gles in cyclopropane and cyclobutane derivatives the hybridizations in aziridine and azetidine should be ca. $sp^{2.3}$ (30% s) and $sp^{2.9}$ (26% s), respectively; R. H. Schwendeman, G. O. Jacobs, and T. M. Krigas, *J. Chem. Phys.*, **40**, 1022 (1964); H. Kim and W. D. Gwinn, *ibid.*, **44**, 865 (1966); S. I. Chan, J. Zinn, and W. D. Gwinn, *ibid.*, **39**, 1319 (1961); see C. A. Coulson, "Valence", Oxford University Press, London, 1952, p 194.

(6) The adiabatic hydrogen affinities and ionization potentials show much the same trends as the vertical data except when there are differences in the relaxation energies of the radical cations (ref 2c). Vertical IP's and HA's have been used for comparisons of hybridization, since the geometry should stay nearly constant for amines and ammonium ions, making all three quantities, HA, IP, and PA, essentially vertical with no change in geometry or hybridization throughout the cycle (eq 1).

(7) Changes in BDE are a linear function of per cent s character for hydrocarbons but about three times smaller than corresponding changes in amine vHA's; S. W. Benson, *J. Chem. Educ.*, **42**, 502 (1965), and ref 2c.

(8) Plots of vIP vs. per cent s character for saturated nitrogen heterocycles have been reported, but the polarizability effects were not taken into account; K. Yoshikawa, M. Hashimoto, and J. Morishima, *J. Am. Chem. Soc.*, **96**, 288 (1974).

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(10) Such resonance effects must also operate for the nitriles, so the significance of the lines drawn through these points in Figure 1 is quantitatively doubtful. In fact, for strained amines with less than 25% s character, it can be deduced that the PA's and vIP's will show large positive deviations from the lines in Figure 1; D. H. Aue, H. M. Webb, and M. T. Bowers, *J. Am. Chem. Soc.*, **97**, 4136 (1975). A plot of ΔvHA vs. per cent s character like Figure 1 shows a more regular behavior since resonance effects on ΔPA and ΔvIP nearly cancel.

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(12) Polarizability effects on PA, vIP, and vHA for oxygen bases are very similar to those in alkylamines. A plot of PA vs. vIP for oxygenated compounds yields lines of slopes about the same as those found in alkylamines (ref 2c).

(13) In π ionization of methylenecyclopropane and isobutylene we see a comparable difference (9.5 kcal/mol) in the vIP's, which must result from indirect ring angle strain effects rather than direct orbital hybridization effects if σ–π separation is to be preserved. A possible explanation lies in Walsh's suggestion [A. D. Walsh, *J. Chem. Soc.*, 2260 (1953)] that the p orbital energy at Y should depend on the angle in X-Y-X compounds (but not for H-Y-H). In Hartree-Fock calculations with an extended basis set for water, however, the p orbital energy decreases by ca. 10 kcal/mol on changing the HOH angle from 109 to 60°. These calculations suggest that electron repulsions at small angles cause a decreased electron density at oxygen with a corresponding lowering in the energy of the oxygen p orbital; D. M. Chipman, B. Kirtman, and W. E. Palke, unpublished results. Such an effect may also operate in oxirane or methylenecyclopropane.

Donald H. Aue,* Hugh M. Webb, Michael T. Bowers
Department of Chemistry, University of California
Santa Barbara, California 93106

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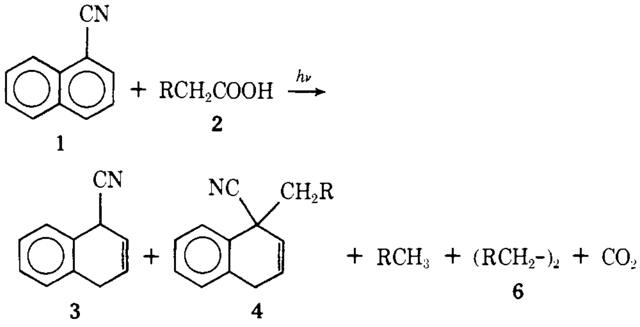
Light Induced Charge Transfer Processes. The Photochemical Behavior of 1-Cyanonaphthalene in the Presence of Phenylacetic Acid Derivatives

Sir:

Compounds of pronounced electron donating[1] or electron accepting properties[2,3] are known to form complexes with photoexcited arenes which are deactivated via exciplex emission in nonpolar solvents, but via electron transfer in polar solvents.[1,4,5] The possibility that such light induced electron transfer interactions may be followed by chemical transformations under favorable conditions is receiving increasing attention.[6] Thus charge transfer interactions have been demonstrated to be involved in the photoreactions of arenes[7,8] and ketones[9,10] with olefins and amines and the photosensitized decarboxylation of carboxylic acids[11] and amino alcohols.[12] This communication describes the photochemical reduction and reductive alkylation of 1-cyanonaphthalene (**1**) by *p*-methoxyphenylacetic acid (**2a**), *m*-methoxyphenylacetic acid (**2b**), and phenoxyacetic acid (**2c**). Mechanistic investigations suggest that photoexcited cyanonaphthalene **1** reacts with carboxylic acids **2a–d** to give excited complexes which deactivate preferentially via exciplex emission in benzene, but via electron transfer followed by chemical reactions in acetonitrile.

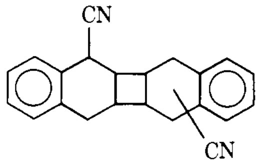
Irradiation of an acetonitrile solution (200 ml) of **1** (0.1 *M*) and **2a** (0.1 *M*) with a medium pressure mercury lamp through Corex filter for 5 hr resulted in 35% consumption of **1** and quantitative conversion of **2a.** Five products were isolated from the crude reaction mixture by chromatography on silica gel: *p*-methoxytoluene, 1-cyano-1,4-dihydronaphthalene (**3**), 1-cyano-1-*p*-methoxybenzyl-1,4-dihydronaphthalene (**4a**), dimer **5** (mp 194–196°; uv$_{max}$ (EtOH) 276 (ϵ 1830), 268 (ϵ 2030), and 263 nm (ϵ 1590); molecular ion *m/e* 310) and bibenzyl **6a**.[13]

Adduct **4a** exhibits the following: uv$_{max}$ (EtOH) 282 (ϵ 1985) and 273 nm (ϵ 2300); NMR ($CDCl_3$) δ 2.68 (d t, 1, J_{gem} = 22 Hz, $J \sim 1.5$, C=CC*H*), 3.24 (dd, 1, J_{gem} = 22 Hz, J_{vic} = 4.5 Hz, C=CC*H*), 3.10 (s, 2, ArCH_2), 3.72 (s, 3, OCH_3), 5.82 (pair of dd, 1, J_{2-3} = 10 Hz, J_{2-4} = 2.5 Hz, $J_{2-4} \sim 1$ Hz, C=C^2*H*), 6.08 (pair of dd, 1, J_{3-2} = 10 Hz, $J_{3-4_{aeq}}$ = 4.5 Hz, $J_{3-4_{ax}}$ = 2.5 Hz, C=C^3*H*), and 6.7–7.65 ppm (m, 8, Ar*H*); molecular ion *m/e* 275.



1 **2** **3** **4** **6**

a, R = *p*-$CH_3OC_6H_4$
b, R = *m*-$CH_3OC_6H_4$
c, R = C_6H_5O-



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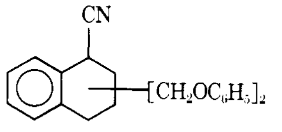

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1-Cyanonaphthalene (**1**) reacted under analogous conditions with *m*-methoxyphenylacetic acid (**2b**) to give *m*-methoxytoluene, dihydrocyanonaphthalene (**3**), addition product **4b** (uv$_{max}$ (EtOH) 284 (ϵ 2250) and 276 nm (ϵ 2570); NMR ($CDCl_3$) δ 2.68 (dt, 1, J_{gem} = 22 Hz, $J \sim 1.5$ Hz, C=CC*H*), 3.24 (dd, 1, J_{gem} = 22 Hz, J_{vic} = 4.5 Hz, C=CC*H*), 3.13 (s, 2, ArCH_2), 3.58 (s, 3, OCH_3), 5.82 (pair of dd, 1, J_{2-3} = 9.5 Hz, J_{2-4} = 2 Hz, $J_{2-4} \sim 1$ Hz, C=C^2*H*) 6.19 (pair of dd, 1, J_{3-2} = 9.5 Hz, $J_{3-4_{aeq}}$ = 4.5 Hz, $J_{3-4_{ax}}$ = 2.5 Hz, C=C^3*H*), and 6.25–7.65 (m, 8, *ArH*); molecular ion *m/e* 275), and bibenzyl **6b.**[13] Irradiation of 1-cyanonaphthalene (**1**) with phenoxyacetic acid (**2c**) gave anisole, dihydrocyanonaphthalene (**3**), diphenoxyethane (**6c**),[14] and two additional products, **4c** and **7.** Compound **4c** exhibits the following: uv$_{max}$ (EtOH) 278 (ϵ 2150), 271 (ϵ 2500), and 265 nm (ϵ 2040); NMR ($CDCl_3$) δ 3.45 (m, 2, C$^4H_2$), 3.97 (d, 1, J_{gem} = 9 Hz, ArOC*H*), 4.15 (d, 1, J_{gem} = 9 Hz, ArOC*H*), 6.18 (m, 2, C*H*=C*H*), 6.65–7.5 (m, 8, Ar*H*), and 7.65 ppm (m, 1, Ar*H*); molecular ion *m/e* 261. Compound **7** exhibits the following: uv$_{max}$ (EtOH) 277 (ϵ 1665), 271 (ϵ 2040), and 265 nm (ϵ 1700); NMR ($CDCl_3$) δ 1.5–3.2 (m, 4, -C*H*-), 3.4–4.4 (m, 5, ArCH_2O- and ArC*H*), and 6.5–7.6 ppm (m, 14, Ar*H*); molecular ion *m/e* 369.

Table I. Quenching of 1-Cyanonaphthalene Fluorescence by Phenylacetic Acids and Quantum Yields for the Reactions of 1-Cyanonaphthalene with Phenylacetic Acids

Quencher	Quenching constant $k_q\tau_s$ (M^{-1})[a] Acetonitrile	Benzene	Quantum yield Φ Acetonitrile	Benzene
p-Methoxyphenylacetic acid (2a)	82 ± 5	19 ± 2	0.18[b] ± 0.02	0.026[c] ± 0.002
p-Methoxyphenylacetic acid-*d* (2d)[d]	77 ± 5		0.18[b] ± 0.02	
p-Methoxyphenylacetic acid ethyl ester (2f)	56 ± 5	13 ± 2		
m-Methoxyphenylacetic acid (2b)	60 ± 5		0.34[b] ± 0.03	
m-Methoxyphenylacetic acid ethyl ester (2g)	35 ± 2			
Phenoxyacetic acid (2c)	20 ± 2	4 ± 0.5	0.11[c] ± 0.01	
Phenylacetic acid (2e)	<0.1		<0.004[b]	
Anisole	108 ± 5	1.5 ± 0.1		

[a] The slope of the Stern–Volmer plot of the fluorescence quenching of 1-cyanonaphthalene (10^{-4} mol/l.); excitation wavelength, λ 310 nm; monitoring wavelength, λ 340–550 nm: solutions deoxygenated by purging with nitrogen. [b,c] The quantum yield for the consumption of 1-cyanonaphthalene (10^{-2} mol/l.) in the presence of the quencher (10^{-1} mol/l.)[b] and (2.10^{-1} mol/l.); [c]excitation wavelength, λ 313 nm. [d]Isotopic purity 85% D.

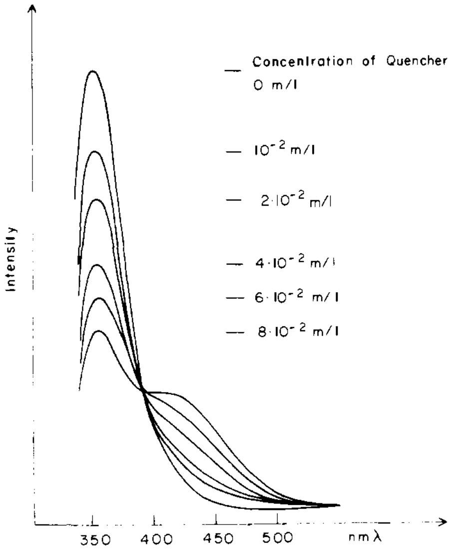

Figure 1. Fluorescence of 1-cyanonaphthalene (10^{-4} mol/l.) in benzene in the presence of *p*-methoxyphenylacetic acid.

While treatment of **3** with Pd–C (10%) in xylene under reflux yielded quantitatively **1**, **4a** remained unchanged under identical conditions.

When cyanonaphthalene **1** was irradiated in the presence of *p*-methoxyphenylacetic acid-*d* (**2d**, 85% isotropic purity) in acetonitrile until 36% of **1** had been consumed, deuterium incorporation was observed in the recovered starting material **1** (9% D), in the reduction product **3** at positions 1 and 4 (50% D in each position) and in the addition product **4a** at position 4 (60% D), as determined by either mass spectrometry or NMR analysis. On the other hand photoexcited cyanonaphthalene **1** failed to react with phenylacetic acid (**2e**) in acetonitrile solution. Irradiation of **1** in the presence of *p*-methoxy phenylacetic acid ethyl ester (**2f**) in acetonitrile or in the presence of *p*-methoxyphenylacetic acid (**2a**) in benzene resulted in only sluggish consumption of **1**.

Phenylacetic acid derivatives **2a–d** as well as their ethyl esters **2f–g** were found to quench the fluorescence of 1-cyanonaphthalene (**1**) in contrast to phenylacetic acid (**2e**) which did not act as quencher (Table I).[15] While the quenching in acetonitrile was not accompanied by the appearance of a new emission, the quenching in benzene was accompanied by the appearance of a new emission, bathochromic to that of **1**, which may be assigned to an exciplex formed between 1-cyanonaphthalene (**1**) and the quencher (Figure 1). The quenching efficiences varied with the quencher and were higher in acetonitrile than in benzene. Similarly the quantum yields for the photoreactions of **1** with acids **2a–d** were found to depend on the nature of the acid and to be higher in acetonitrile than in benzene.

These results suggest that the fluorescence quenching of 1-cyanonaphthalene (**1**) by carboxylic acids **2a–d** and the photoreactions of 1-cyanonaphthalene (**1**) with carboxylic acids **2a–d** are related processes. The higher efficiency of the quenching and the photoreaction in the polar solvent and the fact that the presence of an ether function in the phenylacetic acid is essential for quenching and photoreaction to occur suggest that charge transfer from the quencher to the quenchee is involved in both processes. The absence of a significant kinetic deuterium isotope effect on the quenching efficiency and on the quantum yield of the photoreaction indicates that proton transfer is not involved in the rate determining step of either process.[16] It is thus likely that photoexcited cyanonaphthalene **1** reacts with carboxylic acids **2a–d** and their ethyl ester **2f–g** in acetonitrile to give a complex of charge transfer character which undergoes electron transfer from the quencher (**2a–d, 2f–g**) to the quenchee (**1**) to give a radical cation and radical anion, respectively.

$$\begin{tikzcd}
\mathrm{ArCN^*} + \mathrm{RCH_2COOH} \arrow[r] & {} & \\
& & \mathrm{ArCN} + \mathrm{RCH_2COOH} + h\nu \\
& {[\mathrm{ArCN} \cdots \mathrm{RCH_2COOH}]^*} \arrow[ur, "\text{benzene}"] \arrow[dr, "\text{acetonitrile}"'] & \\
& & \mathrm{ArCN}^{\cdot -} + {}^{+\cdot}\mathrm{RCH_2COOH} \arrow[d] \\
& & \mathrm{HArCN}\cdot + \mathrm{RCH_2}\cdot + \mathrm{CO_2} \arrow[d] \\
& & \text{photoproducts}
\end{tikzcd}$$

If the radical cation contains an acidic proton (quencher **2a–d**), proton transfer from the radical cation to the radical anion with concurrent loss of carbon dioxide may occur to give a radical pair, which may collapse to an addition product (**4a–d**). Alternatively the radical pair may escape the

Table II. Product Distribution in the Reaction of 1-Cyanonaphthalene with Phenylacetic Acid Derivatives in Acetonitrile

Carboxylic acid	% chemical yield[a] 3	4	6	Others
p-Methoxyphenylacetic acid (2a)	15	10	28	18 of **5**
m-Methoxyphenylacetic acid (2b)	65	16	32	
Phenoxyacetic acid (2c)	10	6.5	5	14 of 7

[a] Chemical yield of isolated material relative to consumed starting material.

solvent cage to give, after hydrogen abstraction from a suitable hydrogen source, the various reduction products. If, on the other hand, the radical cation does not contain an acidic proton (quencher **2f**) proton transfer is unfavorable and consequently chemical transformations sluggish. In benzene the complex formed between photoexcited cyanonaphthalene **1** and the quencher cannot decay to ion pairs. Proton transfer and subsequent chemical transformations become thus unfavorable, while complex emission appears as significant deactivation mode.

The structure of the photoproducts obtained from irradiation of **1** with **2a–d** in acetonitrile and the product distribution as function of the acids used (Table II) are compatible with the suggested reaction pathway. 1-Cyanonaphthalene reacts at the substituted ring as expected for a process in which the naphthalene acts as electron acceptor. Deuterium incorporation in the reduction product **3** and addition product **4d** upon irradiation of cyanonaphthalene **1** in the presence of p-methoxyphenylacetic acid-d (**2d**) establishes that proton transfer from the acid to the cyanonaphthalene (**1**) is involved in the photoreaction. Deuterium incorporation in the recovered starting material indicates that the reduction product **3** is formed by disproportionation of 1-cyano-4-hydronaphthyl radical to cyanonaphthalene **1** and 1-cyano-1,4-dihydronaphthalene (**3**). The ratio between reductive alkylation and reduction products varies with the nucleophilicity of the benzyl radical involved; the more nucleophilic p-methoxybenzyl radical reacts faster with the 1-cyano-4-hydronaphthyl radical than the less nucleophilic m-methoxybenzyl radical, resulting in a more favorable ratio of reductive alkylation vs. reduction product.

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Jacqueline Libman

Department of Organic Chemistry,
The Weizmann Institute of Science
Rehovot, Israel

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Stereochemistry at the Origin of 1,2-Hydride Shifts. Evidence for Micellar Control in Nitrous Acid Deamination Reactions

Sir:

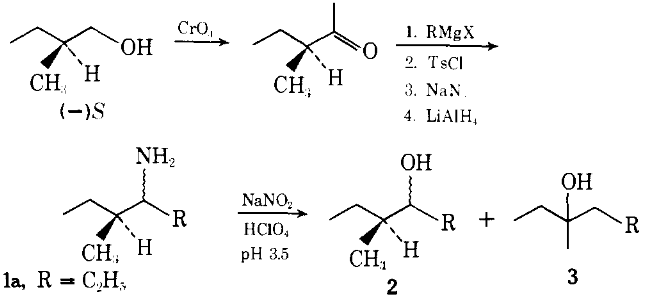
Wagner–Meerwein rearrangements of many chiral molecules afford optically active compounds rather than the racemic products expected from the intermediacy of trigonal planar carbocations. Obvious mechanisms for the conservation of chirality are: (i) formation of bridged, chiral cations; (ii) asymmetric solvation, including the formation of ion pairs. The response of a specific rearrangement to variations of the reaction medium may serve to distinguish between these alternatives. Moss[1] has shown that the stereochemistry of the nitrous acid deamination of 2-aminooctane is profoundly affected by aggregation of the alkylammonium ions in micelles. We report here on related observations concerning the stereochemistry at the origin of deaminatively induced 1,2-hydride shifts.

A series of 4-amino-3-methylalkanes (**1**) was prepared according to Scheme I. These amines were mixtures of 3S,4S and 3S,4R diastereoisomers which could not be separated. Nitrous acid deamination in aqueous perchloric acid (pH 3.5) afforded 55–60% alkenes, 15–20% 3-methyl-4-alkanols (by direct displacement), and 20–30% 3-methyl-3-alkanols (by 1,2-H shift) as the major products. Alcohols resulting from alkyl shifts were identified in minor quantities.[2]

The absolute configuration of the tertiary alcohols **3** was established by correlation with 2-hydroxy-2-methylbutyric acid[3] (Scheme II). The unsaturated alcohols **4** were prepared optically active by Grignard reactions in the presence of 1,2,5,6-diisopropylidene-D-glucofuranose (DIPG).[4] Catalytic hydrogenation of **4** afforded **3** whereas ozonolysis yielded **5**. The alcohol **3d** had previously been correlated with linalool.[5] The configuration of **3a–d** is uniformly (+)R.

When deaminations of **1a–c** were run in 1 M solution, the stereochemistry of **3** was found to depend on the length

Scheme I



1a, R = C_2H_5
b, R = n-C_4H_9
c, R = n-C_6H_{13}
d, R = $CH_2CH_2CH(CH_3)_2$