Arylcyclopropane Photochemistry. The Photochemical Cyclopropylcarbinyl–Homoallyl Rearrangement of 2-Arylcyclopropylcarbinyl Acetates

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Summary Photolysis of 2-arylcyclopropylcarbinyl acetates results in rearrangement to the corresponding homoallyl acetates.

Reaction of cyclopropylcarbinyl derivatives to give homoallyl products is a frequently observed ground-state process.[1] A previous observation of a corresponding photochemical transformation was later shown to be a thermal acid-catalysed reaction[2] and so we now report the first examples of a photochemical cyclopropylcarbinyl–homoallyl rearrangement of cyclopropylcarbinyl esters.

Irradiation† of a cyclohexane solution of the *trans*-acetate (**1a**) for 43·5 h provided in addition to the *cis*-isomer (**2a**) one major photoproduct. This product, isolated in 25% yield by silica gel chromatography, was shown to be the homoallyl acetate (**3a**) by comparison with an authentic sample. Benzylcyclohexane (10%; from phenylcarbene[3]) and 1-phenylbutadiene (traces) were also detected by gas chromatography. The (**1a**) to (**3a**) transformation is inefficient; ϕ *ca.* 0·01.

Appropriate controls showed that the production of (**3a**) is not an acid-catalysed thermal process. Acetone sensi-

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† A Corex-filtered Hanovia 450-watt medium pressure mercury arc was used.

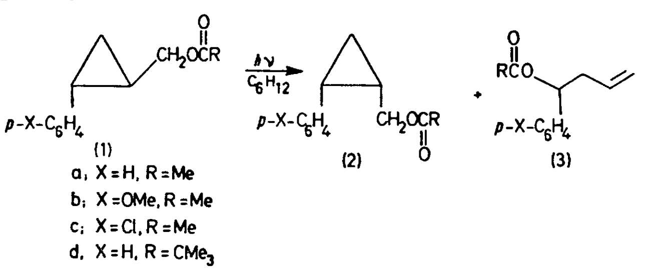
tisation of (**1a**) produced the *cis*-isomer (**2a**) and small amounts of other products, but no (**3a**), indicating that the triplet of (**1a**) is not involved in the formation of (**3a**). Irradiation of (**1a**) in methanol provided both (**3a**) and the ether (**4**) in a 1·4:1 ratio at low conversions of (**1a**).

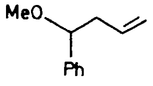
TABLE. Relative quantum yield and rate data for (**1a**—**d**).

Compound	ϕ_r(rel)	k_f(rel)[a]	ϕ_f(rel)[b,c]	k_r(rel)[b]
(**1a**)[d]	1·0	1·0	1·0[f]	1·0
(**1a**)[e]	1·1	1·0	0·72[f]	1·5
(**1b**)[d]	0·12	5·9	2·5[g]	0·28
(**1c**)[d]	0·055	1·5	0·51[h]	0·16
(**1d**)[d]	0·86	1·0	0·87[f]	0·99

[a] The absorption spectra of (**1a**—**d**) are basically similar to those of toluene (**1a**,**d**), *p*-chlorotoluene (**1c**) and *p*-methylanisole (**1b**). Consequently we have used the natural singlet lifetimes[5] of these compounds in computing the relative k_r's. [b] Computed as in ref. 4a. [c] λ(excitation) 250 nm. [d] Cyclohexane solution. [e] Acetonitrile solution. [f] λ_{max} 294 nm. [g] λ_{max} 311 nm. [h] λ_{max} 302 nm.

So far, the rearrangement observed for (**1a**) appears to be general for 2-arylcyclopropylcarbinyl acetates. The diphenyl compound (**5**) rearranges predominantly to (**6**) in cyclohexane and forms both (**6**) and ether (**7**) (0·64:1) in methanol. Similarly, the bicyclic acetate (**8**) (a mixture of epimers) provides (**9**)‡ as the major product. On the other hand, 1-phenylcyclopropylcarbinyl acetate proved relatively stable to irradiation, forming only very small amounts of as yet unidentified materials after prolonged photolysis.

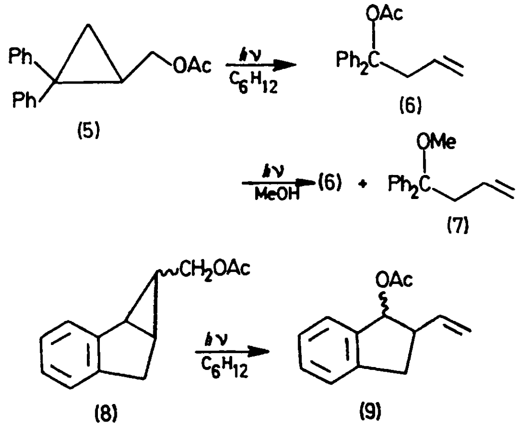


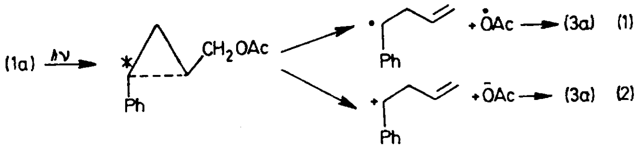


(**4**)

The results of some substituent effect studies are reported in the Table. Significant points to note are (a) both *p*-chloro (**1c**) and *p*-methoxy (**1b**) substituents decrease the rate[4] and efficiency of rearrangement; (b) the rearrangement of (**1a**) proceeds only slightly faster in acetonitrile relative to cyclohexane; (c) changing the acetyl group of (**1a**) to a pivaloyl group (**1d**) has a negligible effect.

We feel a radical mechanism for rearrangement (Equation 1) is unlikely as the predominant pathway in view of the similarity in rates and efficiencies of rearrangement of (**1a**) and (**1d**) for it is known that acetoxy and pivaloyloxy radicals lose carbon dioxide extremely rapidly and that the pivaloyloxy radical is much less stable to dissociation than the acetoxy radical.[6] On the other hand, the observation of both rearranged acetates and ethers when (**1a**) and (**5**) are irradiated in methanol is strong evidence for an ionic process leading to a carbonium ion for which counter ion acetate and solvent methanol compete (Equation 2). However, the negligible polar solvent effect and the deactivating effect of a p-methoxy group would seem to argue against such an ionic process.[7] We note, though, that substituent effects on photochemical ionic processes often differ from those found for analogous ground-state reactions.[8] However, no consistent pattern has emerged for photochemical ionic reactions. Excited state precedent is not clear, and we do not know what sort of substituent effects to expect.[8] Similarly unclear is the magnitude of the solvent effect to be expected in a photochemical ionic process. Thus an ionic mechanism for rearrangement is reasonable. A concerted migration process however remains a possibility and is under investigation.





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‡ Only one isomer of undetermined stereochemistry was found.

[1] R. Breslow, in 'Molecular Rearrangements,' Part 1, ed. P. de Mayo, Interscience, New York, 1963, p. 259; J. W. Wilt, in 'Free Radicals' vol. 1, ed. J. K. Kochi, Wiley, New York, 1973, p. 398.

[2] R. Beugelmans and H. C. de Marcheville, *Chem. Comm.*, 1969, 241; S. J. Cristol, G. A. Lee, and A. L. Noreen, *Tetrahedron Letters*, 1971, 4175.

[3] G. W. Griffin, *Angew. Chem. Internat. Edn.*, 1971, **10**, 537.

[4] (a) S. S. Hixson, *J. Amer. Chem. Soc.*, 1972, **94**, 2507; S. S. Hixson and T. P. Cutler, *ibid.*, 1973, **95**, 3032; (b) H. E. Zimmerman and A. A. Baum *ibid.*, 1971, **93**, 3646; (c) J. C. Dalton and N. J. Turro, *ibid.*, 1971, **93**, 3569.

[5] I. B. Berlman, 'Handbook of Fluorescence Spectra of Aromatic Molecules,' Academic Press, New York, 1971.

[6] J. K. Kochi, in 'Free Radicals,' vol. II, ed. J. K. Kochi, Wiley-Interscience, New York, 1973, p. 698; T. Koenig, *ibid.*, vol. I, p. 113; T. Koenig and H. Fischer, *ibid.*, p. 157, and references therein.

[7] See T. Shono, I. Nishiguchi, and R. Oda, *J. Org. Chem.*, 1970, **35**, 42, for studies on the acetolyses of the *p*-nitrobenzoates analogous to (**1a**—**c**).

[8] H. E. Zimmerman and V. R. Sandel, *J. Amer. Chem. Soc.*, 1963, **85**, 915; M. A. Ratcliffe, Jun., and J. K. Kochi, *J. Org. Chem.*, 1971, **36**, 3112; A. L. Maycock and G. A. Berchtold, *ibid.*, 1970, **35**, 2532.