(11) D. Dodd and M. D. Johnson, *J. Am. Chem. Soc.*, **96**, 2279 (1974).

(12) Free radicals are almost certainly formed during side reactions accompanying the formation of **3**; their detection would not necessarily assist in the understanding of this reaction.

(13) Tetracyanoethylene radical ions have been shown to be important intermediates in a number of reactions of TCNE with organometallic compounds.[14]

(14) (a) P. J. Krusic, H. Stoklosa, L. E. Manzer, and P. Meakin, *J. Am. Chem. Soc.*, **97**, 667 (1975); (b) H. C. Gardner and J. K. Kochi, *ibid.*, **97**, 5026 (1975).

(15) Insertion has been shown to be a consequence of the formation of organic radicals in the presence of the tetracyanoethylene radical anion.[14b] Such a reaction may also be responsible for the formation of unstable insertion products which are formed in the reaction of **1d** with TCNE.

(16) A similar phenomenon has also been observed with 1-(3-methylphenyl)ethylperoxybis(dimethylglyoximato)pyridinecobalt(III),[17] in which the phenyl group also lies close to and parallel with the dioximato ligand plane.[18]

(17) C. Fontaine, K. N. V. Duong, C. Merienne, A. Gaudemer, and C. Gianotti, *J. Organomet. Chem.*, **38**, 167 (1972).

(18) A. Chiaroni and C. Pascard-Billy, *Bull. Soc. Chim. Fr.*, 781 (1973).

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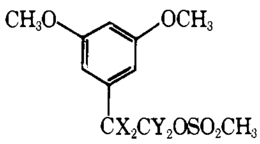
Photochemistry of Aromatic Compounds. Photosolvolysis of 2-(3,5-Dimethoxyphenyl)ethyl Methanesulfonate

Sir:

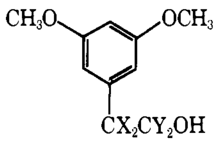
Photochemical solvolyses of numerous substituted and unsubstituted benzyl systems have been studied.[1] We wish to report the first example of photosolvolysis of a 2-arylethyl system which is initiated by excitation of the aryl group and accompanied by its migration.[2] Furthermore, solvolysis product distributions suggest the involvement of a phenonium ion.

Irradiation[3] of a 0.0065 M solution of 2-(3,5-dimethoxyphenyl)ethyl methanesulfonate[4,5] (**1a**) in 50% (v/v) aqueous methanol yielded **2a**[6a] (28.5%),[7] **3a**[5] (19.1%), **4a**[6b] (8.1%), **5a**[8] (5.3%), **6**[6c] (1.1%), **7**[5] (3.3%), and recovered **1a** (8.0%).[9] The ir spectrum (neat) of **5a** displayed bands at 2840 (CH_3O) and 1610 cm^{-1} (aromatic); the uv spectrum (hexane) λ_{max} 275 (ϵ 1600), 277 (ϵ 1600), and 282 nm (ϵ 1670); and the ^1H NMR spectrum (100 MHz, $CDCl_3$) broadened singlets at δ 6.24 and 6.21 (2 H, aromatic), equal singlets at δ 3.78 and 3.67 (6 H, CH_3O), and an A_2B_2 multiplet centered at δ 3.12[10] from δ 2.98 to 3.27 (4 H, CH_2CH_2). Irradiation[3] of a 0.0065 M solution of *n*-octyl methanesulfonate[11] in 50% aqueous methanol yielded only recovered ester. Therefore, photosolvolysis and other processes of **1** are the result of an initial interaction of the excited 3,5-dimethoxyphenyl chromophore with the methanesulfonate group.[12]

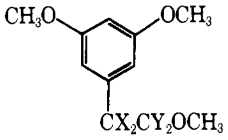
Irradiation[3] of a 0.0065 M solution of **1b**[13] in 50% aqueous methanol yielded **2** (26.7%),[7] **3** (21.7%), **4** (9.3%), **5** (6.3%), **6** (0.4%), **7** (2.1%), and recovered **1** (10.7%). By mass spectrometry[15] **1, 2, 3,** and **5** each contained $\geq$1.98 atoms of excess deuterium per molecule, and by ^1H NMR **1** consisted of a 6.1:1 mixture respectively of **1b** and **1c**, **2** of a 1.1:1 mixture respectively of **2b** and **2c**, **3** of a 1.1:1 mixture respectively of **3b** and **3c**, and **5** of a 2.4:1 mixture of **5b** and **5c**.[16] By mass spectrometry[15] **4** contained 1.89 atoms of excess deuterium per molecule, and by ^1H NMR only **4b** was detected. The spectrum consisted of a doublet at δ 2.53, J = 7.5 Hz (2 H, benzyl), a broad multiplet centered at δ 1.19 from δ 1.07 to 1.30 (1 H, methyl), and resonances for aromatic (3 H) and methoxy protons (6 H) unaltered with respect to the spectrum of **4a**. For minor components **6** and **7** deuterium content and location were not determined. A second photolysis[3] of **1b** resulted in a comparable product distribution and in almost identical mass spectral and ^1H NMR analyses.



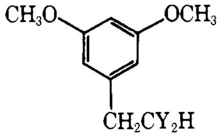
1a, X = Y = H
1b, X = H; Y = D
1c, X = D; Y = H



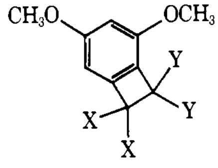
2a, X = Y = H
2b, X = H; Y = D
2c, X = D; Y = H



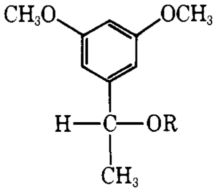
3a, X = Y = H
3b, X = H; Y = D
3c, X = D; Y = H



4a, Y = H
4b, Y = D

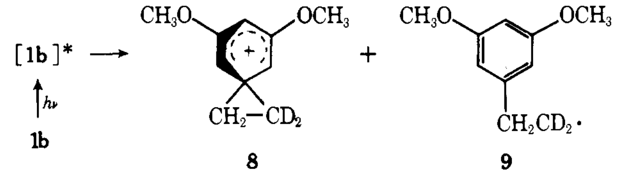


5a, X = Y = H
5b, X = H; Y = D
5c, X = D; Y = H

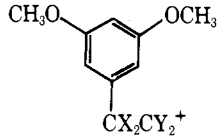


6, R = H
7, R = CH_3

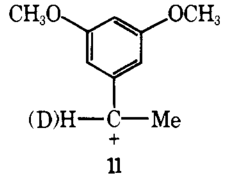
There are several mechanistic interpretations consistent with the product distribution obtained with **1b**, but all of them include phenonium ion **8** as an intermediate or transition state. One possible mechanism involves initial photoinduced cleavages to give **8** and free radical **9**. For **9** intramolecular substitution yields **5b** and hydrogen abstraction from methanol **4b**. If **8** is simply a transition state, it opens to essentially equal amounts of carbenium ions **10a** and **10b**, which then undergo several processes: (a) capture by solvent to give **2** and **3**; (b) capture by methanesulfonate to give **1**; (c) intramolecular alkylation to give **5**; and (d) hydride migration to give carbenium ion **11**. Capture of **11** by solvent yields deuterated analogues of **6** and **7**.[17]



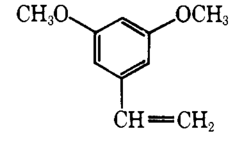
8 **9**



10a, X = H; Y = D
10b, X = D; Y = H



11



12

If **8** is an intermediate, capture by water, methanol, and methanesulfonate would lead directly to **2, 3,** and **1**, respectively, and rearrangement to **5**. Leakage of **8** to **10** would lead to **6** and **7** through **11**.[18,19]

If formed, **12**[5] would not be expected to survive the photolysis conditions used for **1**. Irradiation[3] of a 0.0029 M solution of **12** in 50% aqueous methanol containing 0.0042 M methanesulfonic acid yielded (GLC analysis, *n*-octadecane internal standard) **4a** (26.2%), **6** (0.5%), **7** (2.1%), and no recovered **12**.[21,22] However, in photolyses of **1**, **12** is most likely an intermediate in a minor pathway to **4**. As noted, a small amount of deuterium was lost on going from **1b** to **4**, and this is consistent with the intermediacy of a deuterated analogue of **12** produced from **10b** and/or **11**.[23]

The nature of the interaction between excited 3,5-dimethoxyphenyl and the methanesulfonate group is unknown but will be the subject of further investigation. As noted, it is also unknown whether **8** is an intermediate or simply a transition state, but study of an appropriate chiral system may answer this question.

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References and Notes

(1) (a) H. E. Zimmerman and V. R. Sandel, *J. Am. Chem. Soc.*, **85**, 915–922 (1963); (b) S. J. Cristol and G. C. Schloemer, *ibid.*, **94**, 5916–5917 (1972); (c) D. A. Jaeger, *ibid.*, **97**, 902–904 (1975); (d) A. L. Maycock and G. A. Berchtold, *J. Org. Chem.*, **35**, 2532–2538 (1970); (e) M. A. Ratcliff, Jr., and J. K. Kochi, *ibid.*, **36**, 3112–3120 (1971); (f) V. Lillis, J. McKenna, J. M. McKenna, and I. H. Williams, *J. Chem. Soc., Chem. Commun.*, 474 (1974); (g) V. B. Ivanov, V. L. Ivanov, and M. G. Kuzmin, *Mol. Photochem.*, **6**, 125–132 (1974); (h) S. Fujita, Y. Ozaki, and H. Nozaki, *Bull. Chem. Soc. Jpn.*, **45**, 2571–2574 (1972), and references therein.

(2) Photosolvolysis of 2-(4-hydroxy-3,5-di-*tert*-butylphenyl)ethyl *p*-toluenesulfonate in methanol has been reported, V. B. Vol'eva, V. V. Ershov, and A. A. Volod'kin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1207 (1974). However, with this system it is not clear whether photosolvolysis is initiated by excitation of the aromatic leaving group or 2-aryl group.

(3) For each run 250 ml of solution was degassed with purified nitrogen for 40 min prior to and during irradiation for 40.0 min with a 450-W Hanovia lamp through Vycor.

(4) Methanesulfonate **1a**, bp 145 °C (0.02 mm) (Kugelrohr), was prepared from **2a** by an established procedure, R. K. Crossland and K. L. Servis, *J. Org. Chem.*, **35**, 3195–3196 (1970).

(5) The ^{1}H NMR, ir, and mass spectra were consistent with the structural assignment, and carbon and hydrogen analyses were within 0.40% of theory.

(6) (a) S. Winstein and R. Heck, *J. Am. Chem. Soc.*, **78**, 4801–4806 (1956); (b) J. P. Brown, N. J. Cartwright, A. Robertson, and W. B. Whalley, *J. Chem. Soc.*, 859–867 (1949); (c) H. S. Aaron and C. P. Ferguson, *J. Org. Chem.*, **33**, 684–689 (1968).

(7) (a) Figures are actual yields based on materials isolated from the crude product mixture by column chromatography on silica gel with ether–hexane. (b) No additional material ($>\sim 1\%$) other than polymer was detected. (c) Methanesulfonic acid would have been lost on workup.

(8) High resolution mass spectrometry gave $M^{\cdot +}$ = 164.083 23; calculated for $C_{10}H_{12}O_2$, 164.083 73.

(9) Controls demonstrated the absence of thermal solvolysis of **1a** during photolysis and isolation.

(10) The ethylene protons of benzocyclobutene exhibit a chemical shift of δ 3.14 (CCl_4): G. Fraenkel, Y. Asahi, M. J. Mitchell, and M. P. Cava, *Tetrahedron*, **20**, 1179–1184 (1964).

(11) H. R. Williams and H. S. Mosher, *J. Am. Chem. Soc.*, **76**, 2984–2987 (1954).

(12) There is no evidence in the uv spectrum (50% aqueous methanol) of **1a** for ground state interaction of the aryl and methanesulfonate groups.

(13) Reduction of methyl 3,5-dimethoxyphenylacetate[14] with $LiAlD_4$ (99% D) gave **2b**, which was converted[4] to **1b**.

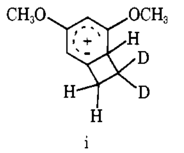
(14) E. Hardegger, W. Rieder, A. Walser, and F. Kugler, *Helv. Chim. Acta*, **49**, 1283–1290 (1966).

(15) For each compound analysis was based on flat-topped peaks of the molecular ion group at 12 eV.

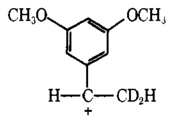
(16) In the spectrum of **5**, singlets in a ratio of 2.4:1 were observed at δ 3.03 and 3.18, respectively. At present it is not known which is the major isomer. However, in view of that fact than an almost equal isomer distribution was obtained for **2** and for **3** from **1b**, it is reasonably assumed that **5b** is the major isomer for purposes of mechanistic discussion.

(17) A control demonstrated that 1-(3,5-dimethoxyphenyl)ethyl methanesulfonate, if produced by a return process with **11**, would have decomposed completely during product isolation if not during photolysis.

(18) An alternative mechanism is formulated by substitution of ions i and ii for free radical **9**. The former ion could result along with **8** from the initial interaction of excited aryl group with methanesulfonate and would be responsible for the excess of **5b** over **5c**. Ion ii could result from hydride transfer concomitant with ionization, and its reduction (see below) would lead to **4b**.



i



ii

(19) Thermal solvolyses of 2-(3,5-dimethoxyphenyl)ethyl *p*-bromobenzenesulfonate,[8a] and its deuterated analogue, 2-(3,5-dimethoxyphenyl)ethyl-*1,1-d₂* *p*-bromobenzenesulfonate,[20] have been reported; **4** and **5** and products analogous to **6** and **7** were not detected. Acetolysis and formolysis of deuterated sulfonate gave ester products containing only partially scrambled deuterium label.

(20) C. C. Lee and L. Noszkó, *Can. J. Chem.*, **44**, 2481–2489 (1966).

(21) By GLC only a few other unknown minor products ($\leq 4\%$) of comparable volatility were detected.

(22) (a) Photochemical reduction of styrenes in methanol and accompanying addition have been reported. For example, see P. J. Kropp, *J. Am. Chem. Soc.*, **95**, 4611–4619 (1973), and references therein. (b) A control demonstrated the absence of thermal reaction.

(23) (a) Irradiation[3] of a 0.0024 M solution of **6** in 50% aqueous methanol containing 0.0044 M methanesulfonic acid yielded (GLC analysis, *n*-octadecane internal standard) **4a** (33.1%), **7** (1.2%), and **6** (0.6%).[21] Likewise, irradiation[3] of a 0.0023 M solution of **7** in the same solvent containing 0.0047 M methanesulfonic acid yielded **4a** (34.8%), **6** (0.5%), and **7** (0.8%).[21] These results are consistent with photoinduced reduction of **12** since reductions of **6**, **7**, and **12** presumably proceed through **11**, which abstracts hydride from methanol. (b) Irradiation[3] of a 0.0023 M solution of **2a** in 50% aqueous methanol containing 0.0045 M methanesulfonic acid yielded (GLC analysis, *n*-octadecane internal standard) recovered **2a** (64.7%) and no **3**, **4**, **5**, **6**, or **7**.[21]

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Solution Structure and Ligand Exchange in the Five-Coordinate Molecular Complexes $NiX_2(PMe_3)_3$

Sir:

Synthesis and determination of the stereochemistries of five-coordinate metal complexes have been subject to a considerable increase of interest during the last decade, but few studies have reported the solution structures of these complexes or kinetic studies of five-coordinate metal centers.[1-7] We wish to present evidence for the solution structure and the ligand exchange mechanism in $NiX_2(PMe_3)_3$ complexes, obtained from $^{31}P\{^1H\}$ NMR spectroscopy.

In earlier papers we have shown[7] that trimethylphosphine Ni(II) complexes, $NiX_2(PMe_3)_3$ (X = CN, Cl, Br, I), are examples of five-coordinate d^8 complexes. They are reasonably stable as crystalline solids, but labile in solution, resulting in different species depending on the concentration, the nature of the solvent, and the presence of excess ligand. Thus the solution structures were not well understood.[5,7]

Figure 1 shows ^{1}H noise decoupled Fourier transform ^{31}P NMR spectra of solutions of $NiX_2(PMe_3)_3$ (X = CN, Cl, Br, I) in 1:1 CH_2Cl_2/CD_2Cl_2 solutions at −75 °C. The slow exchange limit spectra are obtained for the four complexes. They are among the very scarce five-coordinate complexes which exhibit stereochemical rigidity at not too low a temperature.[8]

At −75 °C, the solution spectra present an A_3 pattern for X = CN and an A_2B pattern for X = Cl, Br, and I. These results are consistent with the two trigonal bipyramid (= TBP) configurations: *trans*-TBP (X = CN) and *cis*-TBP (X = Cl, Br, I) previously reported for these complexes.[7] But NMR spectroscopy alone cannot determine unambiguously the geometry of the NiX_2L_3 species in solution for X = halide, since the same A_2B pattern is expected for the cis trigonal bipyramidal and square pyramidal geometries. Nevertheless, the existence of only one isomer in CH_2Cl_2 solution is clearly demonstrated (at least in concentrations detectable by NMR).