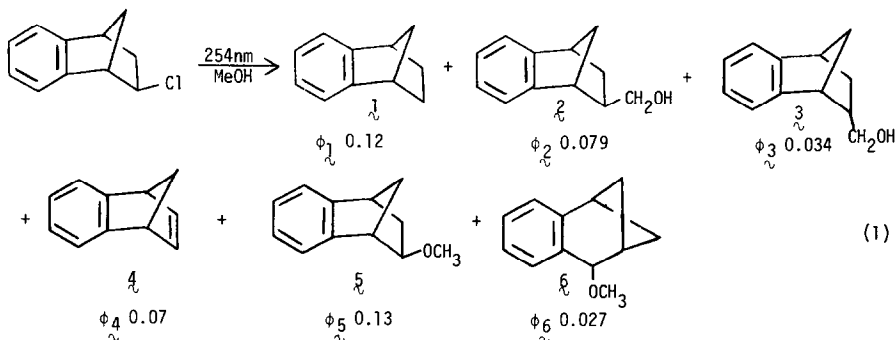


EVIDENCE FOR ANTI-BOND MIGRATION IN THE
 PHOTOREARRANGEMENT OF 2-D-EXO-BENZONORBORNENYL-2-CHLORIDE

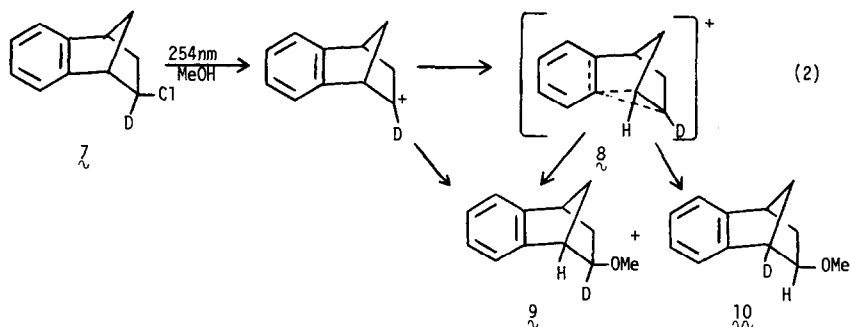
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Abstract : Photosolvolysis of the title compound to exo-2-benzonorbornenyl methyl ether proceeds with scrambling of the deuterium between C₁ and C₂, indicative of migration of the anti aryl group.

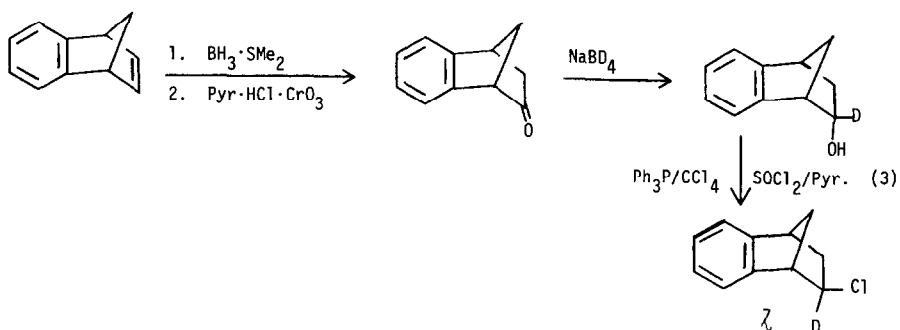
The photolytic cleavage of a group remote from the absorbing chromophore has been a subject of considerable recent interest.^{1,2} A prototypical reaction is shown in eq.1, with the singlet derived cleavage of an exo-2-chloro group occurring at a rate 733 times greater than that observed for the endo isomer.¹



Among the products is an unusual rearranged ether, **6**, which derives from the migration of the C-C bond syn to the nucleofuge.¹ It has been suggested³ that such syn migration is the dominant mode of rearrangement in the photosolvolyses of benzenobicyclic chlorides, but unfortunately any competitive anti migration of the aryl group in eq.1 would be masked by the degenerate formation of the 2-benzonorbornenyl cation. A deuterium atom at C₂ suffices to break this degeneracy, so that rearrangement involving the anti phenyl group should produce a mixture of deuterated ether products, **9** and **10** (eq. 2).



The requisite deuterated chloride, **7**, was prepared as shown in eq. 3. The exo and endo isomers are readily distinguished by ^1H nmr by the characteristic upfield shift of the endo-3 proton in the endo-2-chloro series,¹ and the exo-chloride, (**7**), is cleanly formed in this sequence. Nmr and mass spectral analysis indicated $\geq 85\%$ deuteration at C-2 and no deuteration at C₁.



A high ($\sim 85\%$) conversion photolysis of a methanol solution in a Rayonet Reactor⁴ using 254 nm lamps, followed by preparative vpc, provided deuterated 2-methoxybenzonorbornene which was analyzed by ^1H and ^{13}C nmr, and by mass spectrometry. The major feature of the ^1H nmr (470 MHz) was the appearance of four bands at δ 3.28 (C₄-H), 3.37 (O-CH₃), 3.41 (C₁-H) and 3.44

(C₂-H). Scrambling of deuterium was confirmed by the ^{13}C off-resonance proton decoupled spectrum which showed diminished signal intensities for C₁ and C₂ (due to 1-bond C-D coupling) and doublets for C₇ and C₃ (due to the β -deuterium isotope effect on these positions vicinal to C₁ and C₂).⁵ Mass spectral analysis confirmed the presence of **9** and **10** since fragmentation of the ether gives a base peak corresponding to a retro Diels-Alder reaction^{6,7} to form isoindene (deuterated from **10**).⁸

A quantitative assay of the extent of scrambling was made by photolyzing to low ($\sim 15\%$) conversion in order to minimize any potential ambiguity due to scrambling of λ by internal return. Gc-mass spectral analysis of the photolysis mixture indicated (1) under these conditions there was little, if any, scrambling of unreacted starting material⁹ and (2) the ethers are formed with a $9:10$ ratio of approximately 72:28.¹⁰ These results confirm that photosolvolytic does indeed result in anti migration of the aryl group, in fact with a quantum efficiency which exceeds that for syn migration ($28\% \text{ of } \phi_5 > \phi_6$).^{11,13}

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References and Notes

1. H. Morrison, A. Miller and B. Bigot, *J. Am. Chem. Soc.*, **105**, 2398 (1983) and references therein.
2. S. J. Cristol and M. Z. Ali, *Tetrahedron Lett.*, 5839 (1983) and preceding papers in this series.
3. S. J. Cristol, W. A. Dickenson and M. K. Stanko, *J. Am. Chem. Soc.*, **105**, 1218 (1983).
4. New England Ultraviolet Company.
5. C. Abell and J. Staunton, *J. Chem. Soc. Chem. Comm.*, 856 (1981) and references therein; the precursor chloride, λ showed only the doublet due to C-3.
6. S. J. Cristol and R. Caple, *J. Org. Chem.*, **31**, 2741 (1966).
7. T. Goto, A. Tatematsu, Y. Kata, R. Muneynki, H. Tanida and K. Tori, *Tetrahedron*, **22**, 2213 (1966).
8. A control experiment verified that λ does not solvolyze in acidic aqueous methanol at the temperature of the photolysis (ca. 40°C).
9. In addition to the isoindene peak at 116 m/e, there is a 115 peak which is not solely due to 116-H, as evidenced by a change in the 115/116 ratio upon deuteration at C₂ (see also reference 7). This creates some uncertainty in the interpretation of 117 (deuterated isoindene) relative to 116 (undeuterated isoindene plus contributions from deuterated 115 ions). However, the measured values of 117 relative to 116 before ($\sim 9\%$) and after ($\sim 10\%$) photolysis are within the range of instrumental scatter.
10. Though the problem outlined in footnote 9 does not appear to be as severe in the ether series, our calculated value for 10 presumes no deuterated "115" ions in the 116 peak and therefore represents a minimum value.

11. We have proposed¹ that syn migration proceeds via the formation of a "hot" carbocation unique to the photosolvolysis while Cristol¹² has suggested that this migration occurs in concert with the loss of the nucleofuge.
12. S. J. Cristol and T. H. Bindel, *Org. Photochem.*, **6**, 402 (1983).
13. The fact that we do not appear to be observing total scrambling of the ether is striking, and contrasts with reports on the ground state solvolysis of the brosyiates, c.f. J. P. Dirlam, A. Diaz, S. Winstein, W. P. Giddings and G. C. Hanson, *Tetrahedron Lett.*, 3133 (1969) and references therein. Ground state solvolytic studies on the chloride in aqueous methanol are in progress.

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