Table I. Proton Affinities and Adiabatic and Vertical Ionization Potentials and Hydrogen Affinities of Manxine and Related Amines at 25°[a]

Amine	PA[b]	aIP[c]	aHA[d]	vIP	vHA[d]
NH_3	207 ± 3	235	128 ± 3	250.0[e]	143 ± 3
Et_3N	235.6	166	88	186.3	108.3
Quinuclidine	235.8	173	95	185.6	107.8
n-Pr_3N	237.8	162	86	182.6	107.0
Manxine	235	160	82	161.7	*f*

[a] All values in kcal/mol. [b] PA's are relative to methylamine (218.4 kcal/mol) (see ref 8). [c] The aIP's are quoted to ±2 kcal/mol and are taken at the peak onset except for NH_3 where a 10.18 eV adiabatic value is taken (see ref 7). [d] The adiabatic and vertical hydrogen affinities correspond to the homolytic bond dissociation energies of the $\equiv N^+$ —H bonds and can be derived from the IP and PA data (see ref 8 and 13). It is assumed that the geometry of NH_3 and the alkylamines is unchanged on protonation, so that the PA's are near vertical. The vHA's are then calculated from the PA's. [e] The vIP of ammonia was taken halfway between the two largest vibrational bands at 10.78 and 10.90 eV to make the value most comparable to the vIP's derived from the broadened alkylamine bands. [f] Since manxine appears to change geometry from $\angle CNC \cong 120°$ to 115° on protonation, no vHA can be directly calculated.

Typically, bridgehead amines like quinuclidine, **2,** show a vertical IP very similar to an acyclic model (triethylamine in Figure 1), but they have a narrower band width because of the strain introduced into the bicyclic structure as the bridgehead becomes more planar.[9,10] The photoelectron spectrum for the bridgehead lone pair in manxine, however, has a remarkably different appearance (Figure 1). We interpret the sharp onset and narrow band width in this spectrum as indicative of vertical ionization from a preferred planar geometry in manxine to a planar radical cation.[11] The assignment of the adiabatic band in ammonia and the model acyclic tri-*n*-propylamine reinforces this interpretation, since the vertical IP of manxine is nearly identical with the adiabatic IP (onset) of tri-*n*-propylamine, as expected.

The intrinsic basicity of the lone pair p electrons in manxine was measured by equilibrium ion cyclotron resonance techniques in the gas phase relative to tri-*n*-propylamine.[8,12,13] The proton affinity (PA) of manxine was found to be only 3 kcal/mol lower than that for tri-*n*-propylamine. Competition between large hybridization[14] and strain energy effects[3,4] apparently results in a small net effect on the PA of manxine relative to tri-*n*-propylamine. On the basis of hybridization effects and its low vertical ionization potential, manxine's PA would be expected to be greater than that of a comparable sp^3 hybridized amine like tri-*n*-propylamine.[14] Strain energy effects associated with bond angle distortion at nitrogen in the manxinium ion and steric interactions within the ring oppose this hybridization effect, however.[15]

Not only is manxine less basic than tri-*n*-propylamine by 3 kcal/mol in the gas phase but it is also less basic in aqueous solution by ca. 1.0 kcal/mol than tri-*n*-propylamine or ca. 1.5 kcal/mol than quinuclidine in terms of $\Delta G°_{\text{prot}}$.[1] Thus, these gas-phase and solution-phase basicities show similar, though small, effects.

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(4) W. Parker, R. L. Tranter, C. I. F. Watt, L. W. K. Chang, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **96**, 7121 (1974).

(5) Microwave inversion barriers are 5.78 kcal/mol for NH_3 (M. T. Weise and M. W. P. Strandberg, *Phys. Rev.*, **83**, 567 (1951)), 2.07 kcal/mol for $MeNH_2$ (D. R. Lide, Jr., *J. Chem. Phys.*, **27**, 343 (1957)), and 4.4 kcal/mol for Me_2NH (J. E. Wolbrab and V. W. Laurie, *ibid.*, **48**, 5058 (1968)).

(6) (a) A. W. Potts and W. C. Price, *Proc. R. Soc. London, Ser. A*, **328**, 181 (1972); (b) D. W. Turner, C. Baker, A. D. Baker, and C. R. Brundle, "Molecular Photoelectron Spectroscopy", Wiley-Interscience, London, 1970, p 350.

(7) Bands at 10.02 and 10.15 eV in ammonia were observed by Potts and Price (ref 6a), but it was not established whether the 10.02-eV band was a hot band or not. Our band energies were calibrated directly vs. methyl iodide at 10.16 eV (ref 6b). The 10.07-eV band was shown to increase in intensity relative to the 10.18-eV band at high temperature (ca. 300°). Since the 10.07-eV band may be a hot band, we continue to use the 10.18 eV value, then for a tentative adiabatic (0,0) band assignment (see ref 6a and references therein).

(8) D. H. Aue, H. M. Webb, and M. T. Bowers, *J. Am. Chem. Soc.*, in press.

(9) (a) The half-widths of quinuclidine, 1-azatwistane and 1-azaadamantane are all similar; G. Bieri and E. Heilbronner, *Helv. Chim. Acta*, **57**, 546 (1974). (b) A series of 3-substituted quinuclidines have a similarly narrow bandwidth for the lone pairs; D. H. Aue, H. M. Webb, and M. T. Bowers, unpublished results.

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(11) The detailed interpretation of the stuctural features in the first band of manxine is as yet uncertain, but it appears clear that manxine is planar or near-planar. Similar conclusions have been reached from analyses of absorption spectra of manxine and quinuclidine; A. M. Halpern, *J. Am. Chem. Soc.*, **96**, 7655 (1974).

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(13) D. H. Aue, H. M. Webb, and M. T. Bowers, *J. Am. Chem. Soc.*, **94**, 4726 (1972).

(14) The PA of manxine would be expected to be much higher than n-Pr_3N based on pure p-hybridization and the correlations with percent s character observed by D. H. Aue, H. M. Webb, and M. T. Bowers, *J. Am. Chem. Soc.*, submitted.

(15) For ammonia, the PA, IP, and HA may be calculated for a planar geometry from the inversion barrier (5.8 kcal/mol) (ref 5), the calculated angle bending energy to make three hydrogens in NH_4^+ coplanar with the nitrogen (ca. 8 kcal/mol) (ref 3), and the aIP of NH_3 (Table I). From these data, the derived PA is ca. 2 kcal/mol lower for planar NH_3 than for pyramidal NH_3, the vHA (or $\equiv N^+$—H bond strength) is ca. 23 kcal/mol lower, and the vIP is ca. 21 kcal/mol lower. Thus, the basicity (PA) of planar NH_3 is only slightly lower than pyramidal NH_3 as a result of competition between a strongly lowered $\equiv N^+$—H bond strength and a low ionization potential.

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Proton Affinities, Ionization Potentials, and Hydrogen Affinities of Nitrogen and Oxygen Bases. Hybridization Effects[1]

Sir:

The effect of alkyl group polarizabilities on quantitative proton affinities has been reported previously and the proton affinity changes analyzed in terms of changes in ionization potentials (IP's) and hydrogen affinities (HA's).[2] These quantities are related according to eq 1. In this report we describe how changes in hybridization at nitrogen and oxygen affect the PA's, IP's, and HA's of several amines and oxygenated compounds.

$$\begin{aligned} &B{:} + H^+ \longrightarrow BH^+ \quad -\Delta H° = PA \\ &B^{+\cdot} + H\cdot \longrightarrow BH^+ \quad -\Delta H° = HA \\ &PA(B{:}) = HA(B^{+\cdot}) - IP(B{:}) + IP(H\cdot) \qquad (1) \end{aligned}$$

Nitrogen compounds with lone-pair electrons of high s character are compared in the first part of Table I with saturated model compounds of similar polarizability[3] but with sp^3 hybridization at nitrogen. Differences between the proton affinities of pairs of compounds with similar polarizabil-

Table I. Proton Affinities(PA), Vertical Ionization Potentials (vIP), and Vertical Hydrogen Affinities (vHA) of Nitrogen and Oxygen Bases

	PA[a] (kcal/mol)	vIP[b] (kcal/mol)	vHA (kcal/mol)	% s character[c]
Pyridine	224.8	223.7[d]	134.9	33
Piperidine	230.3	199.7	116.4	25
Aziridine	220.1	226[g]	122	30
Me_2NH	224.9	205.9	117.2	25
MeCH=NEt	227.6	217.7	131.7	33
Et_2NH	230.1	199.0	115.5	25
1-Azabicyclo-[1.1.0]butane	~217[i]	~225[f]	~128	34
Me_3N	229.1	197.4	112.9	25
Azetidine	227.5	208.5[k]	122.4	26
N-Methylaziridine	226.5	213.5	126.4	30
MeCN	188[i]	303.0[e]	177	50
$EtNH_2$	221.1	218.4	125.9	25
EtCN	189[i]	297.7[e]	173	50
H_2O	168[j]	290.8[g]	145	25
MeOH	183[i]	252.8[h]	122	25
Oxirane	185[i]	243.7	115	30
Me_2O	190[i]	231.8	108	25
Et_2O	198[i]	223.7	108	25
Oxetane	194[i]	223.2	103	26
$Me_2C{=}O$	195[i]	223.9	105	33

[a] PA's of amines relative to $MeNH_2$ (218.4 kcal/mol) (see ref 2c). [b] vIP's were measured on a Perkin-Elmer PS-18 spectrometer and were taken at the maximum of the first band. [c] See ref 5. [d] C. Batich, E. Heilbronner, V. Hornung, A. J. Ashe, III, P. T. Clark, V. T. Cobley, D. Kilcast, and I. Scanlon, *J. Am. Chem. Soc.*, 95, 928 (1973). [e] R. F. Lake and H. Thompson, *Proc. R. Soc. London*, 317, 187 (1970). [f] This value is quoted to only ca. ±5 kcal/mol because of uncertainties in the assignment of the n and first σ bands which appear to overlap. [g] D. W. Turner, C. Baker, A. D. Baker, and C. R. Brundle, "Molecular Photoelectron Spectroscopy", Wiley-Interscience, New York, N.Y., 1970. [h] M. B. Robin and N. A. Kuebler, *J. Electron Spectrosc. Relat. Phenom.*, 1, 13 (1972). [i] Semiquantitative values by high pressure and double resonance experiments. Absolute values assigned relative to CH_3CHO [ΔH_f ($CH_3CH{=}OH^+$) = 140 ± 1 kcal/mol (PA = 186 kcal/mol), B. H. Solka and M. E. Russell, *J. Phys. Chem.*, 78, 1268 (1974)] and $(CH_3)_2C{=}CH_2$ [ΔH_f $(CH_3)_3C^+$ = 169 kcal/mol (PA = 193 kcal/mol), J. J. Solomon and F. H. Field, *J. Am. Chem. Soc.*, 95, 4483 (1972)]. [j] S.-L. Chong, R. A. Meyers, and J. L. Franklin, *J. Chem. Phys.*, **56**, 2427 (1973).

ity but different hybridization are then ascribed to lone-pair hybridization effects. For example, the proton affinity of pyridine (sp^2N) is 6 kcal/mol lower than that of piperidine (sp^3N). Thus, the usual explanation that the low basicity of pyridine in solution stems from a hybridization effect is valid in the gas phase when polarizability effects are taken into account.[2,3] Such polarizability effects are highly attenuated, however, in solution, while the hybridization effects are not.[2a,d,g] This leads to reversals in the orders of basicity of pyridine vs. ammonia and methylamine in going from the gas phase to aqueous solution.[2d,4] Similarly, aziridine's[5] proton affinity is 5 kcal/mol lower than dimethylamine; 1-azabicyclobutane[5] has a proton affinity about 12 kcal/mol lower than trimethylamine, and acetonitrile has a PA 34 kcal/mol lower than that of ethylamine. These PA's then show a distinct base weakening effect in compounds with high s character.

The changes in proton affinity with hybridization are accompanied by larger and partially canceling changes in vertical ionization potentials and hydrogen affinities. The vertical hydrogen affinities[6] increase with increasing s character in the N^+-H bond, consistent with the known increases in bond dissociation energies of C-H bonds with increasing s character.[7] For example, in aziridine, the vHA is 16 kcal/mol higher than in dimethylamine.

The differences in PA and vIP between molecules with

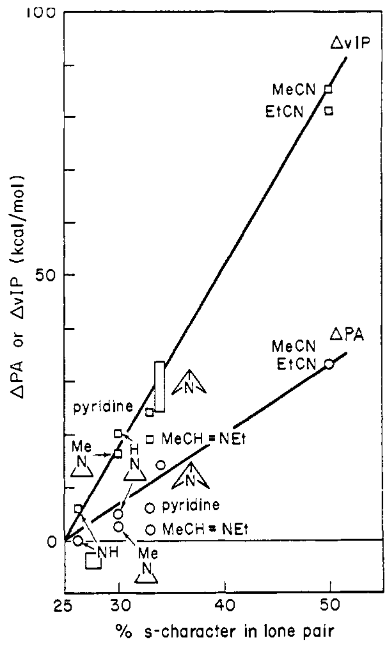

Figure 1. Plot of the differences in PA (○) and vIP (□) between molecules with high s character and model compounds with sp^3 hybridization vs. per cent s character. The lines through ΔPA and ΔvIP points are to show only a semiquantitative correlation, not necessarily linear (ref 10).

high s character in the nitrogen lone pair and models of comparable polarizability can be seen in Figure 1 to correlate reasonably regularly with the fraction of s character of the lone pair.[7,8] The negative deviations by pyridine and imines may be attributed to the resonance stabilization of the radical cations and the pyridinium and iminium ions.[9,10]

The ΔPA between oxirane and dimethyl ether is about the same (5 kcal/mol) as that between aziridine and dimethylamine; but the vIP and vHA changes are only about half as large. This difference may be the result of ionization of oxygen compounds from a p orbital in both compounds so that the hybridization effects are not directly felt in the ionization process in oxirane.[11,12] The lowering of the vIP of oxirane could be the result of angle strain in the ring rather than a direct lone pair hybridization effect.[13] No such vertical p orbital ionization is possible in nitrogen bases like aziridine, pyridine, or nitriles; so the high ΔvIP's observed there can result from direct lone pair hybridization effects.

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(1) Supported by NSF Grants No. MPS74-18397 and MPS73-04657 and the donors of the Petroleum Research Fund administered by the American Chemical Society.

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(3) Polarizabilities of saturated and unsaturated or cyclic compounds of the same carbon skeleton calculated from the Clausius–Mosotti equation are generally the same within 10%.

(4) The attenuation of polarizability effects in alkylamines can be explained in terms of changes in the effective ionic radii on charge densities of the ammonium ions (ref 2d). For hybridization effects on PA, little change in effective ionic radius or charge density in the ion is expected, so hybridization effects are usually strongly felt in solution basicities, especially for acetonitrile ($pK_a \simeq -10$); I. M. Kolthoff and M. K. Chantooni, Jr., *J. Am. Chem. Soc.*, 95, 4768, 8539 (1973); and see ref 2d.

(5) The lone pair hybridization would be expected to be ca. $sp^{2.2}$ (31% s) for aziridine and ca. $sp^{1.9}$ (34% s) for 1-azabicyclobutane on the basis of ^{13}C–H coupling constants in corresponding hydrocarbons; D. Seebach, *Angew Chem., Int. Ed. Engl.*, 4, 121 (1965); K. B. Wiberg and G. M. Lampman, *Tetrahedron Lett.*, 2173 (1963). From the HCH bond an-

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).

(9) D. H. Aue, H. M. Webb, and M. T. Bowers, *J. Am. Chem. Soc.*, to be submitted.

(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.

(11) For leading references see O. Eisenstein, N. T. Anh, A. Devaquet, J. Cantacuzene, and L. Salem, *Tetrahedron*, **30,** 1717 (1974); D. A. Sweigart, *J. Chem. Educ.*, **50,** 322 (1973); D. W. Turner, C. Baker, A. D. Baker, and C. R. Brundle, "Molecular Photoelectron Spectroscopy", Wiley-Interscience, New York, N.Y., 1970.

(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.

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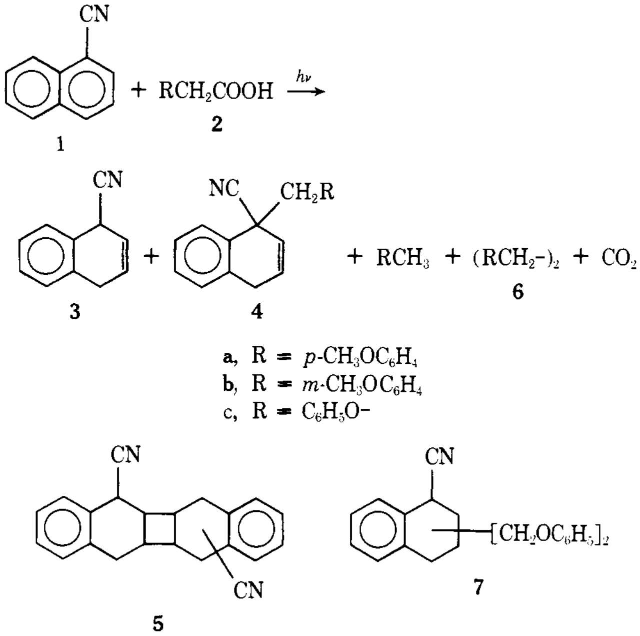
Light Induced Charge Transfer Processes. The Photochemical Behavior of 1-Cyanonaphthalene in the Presence of Phenylacetic Acid Derivatives

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, $J_{\text{gem}} = 22$ Hz, $J \sim 1.5$, C=CC*H*), 3.24 (dd, 1, $J_{\text{gem}} = 22$ Hz, $J_{\text{vic}} = 4.5$ Hz, C=CC*H*), 3.10 (s, 2, ArCH_2), 3.72 (s, 3, OCH_3), 5.82 (pair of dd, 1, $J_{2\text{-}3} = 10$ Hz, $J_{2\text{-}4} = 2.5$ Hz, $J_{2\text{-}4} \sim 1$ Hz, C=C^2H), 6.08 (pair of dd, 1, $J_{3\text{-}2} = 10$ Hz, $J_{3\text{-}4_{\text{aeq}}} = 4.5$ Hz, $J_{3\text{-}4_{\text{ax}}} = 2.5$ Hz, C=C^3H), and 6.7–7.65 ppm (m, 8, Ar*H*); molecular ion *m/e* 275.



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

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, $J_{\text{gem}} = 22$ Hz, $J \sim 1.5$ Hz, C=CC*H*), 3.24 (dd, 1, $J_{\text{gem}} = 22$ Hz, $J_{\text{vic}} = 4.5$ Hz, C=CC*H*), 3.13 (s, 2, ArCH_2), 3.58 (s, 3, OCH_3), 5.82 (pair of dd, 1, $J_{2\text{-}3} = 9.5$ Hz, $J_{2\text{-}4} = 2$ Hz, $J_{2\text{-}4} \sim 1$ Hz, C=C^2H) 6.19 (pair of dd, 1, $J_{3\text{-}2} = 9.5$ Hz, $J_{3\text{-}4_{\text{aeq}}} = 4.5$ Hz, $J_{3\text{-}4_{\text{ax}}} = 2.5$ Hz, C=C^3H), 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, $J_{\text{gem}} = 9$ Hz, ArOC*H*), 4.15 (d, 1, $J_{\text{gem}} = 9$ 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.