

National Science Foundation and the National Institutes of Health is gratefully acknowledged.

References and Notes

- (1) (a) K. N. Houk, *J. Am. Chem. Soc.*, **94**, 8953 (1972); (b) K. N. Houk, J. Sims, R. E. Duke, Jr., R. W. Strozier, and J. K. George, *ibid.*, **95**, 7287 (1973); (c) K. N. Houk, J. Sims, C. R. Watts, and L. J. Luskus, *ibid.*, **95**, 7301 (1973); (d) K. N. Houk, *Acc. Chem. Res.*, **8**, 361 (1975).
- (2) J. Sims and K. N. Houk, *J. Am. Chem. Soc.*, **95**, 5798 (1973).
- (3) The nucleophilic terminus is that with greater negative charge and highest HOMO coefficient; the electrophilic terminus has largest LUMO coefficient and the least negative (or most positive) charge.^{1b,c,4}
- (4) MINDO/2 and MINDO/3 optimized geometries: P. Caramella, R. W. Gandour, J. A. Hall, C. G. Deville, and K. N. Houk, *J. Am. Chem. Soc.*, in press. These calculations also predict the trends obtained here by ab initio techniques: in MINDO/3 (MINDO/2) the HCN angles are 116° (114°), 126° (122°), and 159° (150°) for the ylide, imine, and oxide, respectively. The linear nitrile oxide is only 0.1 (0.2) kcal/mol higher in energy than the bent.
- (5) A. Padwa, M. Dharan, J. Smolanoff, and S. I. Wetmore, Jr., *J. Am. Chem. Soc.*, **95**, 1945, 1954 (1973).
- (6) R. Huisgen, *Helv. Chim. Acta*, **50**, 2421 (1967); K. Bunge, R. Huisgen, R. Raab, and H. J. Sturm, *Chem. Ber.*, **105**, 1307 (1972), and references therein; B. Jackson, M. Marky, H.-J. Hansen, and H. Schmid, *Helv. Chim. Acta*, **55**, 919 (1972).
- (7) A. Padwa and J. Smolanoff, *J. Chem. Soc., Chem. Commun.*, 342 (1973).
- (8) N. Gakis, H. Heimgartner, and H. Schmid, *Helv. Chim. Acta*, **58**, 748 (1975), and references therein.
- (9) (a) A. Padwa and S. I. Wetmore, Jr., *J. Am. Chem. Soc.*, **96**, 2414 (1974); (b) A. Padwa and P. H. J. Carlsen, *ibid.*, **97**, 3862 (1975); A. Padwa, A. Ku, A. Mazzu, and S. I. Wetmore, Jr., *ibid.*, **98**, 1048 (1976); A. Padwa and P. H. J. Carlsen, submitted for publication.
- (10) The GAUSSIAN 70 series of programs was used: W. J. Hehre, W. A. Lathan, R. Ditchfield, M. D. Newton, and J. A. Pople, Program No. 236, Quantum Chemistry Program Exchange, Indiana University, Bloomington, Ind. The optimizations were carried out by variations of all geometrical parameters by the procedure described by Pople,¹¹ using the minimal STO-3G basis set.¹² While energies of optimized geometries were recalculated using the split-valence 4-31G basis set.^{13,14} See W. A. Lathan, L. A. Curtiss, W. J. Hehre, J. B. Lisle, and J. A. Pople, *Prog. Phys. Org. Chem.*, **11**, 175 (1974), for extensive comparisons of the results of this methodology with experiment.
- (11) M. D. Newton, W. A. Lathan, W. J. Hehre, and J. A. Pople, *J. Chem. Phys.*, **52**, 4064 (1970).
- (12) W. J. Hehre, R. F. Stewart, and J. A. Pople, *J. Chem. Phys.*, **51**, 2657 (1969).
- (13) R. Ditchfield, W. J. Hehre, and J. A. Pople, *J. Chem. Phys.*, **54**, 724 (1971).
- (14) (a) R. Huisgen (*Angew. Chem., Int. Ed. Engl.*, **2**, 633 (1963)) postulated that the HCN-bent geometries of nitrilium betaines would be less stable than the planar, because allyl resonance would be maximum for the planar geometries. (b) L. Salem (*J. Am. Chem. Soc.*, **96**, 3486 (1974)) has discussed the photochemical ring-opening of azirines and mentions the possibility of initial formation of a diradical (bent) species which may undergo reactions different from the dipolar (linear) species. Padwa has suggested that the stable linear geometry can undergo rehybridization to a higher energy bent (carbene) form, which may undergo carbene-like cycloadditions.⁹
- (15) STO-3G calculations on the allenyl-propargyl anion system indicate the following geometries (relative energies): propargyl (planar), $r_{HC_1} = 1.05 \text{ \AA}$, $r_{C_1C_2} = 1.19 \text{ \AA}$, $r_{C_2C_3} = 1.37 \text{ \AA}$, $r_{C_3H} = 1.07 \text{ \AA}$, $\angle HC_3H = 116.4^\circ$, ($E_{rel} = +6 \text{ kcal/mol}$); allenyl (nonplanar); $r_{HC_1} = 1.10 \text{ \AA}$, $r_{C_1C_2} = 1.26 \text{ \AA}$, $r_{C_2C_3} = 1.33 \text{ \AA}$, $r_{C_3H} = 1.08 \text{ \AA}$, $\angle HC_3H = 113.8^\circ$, $\angle H_1C_1C_2 = 115.8^\circ$ ($E_{rel} = 0$). This energy difference is reduced to 5 kcal/mol in 4-31 G calculations.
- (16) Although microwave data on fulminic acid were originally interpreted in terms of a linear geometry ($r_{HC} = 1.027 \text{ \AA}$; $r_{CN} = 1.168 \text{ \AA}$; $r_{NO} = 1.199 \text{ \AA}$),¹⁷ recent ir data imply that this molecule is "quasi-linear", with the linear geometry $\sim 0.1 \text{ kcal/mol}$ less stable than a bent species ($\angle HCN = 165^\circ$; $r_{HC} = 1.060 \text{ \AA}$; $r_{CN} = 1.168 \text{ \AA}$; $r_{NO} = 1.199 \text{ \AA}$).¹⁸ Although the STO-3G calculations do not reproduce this hump at the bottom of the surface, the flatness of the HCN bending surface is reproduced: the optimized molecule with $\angle HCN = 165^\circ$ is only 1.4 kcal/mol (4-31G) less stable than the linear. MINDO/3 calculations reproduce this hump quantitatively.⁴
- (17) H. K. Bodenseh and K. Winnewisser, *Z. Naturforsch.*, **24**, 1973 (1969).
- (18) B. P. Winnewisser, M. Winnewisser, and F. Winther, *J. Mol. Spectrosc.*, **51**, 65 (1974).
- (19) Similar reasoning has been used to rationalize inversion barriers in AH_3 molecules: W. Cherry and N. Epiotis, *J. Am. Chem. Soc.*, **98**, 1135 (1976).
- (20) R. Huisgen, R. Sustmann, and K. Bunge, *Chem. Ber.*, **105**, 1324 (1972).
- (21) L. A. Wendling and R. G. Bergman, *J. Am. Chem. Soc.*, **96**, 308 (1974); A. Demoulin, H. Gorissen, A.-M. Hesbain-Frisquen, and L. Ghosez, *J. Org. Chem.*, **41**, 83 (1976); *J. Am. Chem. Soc.*, **97**, 4409 (1975).
- (22) K. Burger, W. Thenn, and E. Müller, *Angew. Chem., Int. Ed. Engl.*, **12**, 155 (1973); K. Burger, and K. Einhellig, *Chem. Ber.*, **106**, 3421 (1973); K. Burger, K. Einhellig, G. Süß, and A. Gieren, *Angew. Chem., Int. Ed. Engl.*, **12**, 156 (1973).
- (23) A. Padwa and J. K. Rasmussen, *J. Am. Chem. Soc.*, **97**, 5912 (1975).
- (24) Nitrile yields have now been observed spectroscopically in glasses at low temperature: A. Orahovata, H. Heimgarten, H. Schmid, and W. Heinzelmann, *Helv. Chim. Acta*, **58**, 2662 (1975).
- (25) D. Poppinger, *J. Am. Chem. Soc.*, **97**, 7486 (1975).
- (26) K. N. Houk, J. Sims, and Y.-M. Chang, unpublished results.
- (27) Although one cannot be sure that calculations with more extended basis sets, such as are necessary for anion calculations (J. W. Williams, Jr., and A. Streitwieser, Jr., *J. Am. Chem. Soc.*, **97**, 2634 (1975)), and with inclusion of correlation energy (for limited CI calculations on some 1,3-dipoles, see E. F. Hayes and A. K. Q. Siu, *J. Am. Chem. Soc.*, **93**, 2090 (1971)), will continue to favor a particular geometry shown, the trends observed here are expected to be preserved in more extensive calculations, as they are also in MINDO/2 and MINDO/3 calculations.⁴
- (28) (a) On leave from the University of Pavia, Italy; (b) Camille and Henry Dreyfus Teacher-Scholar Grant Recipient, 1972-1977; Fellow of the Alfred P. Sloan Foundation, 1975-1977.
- (29) A previous partial optimization of nitrile imine by ab initio techniques gave $\angle HCN = 107^\circ$, $\angle NNH = 115^\circ$, $r_{CN} = 1.34 \text{ \AA}$, and $r_{NN} = 1.33 \text{ \AA}$: B. T. Hart, *Aust. J. Chem.*, **26**, 461 (1973).

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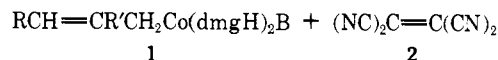
Cyclization and Rearrangement in the Reaction of Allylbis(dimethylglyoximate)cobalt(III) Complexes with Tetracyanoethylene. Crystal Structure of *trans*-3,3,4,4-Tetracyano-2-phenylcyclopentylbis(dimethylglyoximate)imidazolecobalt(III)

Sir:

Mainly because of their biological analogues, 1,2-rearrangements¹ are of considerable importance in organocobalt chemistry. Indeed, despite appreciable efforts to understand 1,2-migrations of functional groups catalyzed by adenosylcobalamin, they are not understood at all² and present theories have had to rely almost exclusively on results from synthetic "model" systems. We here describe a further example of a 1,2-rearrangement in organocobaloxime chemistry which also has analogues in the organic chemistry of other organometallic complexes.³

Several allylbis(dioximate)pyridinecobalt(III) complexes (e.g., **1**) react with tetracyanoethylene (**2**) in dichloromethane to give 3,3,4,4-tetracyanocyclopentylbis(dioximate)pyridinecobalt(III) complexes (e.g., **3**). Thus, allylbis(dimethylglyoximate)pyridinecobalt(III) (**1a**) gives a near quantitative yield of **3a** (eq 1), but the yield of cyclic product from 3-substituted allyl complexes **1b**, **1c** and **1e** is lower⁵ (40-70%) and that from the 2-substituted allyl complex **1d** is negligible.

The ¹H NMR spectra and chromatographic behavior of the products from **1b**, **1c** and **1e** indicate that only a single cyclic product is formed in each case and the solid (**3e**) obtained from



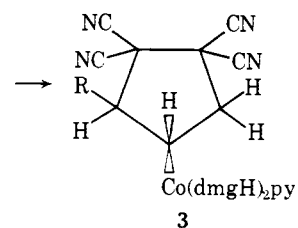
1a, R = R' = H; B = py

1b, R = Me; R' = H; B = py

1c, (trans)R = Ph; R' = H; B = py

1d, R = H; R' = Me; B = py

1e, (trans)R = Ph; R' = H; B = imidazole

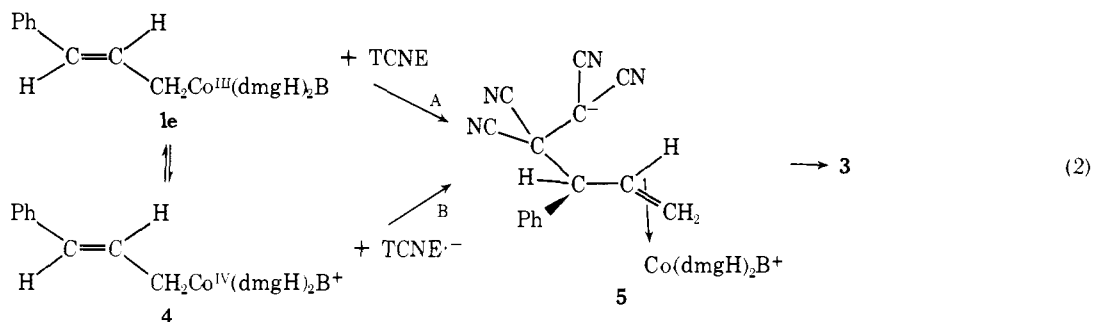


3a, R = H; B = py

3b, R = Me; B = py

3c, R = Ph; B = py

3e, R = Ph; B = imidazole



1e gave only a single crystalline species which remained unchanged through various crystallization processes. Pale yellow crystals were obtained from acetone for structure analysis.

The structure of **3e** was solved by heavy atom analysis, using 2973 independent reflections collected on a Stöe Stadi-2 diffractometer and refined by block diagonal least-squares to a current *R* of 0.082. The cobalt was allowed anisotropic thermal parameters and all other non-hydrogen atoms have been given isotropic parameters.

The structure of **3e** (Figure 1) shows clearly that, though the metal and the phenyl group are in mutual trans-positions with respect to the cyclopentane ring, the phenyl group is constrained to lie (a) close to and almost parallel with the plane of the dioximato ligands, and (b) centered approximately below one of the glyoximato oxygen atoms [O(1)]. These results have both spectroscopic and mechanistic consequences.

(1) The trans-stereochemistry of the product **3e** from the *trans*-cinnamyl complex **1e**⁶ clearly indicates that the reaction must involve either a concerted 2 + 3 cycloaddition⁷ with a 1,2-migration of the cobalt, or attack of the tetracyanoethylene or its radical anion on the γ -carbon of the cinnamyl complex (**1e**; path A, eq 2) or its oxidation product **4** (path B, eq 2), respectively, to give the intermediate **5** with *antarafacial* coordination⁸ of the cobalt to the α,β -double bond. This step determines the stereochemistry and subsequent ring closure accompanied by a further shift of the metal from the α,β -double bond to a σ -bond at the β -position would give the observed *trans*-product **3**.^{9,10}

While there is no evidence that free radicals are directly involved in this reaction,¹² a preliminary electron transfer from the substrate to tetracyanoethylene (eq 2) is possible.¹³ However, any cinnamyl radicals formed by homolysis of the cinnamylcobaloxime(IV) intermediate **4** would react with the tetracyanoethylene radical ion to give either the 1,1,2,2-tetracyano-3-phenylpent-4-enyl or 1,1,2,2-tetracyano-5-phenylpent-3-enyl carbanion which would be expected to have a far greater capacity for reaction with the cobaloxime(III) species at the carbanionic center, giving insertion products,¹⁵ than at the olefinic bond.

(2) The asymmetry of the cyclopentyl substituent and the proximity of the phenyl ring to the plane of the dioximato ligands are also evident in solution, for there is a marked effect in the ¹H NMR spectra of **3c** and **3e**, which is not evident in those of the products **3a** or **3b**. Thus, the two diagonally opposite pairs of methyl groups C₁, C₈, and C₄, C₅ of **3b**, **c** and **e** are diastereotopic and those of **3c** and **e** have markedly different chemical shifts in CDCl₃/CD₃OD; this difference in chemical shift varies, for **3c**, from 0.22 ppm at 60° to 0.30 ppm at -60° and, for **3e** from 0.18 to 0.21 ppm.

(3) Bond lengths and angles are generally unexceptionable. The Co-N bond lengths within the near-planar cobaloxime moiety average 1.89 (1) Å, the Co-N(imidazole) bond length is 2.01 (1) Å and the Co-C bond length is 2.06 (1) Å. The interaction between the asymmetric organic ligand and the dioximato ligands causes some distortion both of the cobaloxime plane and of the axial ligand-cobalt-axial ligand

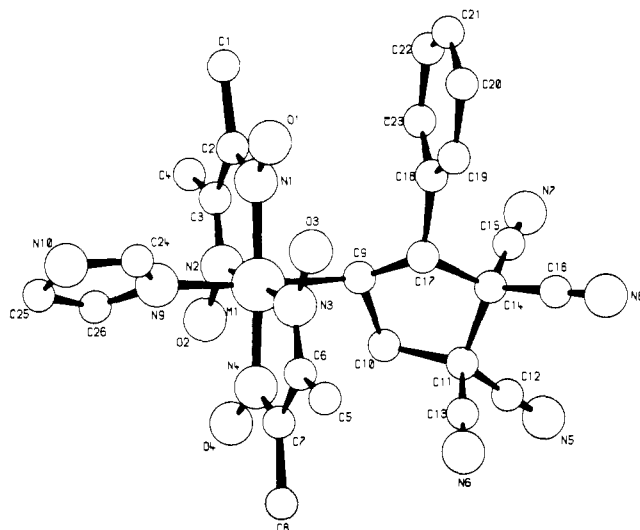


Figure 1.

axis. The O₁-O₂ bond distances are therefore different, O₁-O₂ (2.51 (1) Å) O₂-O₄ (2.44 (1) Å), and the C₉-Co-N₉ angle is 174.94°.

References and Notes

- (1) For a list of nine such rearrangements, with references, see ref 2.
- (2) B. M. Babior, *Acc. Chem. Res.*, **8**, 376 (1975).
- (3) Similar cyclopentylmetal complexes have been described in the corresponding reactions of several allylmetal carbonyl complexes with tetracyanoethylene: cf. (a) J. E. Thomasson, P. W. Robinson, D. A. Ross, and A. Wojcicki, *Inorg. Chem.*, **10**, 2130 (1971); (b) W. P. Giering, S. Raghu, M. Rosenblum, A. Cutler, D. Entholt, and R. W. Fish, *J. Am. Chem. Soc.*, **94**, 8251 (1972); (c) W. P. Giering and M. Rosenblum, *ibid.*, **93**, 5299 (1971); (d) D. w. Lichtenberg and A. Wojcicki, *J. Organomet. Chem.*, **33**, C77 (1971); S. R. Su and A. Wojcicki, *Inorg. Chem.*, **14**, 89 (1975); *Inorg. Chim. Acta*, **8**, 55 (1974). The preparation of **3a** has also been mentioned as a footnote in M. Rosenblum, *Acc. Chem. Res.*, **7**, 122 (1974), and in ref 3b. A full account of the preparation of **3a** has appeared⁴ since the submission of this manuscript.
- (4) A. Cutler, D. Entholt, W. P. Giering, P. Lennon, S. Raghu, A. Rosen, M. Rosenblum, J. Tancrede, and D. Wells, *J. Am. Chem. Soc.*, **98**, 3495 (1976). This paper also describes the stereochemistry of the cycloaddition of tetracyanoethylene to *trans*-CH₃CH:CH-CH₂Fe(CO)₂- η^5 -C₅H₅ based on an examination of the ¹H NMR of the reaction product.
- (5) The yield of **3d** is greatest when a small excess of pyridine and a two-threefold excess of tetracyanoethylene are used. This and other products in this work were characterized by elemental analysis.
- (6) **1c** and **1e** were prepared from cinnamylbis(dimethylglyoximate)aquocobalt(III) which was shown by NMR spectroscopy to be substantially ($\geq 90\%$) the *trans* isomer. No *cis* isomer could be detected. The products **1c** and **1e** also showed sharp single dimethylglyoximate proton resonances characteristic of single isomers. We have been unable to prepare the corresponding *cis* isomer.
- (7) The concerted [$\pi 2_s + \pi 2_s + \sigma 2_s$] process, which cannot be ruled out, has been considered by Rosenblum^{3c} for analogous iron complexes, but was believed to be less likely than a sequential process of appreciable ionic character.
- (8) If the migration of the cobalt were suprafacial, then the *cis* isomers of **3** would be formed.
- (9) Several comparable 1,2- σ - π - σ rearrangements involving cobalt(III) complexes have also been observed, e.g., B. T. Golding, H. L. Holland, U. Horn, and S. Sakrikar, *Angew. Chem., Int. Ed. Engl.*, **9**, 959 (1970).
- (10) Though several allyl-cobaloxime complexes have been shown to have dynamic character in solution,¹¹ the need for a small excess of pyridine⁵ and the higher yields obtained when imidazole is the basal ligand rule out pathways through the π -allyl-cobaloxime species and through a prior rearrangement of *trans*- to *cis*-cinnamylcobaloxime.

- (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. Köchi, *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(dimethylglyoximate)pyridinecobalt(III),¹⁷ in which the phenyl group also lies close to and parallel with the dioximate 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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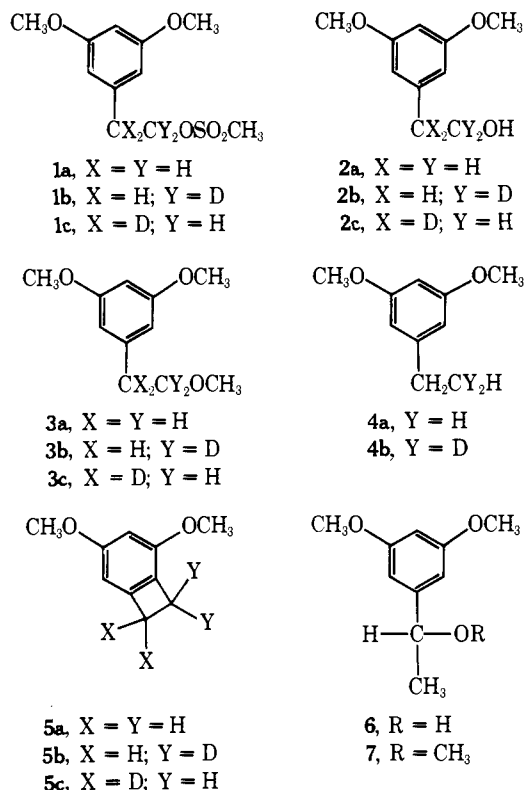
Photochemistry of Aromatic Compounds. Photosolvolysis of 2-(3,5-Dimethoxyphenyl)ethyl Methanesulfonate

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.

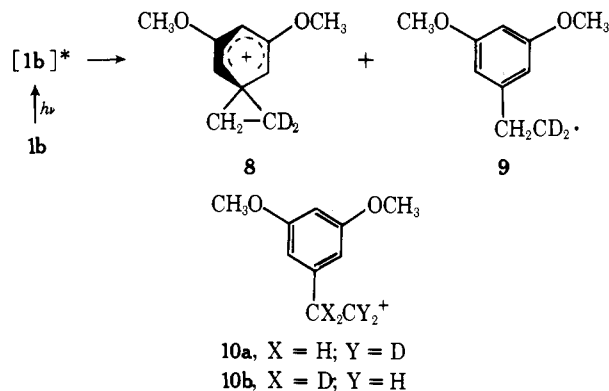
Irradiation³ of a 0.0065 M solution of 2-(3,5-dimethoxyphenyl)ethyl methanesulfonate^{4,5} (**1a**) in 50% (v/v) aqueous methanol yielded **2a**^{6a} (28.5%),⁷ **3a**⁵ (19.1%), **4a**^{6b} (8.1%), **5a**⁸ (5.3%), **6**^{6c} (1.1%), **7**⁵ (3.3%), and recovered **1a** (8.0%).⁹ The ir spectrum (neat) of **5a** displayed bands at 2840 (CH₃O) 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, CDCl₃) broadened singlets at δ 6.24 and 6.21 (2 H, aromatic), equal singlets at δ 3.78 and 3.67 (6 H, CH₃O), and an A₂B₂ multiplet centered at δ 3.12¹⁰ from δ 2.98 to 3.27 (4 H, CH₂CH₂). Irradiation³ of a 0.0065 M solution of *n*-octyl methanesulfonate¹¹ 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

Irradiation³ 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 spectrometry¹⁵ **1**, **2**, **3**, and **5** each contained ≥ 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 spectrometry¹⁵ **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 photolysis³ of **1b** resulted in a

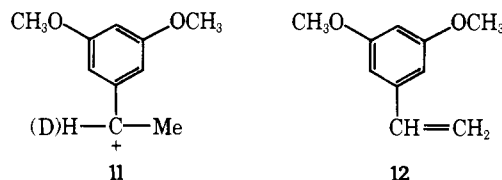


comparable product distribution and in almost identical mass spectral and ¹H NMR analyses.

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



If **8** is an intermediate, capture by water, methanol, and methanesulfonate would lead directly to **2**, **3**, and **1**, respec-