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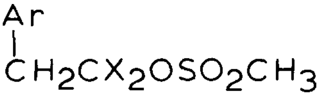
PHOTOLYSIS OF CIS- AND TRANS-2-(3,5-DIMETHOXYPHENYL)CYCLOPENTYL METHANESULFONATE. STEREOELECTRONIC REQUIREMENT FOR PHOTOSOLVOLYSIS

David A. Jaeger* and Emily A. Bernhardt

Department of Chemistry, University of Wyoming, Laramie, Wyoming 82071

Abstract: On irradiation in methanol, trans-2-(3,5-dimethoxyphenyl)cyclopentyl methanesulfonate underwent photosolvolysis whereas the cis-isomer did not; thus, for photosolvolysis there exists a trans-requirement of excited aryl group and leaving group.

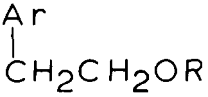
There have been several reports of photosolvolysis of 2-arylalkyl and related systems.[1] In particular, we reported[1a] that of 1a in aqueous methanol, which yielded 2 and 3 as the major products. With deuterated analogue 1b, these products were produced with 100% scrambling of the labeled carbon between the 1- and 2-positions of the ethyl group. A mechanism involving phenonium ion intermediate 4 was proposed based on these and other results.



$\overset{\text{Ar}}{\overset{|}{\text{C}}}H_2CX_2OSO_2CH_3$

1a, X = H

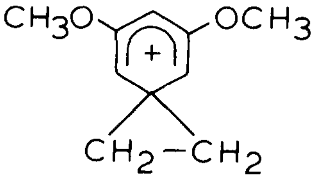
1b, X = D



$\overset{\text{Ar}}{\overset{|}{\text{C}}}H_2CH_2OR$

2, R = H

3, R = CH_3

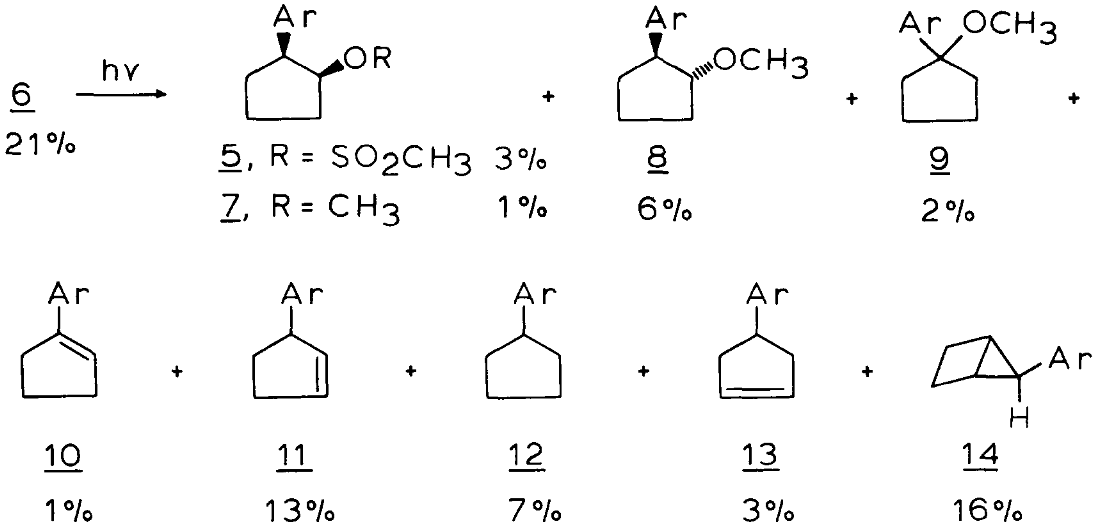


4

Ar = 3,5-$(CH_3O)_2C_6H_3$-

In order to define the stereoelectronic requirement for photosolvolysis of 2-arylalkyl systems such as 1, we have prepared and studied cis- (5) and trans-2-(3,5-dimethoxyphenyl)-cyclopentyl methanesulfonate (6). Dehydration of 1-(3,5-dimethoxyphenyl)cyclopentanol[2] with H_2SO_4-CH_3CO_2H yielded alkene 10.[2] Oxidation of 10 with m-$ClC_6H_4CO_3H$ in benzene yielded the corresponding epoxide, which was converted to 2-(3,5-dimethoxyphenyl)cyclopentanone[2] with $BF_3 \cdot Et_2O$ in benzene. Reduction of this ketone with L-Selectride (Aldrich) in tetrahydrofuran (THF) gave cis-2-(3,5-dimethoxyphenyl)cyclopentanol,[2] which was converted[3] to 5[2] with CH_3SO_2Cl-Et_3N in CH_2Cl_2. Hydroboration-oxidation of 10 in THF gave trans-2-(3,5-dimethoxyphenyl)cyclopentanol,[2] which was converted to 6.[2]

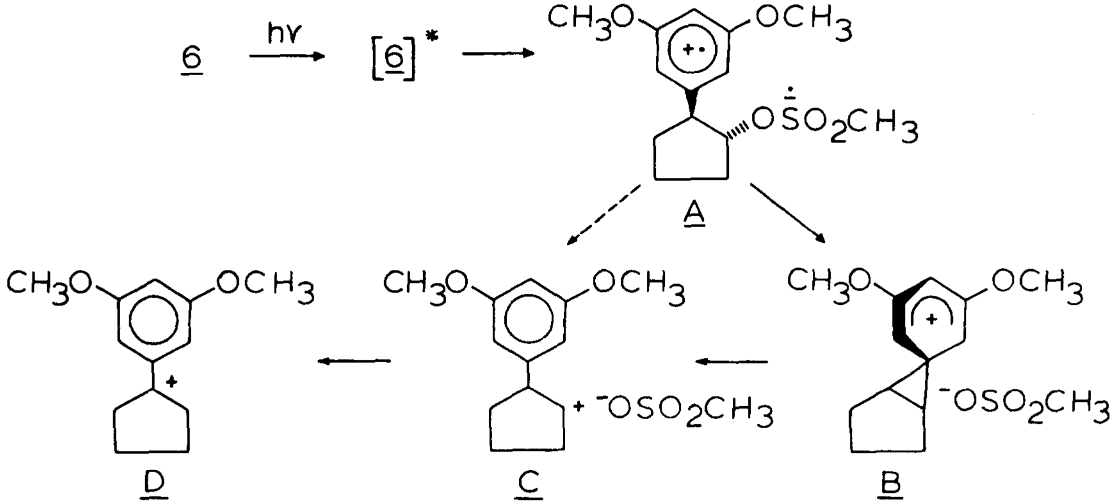
Irradiation of a degassed 4.45×10^{-3} M solution[4] of 6 in CH_3OH yielded the following products in the indicated amounts as determined by direct calibrated analysis of the reaction mixture by high performance liquid chromatography (HPLC).[5,6] The identities of 7-12 were established by comparisons with samples synthesized independently,[2,7] and those of 13 and 14 on the basis of their spectral and chromatographic behavior.[8] Under essentially the same irradiation conditions cis-methanesulfonate 5 was inert.[6]



In contrast to the above photochemical results, thermal solvolysis of a 4.30 x 10^{-3} *M* solution of 5 in CH_3OH at reflux under N_2 for 10 h yielded 11% 8 and 73% 10 as determined by direct calibrated analysis of the reaction mixture by HPLC.[5] Thermal solvolysis of a 3.93 x 10^{-3} *M* solution of 6 in CH_3OH under the same conditions gave 34% 6, 24% 7, 1% 8, 30% 10, and 7% 11. These results parallel those of Kim and Brown for the acetolyses of *cis*- and *trans*-2-arylcyclopentyl *p*-toluenesulfonates.[9] For all of the *cis* and those *trans* systems similar to 6 with deactivating substituents, solvolysis proceeded without aryl participation. On the other hand, solvolysis of *trans* systems with activating substituents (*i.e.*, *p*-MeO) involved aryl participation with the possible intervention of aryl-bridged ions.

In the irradiations of 5 and 6, only the aryl chromophore absorbed.[1a] Thus for 6, photosolvolysis and other reactions must be the result of an interaction between the excited 3,5-dimethoxyphenyl group and the unexcited methanesulfonate leaving group. This interaction cannot involve simple energy transfer because the singlet energy of the latter is greater than that of the former, and it is assumed that the same relationship holds for the respective triplet states. Charge transfer within 6 from the excited aryl group to the methanesulfonate group is a possible energy transfer pathway[10] and is incorporated into the mechanistic scheme below.

Charge transfer species A results from the excited state of 6[11] and then yields bridged ion B, which is partitioned among several processes. Its capture by $CH_3SO_3^-$ and CH_3OH gives starting material 6 and *trans*-ether 8, respectively, and its deprotonation by CH_3OH at a β-carbon atom yields 11, one of the major products. Ion B can also open to give ion C, whose capture by $CH_3SO_3^-$ gives 5 and 6, and by CH_3OH, 7 and 8. Deprotonation of C yields 10 and 11. Rearrangement of ion C gives tertiary ion D, whose capture by CH_3OH yields 9, and deprotonation 10.[12] The formation of 12 probably involves photoinduced ionization of 9 and/or protonation of 10 followed by hydride abstraction from CH_3OH by the resultant excited carbonium ion D.[13] Compound 14 is most likely a secondary product arising from a photoinduced di-π-methane rearrangement of 11. The origin of proposed structure 13 is unknown. It is possible that A gives C directly. However, the predominance of *trans*-ether 8 over *cis*-ether 7 and the formation of a relatively large amount of nonconjugated alkene 11 suggest the involvement of B.



B $\longrightarrow$ 6 + 8 + 11; C $\longrightarrow$ 5 + 6 + 7 + 8 + 10 + 11; D $\longrightarrow$ 9 + 10

In summary, the thermal and photochemical solvolytic properties of methanesulfonates 5 and 6 differ markedly. A *trans*-relationship of the aryl group and methanesulfonate leaving group is necessary for photosolvolysis. Such a *trans*- or *anti*-activation has been reported previously for several benzo- and dibenzo-polycyclic systems.[1b,c]

Acknowledgement. We thank Professor Joseph J. Tufariello for furnishing the ^1H NMR spectra of several *exo*- and *endo*-5-substituted bicyclo[2.1.0]pentanes and Dr. Richard A. Heppner for the high resolution mass spectra. Acknowledgement is made to the Division of Basic Research of the College of Arts and Sciences, University of Wyoming, for support of this research.

References and Notes

1. For examples, see (a) Jaeger, D. A. *J. Am. Chem. Soc.* *1976*, **98**, 6401. (b) Cristol, S. J.; Dickenson, W. A.; Stanko, M. K. *ibid.* *1983*, **105**, 1218. (c) Morrison, H.; Miller, A.; Bigot, B. *ibid.* *1983*, **105**, 2398, and references therein.
2. Satisfactory spectral and analytical data [carbon and hydrogen combustion analyses (±0.4%) or high resolution mass spectrometry of molecular ion] were obtained.
3. Crossland, R. K.; Servis, K. L. *J. Org. Chem.* *1970*, **35**, 3195.
4. Three 5 mL-portions of the solution in 10 mm x 100 mm quartz test tubes fitted with septum caps were degassed for at least 40 min with purified N_2 introduced and vented through syringe needles. The needles were then withdrawn and the septum caps sealed with wax. One tube was covered with aluminum foil, and the three were irradiated simultaneously for 63 min with a 450-W Hanovia lamp through a Corex filter in a merry-go-round apparatus.

5. A 4.6 mm (i.d.) x 250 mm 10 μm LiChrosorb RP-18 column was used with ultraviolet detection at 270 nm and 47:53 (v/v) CH_3CN-H_2O as eluant at a flow rate of 2 mL/min. An internal standard, n-pentyl 3,5-dimethoxybenzoate, was added to each reaction mixture after irradiation.
6. Analysis of the tube held in the dark above indicated the presence of only 6 (5). However, this control alone does not preclude the occurrence of thermal solvolysis during photosolvolysis. The latter generates CH_3SO_3H and the irradiation of CH_3OH an acidic material. Therefore, the following control was performed to demonstrate that acid-catalyzed thermal solvolysis of 6 does not accompany its photosolvolysis. A solution of 4:1 (v/v) CH_3OH-H_2O was degassed with N_2 for 45 min prior to and during irradiation for 40 min with the above lamp through a Vycor filter. Then 6 and CH_3SO_3H were added to give concentrations of 4.9 x 10^{-3} M and 5.7 x 10^{-3} M, respectively. After the resultant solution was held in the dark at room temperature for 40 min, it was worked up to yield only 6 by ^1H NMR analysis. It is reasonably assumed that 6 would be thermally stable under the same conditions in CH_3OH also.
7. In large scale runs, these compounds were isolated by combined column chromatography (silica gel with ether-hexane elution) and gas chromatography (6 ft x 0.25 in. 5% FFAP on 60-80 mesh AW Chromosorb W at 165 °C).
8. For 14, ^1H NMR (80 MHz, $CDCl_3$, TMS): δ 1.53-1.63 (m, 2 H, $H_{2,3\text{-exo}}$), 1.78-1.84 (m, 2 H, $H_{1,4}$), 2.01 (s, 1 H, H_5), 2.19-2.32 (m, 2 H, $H_{2,3\text{-endo}}$), 3.75 (s, 6 H, CH_3O), 6.12 (d, J = 2.1 Hz, 2 H, ArH_2), 6.23 (t, J = 2.1 Hz, 1 H, ArH_4); high resolution mass spectrum: $M^{+\cdot}$, 204.1135; Calcd for $C_{13}H_{16}O_2$, 204.1146. The bicyclo portion of the ^1H NMR spectrum of 14 is very similar to that of exo-5-carbomethoxybicyclo[2.1.0]pentane but not to that of the endo isomer. For 13, high resolution mass spectrum: $M^{+\cdot}$, 204.1146; Calcd for $C_{13}H_{16}O_2$, 204.1146. Further spectral characterization of 13 was precluded by the lack of sufficient material; therefore, the indicated structure is tentative.
9. (a) Kim, C. J.; Brown, H. C. J. Am. Chem. Soc. **1972**, *94*, 5043. (b) Kim, C. J.; Brown, H. C. ibid. **1972**, *94*, 5051.
10. For an example of an analogous proposed charge transfer process, see ref. 1b.
11. The results of sensitization with benzene imply the involvement of the triplet state.
12. If formed by capture of D by $CH_3SO_3^-$, 1-(3,5-dimethoxyphenyl)cyclopentyl methanesulfonate would have thermally decomposed.
13. For demonstration of analogous processes in the study of 1, see ref. 1a.

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