

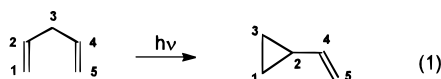
Arylmethyl Ester Photochemistry: The Aryl Version of the Cyclopropyl- π -methane Rearrangement for an Ester Conformationally Restricted from Carbon–Oxygen Bond Cleavage

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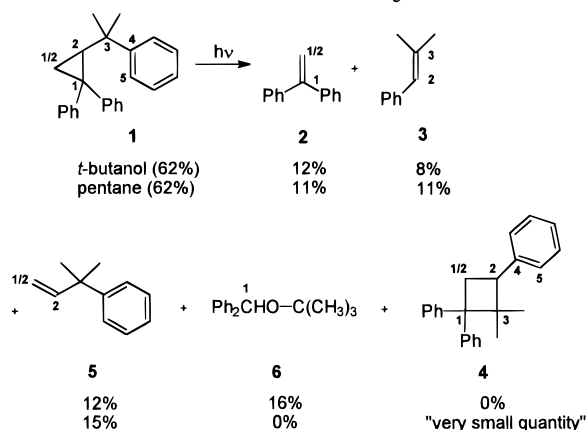
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The di- π -methane reaction is an excellent example of a single research group, in a series of comprehensive papers on structural variations of eq 1,^{1–3} clarifying many mechanistic details of a photochemical reaction. Consequently, the suggestion has been made that this reaction be called the Zimmerman rearrangement.⁴

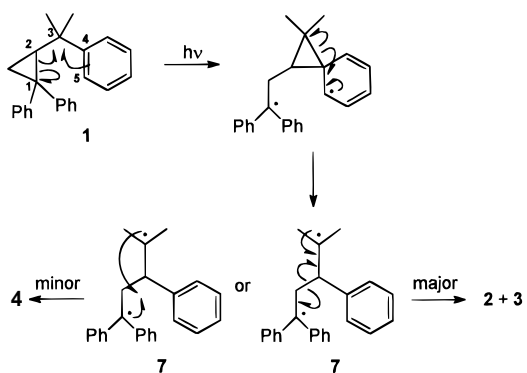


One of the cases studied was the aryl version of the cyclopropyl- π -methane rearrangement.⁵ In that example, Scheme 1, the cyclopropane $\sigma(1,2)$ bond in **1** represents one of the π -components and the aromatic $\pi(4,5)$ bond, the other.⁶ The cyclobutane, **4**, is the expected rearrangement product, and the path proposed for its formation is shown.⁷ However, the yields⁸ of **4** were, in fact, very low, none being observed in 2-methyl-2-propanol solvent and “a very small quantity” in pentane. Photolysis of independently synthesized **4** gave **2** and **3** as products, but isotope dilution experiments demonstrated that in the photolysis of **1** both **2** and **3** were primary, not secondary, photoproducts. Therefore, the intermedi-

Scheme 1. Photochemistry of Ester **1**



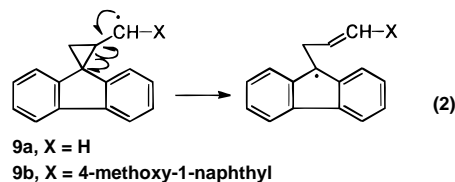
ate biradical, **7**,⁹ fragments preferentially to the two alkenes rather than cyclizing to the cyclobutane. To our



knowledge, this variant of the prototype in eq 1 has not yet been found as a major pathway.¹⁰

Our recent studies on the photochemistry of arylmethyl esters have focused on the chemical reactivity of the intermediate radical and ion pairs.¹¹ The “radical clock” technique¹² has now become a standard method for determining the kinetic behavior of radicals, but since the lifetimes of the radical pair are in the 10^{-9} – 10^{-11} s domain, a very fast radical clock is necessary. With this in mind we synthesized **8**.¹³ This ester proved, serendipitously, to be a substrate ideally suited for observing the arylcyclopropyl- π -methane rearrangement. Of the two diastereomers possible for **8**, the compound isolated was the *R,R/S,S* combination, as shown by an X-ray crystal structure determination.¹⁴ In the solid state, the H–C2–C3–H dihedral angle was calculated to be 166° . The solution (CDCl_3) NMR spectrum gave a value for this vicinal coupling constant of 10.1 Hz, strongly suggesting that the conformation in solution also has a large dihedral angle.

This particular ester was chosen to incorporate the “constrained, aryl-substituted cyclopropylcarbinyl radical” designed by Martin-Esker *et al.*¹⁵ to probe picosecond radical kinetics, eq 2. For **9** (X = H), the rate constant



for ring opening has been estimated at $6 \times 10^{12} \text{ s}^{-1}$; for

(1) Zimmerman, H. E. In *Handbook of Organic Photochemistry and Photobiology*; Horspool, W. M., Song, P.-S., Eds.; CRC Press: Boca Raton, 1995; pp 184–193.

(2) Zimmerman, H. E. In *Organic Photochemistry*; Padwa, A., Ed.; Marcel Dekker: New York, 1991; pp 1–36.

(3) Zimmerman, H. E. In *Rearrangements in Ground and Excited States*; DeMayo, P., Ed.; Academic Press: New York, 1980; Vol. 3, pp 131–164.

(4) Salem, L. As quoted and supported by P. DeMayo in a footnote to the title of ref 3.

(5) Zimmerman, H. E.; Carpenter, C. W. *J. Org. Chem.* **1988**, *53*, 3298–3305.

(6) The symbol 1/2 is used for the carbon between C1 and C2 that would be dormant in the rearrangement.

(7) Products **5** and **6** are derived from fragmentation of the cyclopropane **1** to an alkene and a carbene. In this substrate, the excitation energy is localized in the diphenylcyclopropane chromophore.

(8) The percentage numbers under **1** are for reisolated starting material.

(9) These species are to be considered points on an excited-state hypersurface and are not necessarily energy minima or maxima. This has been discussed in detail in the experimental and review publications by Zimmerman.^{1–3}

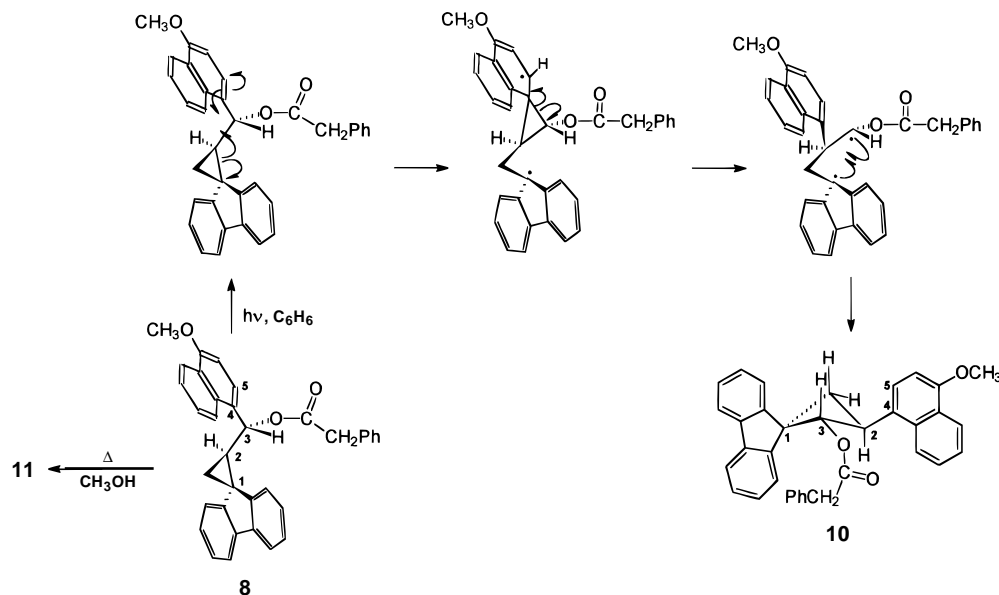
(10) In the photolysis of cyclopropyl phenyl borate salts, products were obtained that are possibly derived from the boracyclobutane: Kropp, M. A.; Baillargeon, M.; Park, K. M.; Bhamidapaty, K.; Schuster, G. B. *J. Am. Chem. Soc.* **1991**, *113*, 2155–2163.

(11) Pincock, J. A. *Acc. Chem. Res.* **1997**, *30*, 43–49.

(12) Griller, D.; Ingold, K. U. *Acc. Chem. Res.* **1980**, *13*, 317–323.

(13) The experimental procedures for the preparation and characterization of new compounds can be found in: Nevill, S. M.; Pincock, J. A. *Can. J. Chem.* **1997**, in press.

(14) Kwiatkowski, W. Department of Chemistry, Dalhousie University, 1996, unpublished results. The author has deposited atomic coordinates for this structure with the Cambridge Crystallographic Data Center. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK.

Scheme 2. Thermal and Photo Reactivity of **8**

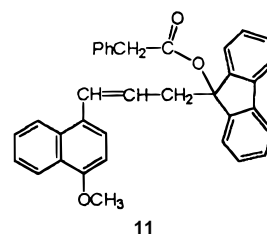
X = 4-methoxy-1-naphthyl (**9b**), the value expected would be smaller but still large enough to probe the reactivity of the radical pair generated after homolytic cleavage of the ester C–O bond in the photolysis of **8**. The 4-methoxynaphthalene moiety was chosen to have a lower singlet energy than the fluorenyl chromophore so that the excitation energy would be localized to activate the arylmethyl ester. This expectation was confirmed by fluorescence results in methanol for **8**, which gave a 0,0 value for the singlet excited state of 87.7 kcal/mol, similar that of 88.8 for 1-methoxynaphthalene.¹⁶ Fluorene has a significantly higher value of 95.1 kcal/mol.^{16,17}

To probe the chemistry of the radical pair, ester **8** was first photolyzed in benzene using a Pyrex-filtered medium-pressure Hanovia lamp. Surprisingly, in the first example that we have found, no detectable arylmethyl ester photocleavage occurred. Instead, as shown in Scheme 2, one major product, **10**,¹⁸ was observed (75% yield based on 68% conversion of ester **8**, as determined by calibrated HPLC). Longer photolysis times led to much poorer mass balance due to the disappearance of the product by secondary photolysis. The assignment of *trans* stereochemistry in **10** is based, in part, on mechanistic grounds; the concerted pathway, known to proceed with inversion of configuration at C3,¹⁹ as shown in Scheme 2, converts (*R,R*)-**8** stereoselectively to (*R,S*)-**10**, i.e., *trans*. Supporting this assignment is the observation of an enhancement by NOE of the C1 fluorenyl hydrogen by both the cyclobutyl hydrogen at the ester carbon (C3) and one of

the hydrogens of the cyclobutyl methylene group but no enhancement between the two *trans* cyclobutyl methine hydrogens at C2 and C3.

The fact that **8** is converted to **10** rather than undergoing arylmethyl ester photochemistry can be rationalized by its preferred conformation.²⁰ The π orbital of the naphthalene chromophore is ideally oriented to induce cyclopropyl bond cleavage and formation of the 1,5-biradical.²¹ In contrast, the ester C–O bond is nearly orthogonal to the same π orbital.^{22,23} The preferred collapse of the 1,4-biradical to the cyclobutane rather than fragmentation to alkenes is consistent with two arguments developed by Zimmerman; the species may still be on the S_1 surface and, perhaps more importantly, will be formed in the required cisoid geometry,⁵ which is less likely to be dominant in **7**. Therefore, conversion of **7** to **4** would be disfavored.

A reviewer has suggested that **10** could be formed by an alternate pathway of homolytic carbon–oxygen bond cleavage to a radical pair followed by rapid electron transfer to form the cyclopropylcarbinyl cation/carboxylate anion ion pair. Collapse of this ion pair, after rearrangement, could give **10**. However, the possibility of the intervention of ion pairs seems unlikely in benzene as the solvent. Moreover, the expected ion pair from **8**, generated by solvolysis in refluxing methanol, does not give **10** but rather the ring-opened rearrangement product, **11** (Scheme 2).¹³



11

(15) Martin-Esker, A. A.; Johnson, C. C.; Horner, J. H.; Newcomb, M. J. *Am. Chem. Soc.* **1994**, *116*, 9174–9181.

(16) Murov, S. L. *Handbook of Photochemistry*; Marcel Dekker: New York, 1973.

(17) Localization of the excitation energy on the naphthalene ring probably prevents the carbene fragmentation observed for **1**.

(18) The structure of **10** was fully established by IR, MS, and correlated ¹H and ¹³C NMR.

(19) Zimmerman, H. E.; Robbins, J. D.; McKelvey, R. D.; Samuel, C. J.; Sousa, L. R. *J. Am. Chem. Soc.* **1974**, *96*, 4630–4642.

(20) As discussed above, we assume that the solid-state and solution conformations are similar.

(21) The dihedral angle from C2 to C5 (**8** in Scheme 2) is 98° and the distance between the two reactive carbons (C2 and C4) is only 2.46 Å.

(22) The dihedral angle from the ester oxygen to C5 is 19°.

(23) This conformational explanation for the formation of **10** from **8** is supported by the photochemical results for an ester where the fluorenyl spiro structure is replaced by a single phenyl group. In that case, normal ester photochemistry occurs and a cyclobutane product analogous to **10** is not observed.¹³

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