}/k_{\rm r} \cong 300$, the ratio of the rate constant for self-quenching to that of abstraction of hydrogen from triethylamine. The reaction is also quenched by naphthalene, $k_{\rm q}/k_{\rm r} \cong 500$. The photoreduction of PAB by 1 M triethylamine in cyclohexane was even more effective, ϕ 0.57 (expt 7), dilution with the nonpolar solvent apparently leading to higher conversion to the reactive $n \rightarrow \pi^*$ triplet.

Finally, photoreduction of PAB by a saturated (0.05 M) solution of triethylenediamine in cyclohexane was also efficient, ϕ 0.25 (expt 8). Abstraction of hydrogen from carbon attached to a heteroatom may be facilitated by a polar contribution to the stability of the transition state

$$[-\ddot{X}-C \cdot H \cdot 0 - \dot{C} < \longleftrightarrow -\dot{X}=C < \cdot H : 0 - C <]$$

While such stabilization may not require full planarity of the -XC < grouping, the high reactivity of the bicyclic amine may indicate that activation by adjacent N may be of a different character. These reactions may proceed by initial electron transfer from the N atom to triplet ketone, followed by proton transfer and electron redistribution.

(9) A. Beckett and G. Porter, Trans. Faraday Soc., 59, 2038 (1963).

An analogy for the electron transfer may be seen in the absence of a deuterium isotope effect in the reaction of peroxy radicals with aromatic amines, acting as antioxidants.¹⁰

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Benzhydryl Benzoate Ion Pairs and the Nitrosoamide Decomposition¹

Sir:

Diaz and Winstein² have recently proposed that essentially the same ion pair (II = II') or spectrum of ion pairs is obtained from the reaction of diphenyldiazomethane (DDM) with benzoic acid in ethanol as from the ethanolysis of benzhydryl benzoate. Their statement was based on the near equivalence of the yield ratio (ester/(ester + ROEt)) for the DDM route (eq 1) and the rate ratio ($k_{eq}/(k_{eq} + k_t)$) for the solvolysis (eq 2) (with the assumption that the O-18 is randomized in II'). The values were 0.558 (or 0.528)^{3,4} and

$$(C_{6}H_{5})_{2}CN_{2} + HOBz \longrightarrow (C_{6}H_{5})_{2}CHN_{2}^{+}OBz$$

$$I$$

$$(C_{6}H_{5})_{2}CHOBz \longleftarrow (C_{6}H_{5})_{2}CH^{+} \xrightarrow{C}CC_{6}H_{5} \xrightarrow{EtOH} \rightarrow HOBz$$

$$II$$

$$(C_{6}H_{6})_{2}CHOEt$$

$$(C_{\mathfrak{e}}H_{\mathfrak{5}})_{2}CHOCO^{16}C_{\mathfrak{e}}H_{\mathfrak{5}} \xrightarrow{k_{\mathfrak{e}q} + k_{\mathfrak{t}}} \longrightarrow (C_{\mathfrak{e}}H_{\mathfrak{5}})_{2}CHO^{16}CO^{16}C_{\mathfrak{6}}H_{\mathfrak{5}} (\longrightarrow k_{\mathfrak{e}q})$$

$$II' \xrightarrow{(C_{\mathfrak{e}}H_{\mathfrak{5}})_{2}CHOEt} + C_{\mathfrak{e}}H_{\mathfrak{5}}CO_{2}H (\longrightarrow k_{\mathfrak{t}}) \qquad (2)$$

0.47, respectively. Similar comparisons with *p*-nitrobenzoic acid in 90% acetone gave values of 0.822 (or 0.754)⁴ and 0.745, respectively. The authors

- (1) This research was supported by the National Science Foundation.
- (2) A. F. Diaz and S. Winstein, J. Am. Chem. Soc., 88, 1318 (1966).
- (3) See also R. A. M. O'Ferrall, W. K. Kwok, and S. I. Miller, *ibid.*, **86**, 5553 (1964).
- (4) Numbers in parentheses are values² of (ester)/(DDM).

165