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

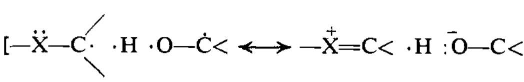
		PAB		Benzophenone	
Expt	Solvent	M	ϕ	M	ϕ
1	1-Propanol	1×10^{-3}	$<0.001^{b,c}$	5×10^{-4}	1.35^{a}
				1×10^{-1}	1.9^{a}
2	*n*-Butylamine	1×10^{-2}	$<0.001^{c}$	2×10^{-1}	$\sim 0.9^{d}$
3	Diisopropylamine	6×10^{-2}	$\sim 0.02^{b}$	2×10^{-1}	$\sim 0.3^{d}$
		1×10^{-3}	0.038^{b}		
4	Cyclohexane	1×10^{-3}	0.07^{b}	. . .	0.5^{e}
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^{b}		
7	1 M triethylamine in cyclohexane	1×10^{-3}	0.57^{b}		
8	0.05 M triethylenediamine in cyclohexane	1×10^{-3}	0.25^{b}		

[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 mμ or 334 mμ. [c] This work, unfiltered light, GE H-85-A3 source. [d] Reference 8, irradiation as in footnote *c*. [e] Reference 3.

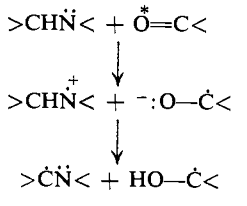
capacity of 1 M 2-propanol to decrease the quantum yield of photoreduction in cyclohexane, or possibly of cyclohexane to increase that due to 2-propanol (expt 5), may indicate a yield of the n → π* triplet in this medium which is intermediate between the negligible value in 2-propanol and the higher 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 ketone[9] (expt 1), but PAB in triethylamine showed quantum yields falling from 0.38 at 10^{-3} M to 0.23 at 2×10^{-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 $k_q/k_r \cong 300$, the ratio of the rate constant for self-quenching to that of abstraction of hydrogen from triethylamine. The reaction is also quenched by naphthalene, $k_q/k_r \cong 500$. 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 → π* 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



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.



$$\begin{array}{c} >\mathrm{CH\ddot{N}}< + \overset{*}{\mathrm{O}}=\mathrm{C}< \\ \downarrow \\ >\mathrm{CH}\overset{+}{\dot{\mathrm{N}}}< + {}^{-}:\mathrm{O}-\dot{\mathrm{C}}< \\ \downarrow \\ >\dot{\mathrm{C}}\ddot{\mathrm{N}}< + \mathrm{HO}-\dot{\mathrm{C}}< \end{array} \qquad (2)$$

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

(10) G. S. Hammond, C. E. Boozer, C. Hamilton, and J. N. Sen, *J. Am. Chem. Soc.*, **77**, 3238 (1955).

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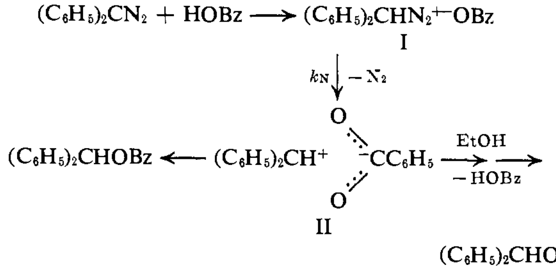
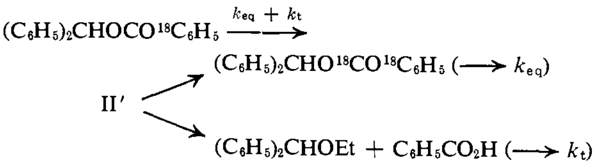
Benzhydryl Benzoate Ion Pairs and the Nitrosoamide Decomposition[1]

Sir:

Diaz and Winstein[2] 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 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





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(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 values[2] of (ester)/(DDM).

Table I. Decomposition of Compound III

Solvent	Benzoate, %	Solvent-derived product, %	Carbonyl-O^{18}: ether-O^{18} in benzoate[f]
CH_2Cl_2[a]	87	....	56:44
Toluene[a]	97	....	54:46
HOAc	40	60 (acetate)	67:33
DOAc	42[b]	52 (acetate)[c]	62:38
Ethanol[d]	43[e]	55 (ethyl ether)[e]	60:40

[a] Experiments of Dr. Jan Bakke. [b] The benzoate contained 0.049 atom % excess deuterium (0.8% of one hydrogen). [c] Containing 0.248 atom % excess deuterium (3.5% of one hydrogen). [d] Containing about 1 equiv of unlabeled benzoic acid. [e] A run carried out with unlabeled amide in the absence of benzoic acid gave 41.7% benzoate and 56.0% ether; see also run 7, Table II. [f] No loss of O^{18} occurred in these runs.

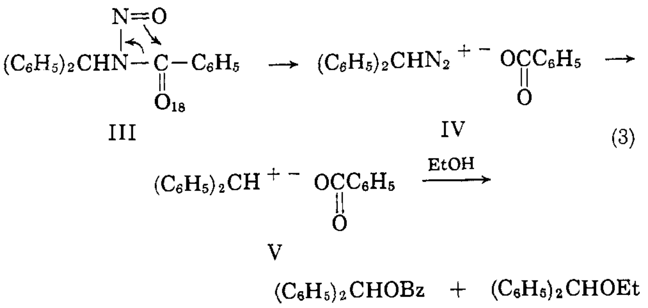
Table II. Decomposition of Nitrosoamides of *p*-Chlorobenzhydrylamine ($ClC_6H_4(C_6H_5)CHN(NO)COR$)

		Yields,[a] %		Retn. of configuration[b]	
R	Solvent	Intramolecular ester	Solvent-derived product	Intramolecular ester	Solvent-derived product
C_6H_5	CH_2Cl_2	91 (77)	....	57 (58)	.....
C_6H_5	Benzene	99	....	53	.....
C_6H_5	CH_3CN	91	....	60	.....
C_6H_5	HOAc	41 (43)	53 (57) (acetate)	72	.....
2-$C_{10}H_7$	CH_2Cl_2	91	....	57	.....
2-$C_{10}H_7$	HOAc	46 (45)[c]	53 (43)[c] (acetate)	70 (67)	53 (54)
2-$C_{10}H_7$	Ethanol	37	55 (ethyl ether)	69	53
CH_3	CH_2Cl_2	89	....	56	.....

[a] By nmr. [b] Calculated as if no real racemization occurred (100 − observed retention)/2 + observed retention = retention reported. [c] Corrected for the recovery of 5% starting amide.

pointed out that ion-pair return appeared to be more important in the DDM reaction than in solvolysis (ratio of 0.558 *vs.* 0.47, *e.g.*), and they proposed that a lack of equivalence of the oxygen atoms in the solvolytic ion pair might account for this.

We now report on a nitrosoamide decomposition[5] that could, in principle, lead (eq 3) to the same ion



$$(C_6H_5)_2CHN(N{=}O)-\underset{\underset{O_{18}}{\|}}{C}-C_6H_5 \longrightarrow (C_6H_5)_2CHN_2{}^{+}\ {}^{-}O\underset{\underset{O}{\|}}{C}C_6H_5 \longrightarrow \quad (3)$$

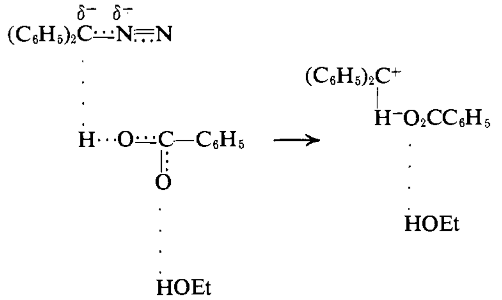
III IV

$$(C_6H_5)_2CH^{+}\ {}^{-}O\underset{\underset{O}{\|}}{C}C_6H_5 \xrightarrow{EtOH} (C_6H_5)_2CHOBz + (C_6H_5)_2CHOEt$$

V

pairs (I and II = IV and V?). The O-18 results indicate that in ethanol 60% of the O-18 is retained in the carbonyl group (Table I). If, for the moment, we assume that ion pair V = II = II′, we can state that a *minimum* of 20% of the ion pairs in solvolysis (II′) returns without O-18 scrambling (if V ≠ II′ (II), we would expect more equilibration from V than from II′ (II) because the nitrogen atoms in IV would ensure an *initial* separation of the ions greater than that in II′ (II)). Applying this correction to Diaz and Winstein's results, their ratio for solvolytic return becomes 0.52, which is closer to the DDM result (0.558). Our measurement was made at 25° and theirs at 100°, but preliminary evidence suggests that neither their ratio[2] nor O-18 scrambling[5] is very sensitive to temperature.

More significant is our finding that the ratio (ester/(ester + ROEt)) for the decomposition of III in ethanol at 25° (0.44, 0.43; Table I)[6] is different than the ratio from the DDM route at 25° (0.593, 0.609)[2] (we find 0.63 for DDM). Thus I and IV must be different. Possibly, they are related as *cis–trans* isomers or, alternatively, I may be a hydrogen-bonded complex (VI). In any event, the DDM reaction could lead (VI → VII) to a carboxylate ion closer to the electron-deficient carbon atom than would the nitrosoamide reaction, since the ions of V were initially separated (IV) by two nitrogen atoms. Thus V could be considered a vibrationally excited ion pair; certain of the unique features of the deamination reactions can be accounted for on this basis if isomerization of the cation, or con-



VI VII

version of V to a solvent-separated ion pair, *e.g.*, can compete with relaxation. A more detailed interpretation must await further data and a determination of the role, if any, of $(C_6H_5)_2CHN_2OEt$.

The decomposition of III in benzene in the presence of a fivefold excess of diazomethane yielded about 4% DDM. The decomposition of III in O-deuterioacetic acid yielded benzoate and acetate esters that did not contain significant amounts of deuterium (Table I). Diphenyldiazomethane is apparently not an intermediate under these conditions. Since ethanol is more polar than acetic acid and since the stereochemical results in acetic acid and ethanol are similar (Table II), it is unlikely that significant amounts of DDM were formed in the nitrosoamide runs in ethanol.

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(5) E. H. White and C. A. Aufdermarsh, Jr., *J. Am. Chem. Soc.*, **83**, 1179 (1961) (includes effect of temperature on the O-18 scrambling in a nitroamide).

(6) Determined by nmr. Titration gave a ratio of 0.43 for the first run.

The stereochemical results[7] (Table II) indicate a high per cent retention which is approximately the same as that reported for the nitrosoamide decompositions of 1-phenylethylamine[5] and 3β-cholestanylamine[8] in acetic acid (OH and OD). Note that the solvent-derived products were formed with net retention of configuration (Table II).[9] The mechanism for the decomposition of III is presumably the same as that outlined for 1-phenylethylamine.[5]

[7] Using values of G. H. Green and J. Kenyon (*J. Chem. Soc.*, 751 (1950)) for benzhydrol, values of G. R. Clemo, C. Gardner, and R. Raper (*ibid.*, 1958 (1939)) for the amine, and the fact that all previous nitrosoamide reactions in polar solvents have proceeded with retention of configuration. Suitable controls were run to ensure the validity of the O-18 and stereochemical results.

[8] E. H. White and F. W. Bachelor, *Tetrahedron Letters*, 77 (1965).

[9] For a related example, see E. H. White and J. E. Stuber, *J. Am. Chem. Soc.*, **85**, 2168 (1963), and for an example of retention observed in the solvolysis of a benzhydryl ester, see H. L. Goering, R. G. Briody, and J. F. Levy, *ibid.*, **85**, 3059 (1963).

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Anomalous Rotatory Dispersion of 1-Butyl-1-*d* Acetate

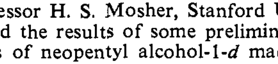
Sir:

It is now established, both theoretically[1] and experimentally,[2] that molecules which are optically active because of hydrogen–deuterium asymmetry[3] do not differ in principle from normally asymmetric molecules.

Investigation of the optical rotatory dispersion (ORD) of several deuterium compounds, R_1CHDR_2, resulted in the observation of plain dispersion curves.[2] However, measurements could not be carried out in the region of electronic absorption due to the small optical activity and high absorptivity exhibited by these compounds. Since the Cotton effect is observed only in the vicinity of an absorption band, it was not possible to demonstrate experimentally whether molecules which are optically active because of H–D asymmetry are capable of exhibiting measurable Cotton effects.

We wish to report what we believe to be the first observation of a Cotton effect in a molecule which owes its optical activity solely to isotopic substitution.

(*R*)-(+)-1-Butyl-1-*d* acetate, (+)-**1**, $[\alpha]^{27}D$ +0.687°,



$$CH_3CH_2CH_2\text{—}\overset{D}{\underset{H}{C}}\text{—}O_2CCH_3$$

(+)-**1**

was prepared from (*R*)-(−)-butanol-1-*d*[4] by treatment with acetyl chloride and pyridine. Since preparation of the ester does not involve the asymmetric center, (+)-**1** is also 59% of optical purity.

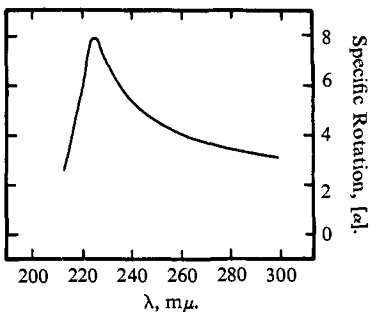


Figure 1. Optical rotatory dispersion curve of (*R*)-(+)-1-butyl-1-*d* acetate in isooctane solution.

The ultraviolet ORD curve of (+)-**1** in isooctane solution is shown in Figure 1. The first extremum of a positive Cotton effect is observed with a peak at 226 mμ. Because of a decreasing rotation:absorption ratio, measurements were possible only to 212 mμ.[6] The results of the ORD data for (+)-**1** indicate that optically active deuterium compounds can be expected to exhibit weak but measurable Cotton effects.

Acknowledgment. This work was supported in part by U. S. Public Health Service Grant GM 14068 from the National Institute of General Medical Sciences. The author is grateful to Mr. P. Swender for technical assistance.

[1] W. Fickett, *J. Am. Chem. Soc.*, **74**, 4204 (1952).

[2] A. Streitwieser, Jr., L. Verbit, and S. Andreades, *J. Org. Chem.*, 30, 2078 (1965); M. Sprecher, R. Berger, and D. B. Sprinson, *J. Biol. Chem.*, **239**, 4268 (1964); J. W. Cornforth, G. Ryback, G. Popjak, C. Donninger, and G. Schroepfer, Jr., *Biochem. Biophys. Res. Commun.*, **9**, 371 (1962). Professor H. S. Mosher, Stanford University, has very kindly communicated the results of some preliminary ORD measurements of derivatives of neopentyl alcohol-1-*d* made in 1960: H. S. Mosher and V. E. Althouse, unpublished work.

[3] A. Streitwieser, Jr., J. R. Wolfe, Jr., and W. D. Schaeffer, *Tetrahedron*, **6**, 338 (1959).

[4] The 1-butanol-1-*d* was prepared *via* the asymmetric hydroboration reaction (A. Streitwieser, Jr., and L. Verbit, 147th National Meeting of the American Chemical Society, Philadelphia, Pa., April 1964, Abstracts, p 50N) and was 59% optically pure.[5] Nmr analysis indicated the presence of 0.97 ± 0.05 D per molecule.

[5] V. E. Althouse, D. M. Feigl, W. A. Sanderson, and H. S. Mosher, *ibid.*, **88**, 3595 (1966), report $[\alpha]^{27.5}D$ 0.471° for 1-butanol-1-*d* prepared enzymatically.

[6] A JASCO recording spectropolarimeter was used. Measurements were carried out under constant nitrogen flush using the ±30 millidegree scale. In order to guard against instrument artifacts such as stray light, the sample absorbance was kept below 2. Base-line measurements were taken using unlabeled (thus inactive) *n*-butyl acetate in isooctane at the same concentration at which the optically active sample was run. A 450-w high-pressure xenon arc with less than 50 lamp-hr was used as the source.

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Fluorescence and Room-Temperature Laser Action of Trivalent Neodymium in an Organic Liquid Solution

Sir:

In two recent communications, we reported fluorescence and laser action of trivalent neodymium in an aprotic inorganic solvent.[1,2] The present communication extends this study to organic liquid systems.

Excited neodymium undergoes radiationless relaxation by two mechanisms: direct energy transfer to a vibration of the environment[3] and self-quenching.[4] Both the choice of the solvent and the design of the solute for the present system were aimed to reduce these.

[1] A. Heller, *Appl. Phys. Letters*, **9**, 106 (1966).

[2] A. Lempicki and A. Heller, *ibid.*, **9**, 108 (1966).

[3] A. Heller, *J. Am. Chem. Soc.*, **88**, 2058 (1966).

[4] G. E. Peterson and P. M. Brindenbaugh, *J. Opt. Soc. Am.*, **54**, 644 (1964).