Tetrahedron Vol. 42, No. 2, pp. 753 to 754, 1986
Printed in Great Britain.

0040-4020/86 $3.00 + .00

EVIDENCE FOR INTRAMOLECULAR [2+2] CYCLOADDITION PROCESS IN THE PHOTO-CLAISEN REARRANGEMENT[1]

BORIS ŠKET, NATAŠA ZUPANČIČ and MARKO ZUPAN*
Department of Chemistry and "Jožef Stefan" Institute, "E. Kardelj" University of Ljubljana, Yugoslavia

(*Received in UK* 25 *March* 1985)

Abstract—Photoreaction of pentafluorophenyl-prop-2-enyl ether in cyclohexane at $\lambda = 253.7$ nm resulted in intramolecular [2+2] cycloaddition, forming 2,3,4,5,6-pentafluoro-1,8-epoximethano bicyclo[4.2.0]octa-2,4-diene, while a similar reaction of the thio analogue led to C—S bond cleavage.

The photochemical behaviour of aromatic molecules has been widely investigated in the last three decades.[2] It is well known that several rearrangements of aromatic molecules can also occur under photochemical conditions.[3] Photo-Claisen rearrangements of aryl-allyl ethers lead to 2-, 3-, and 4-substituted phenols, dienons, and other products, with the course of the reaction depending on the substituent and the reaction conditions.[4,5] Photoreactions of non-conjugated phenyl-vinyl bichromophoric systems lead to various types of intramolecular cycloaddition products, and the position of attack strongly depends on the structure of the molecule:[6] benzyl-prop-2-enyl ether is transformed after 2,6- and 1,3-attack to three products with quantum yields between 0.017 and 0.03. The use of fluorine as a convenient substituent to follow the photochemical behaviour of molecules has been variously reported.[7] For the last ten years Brooke intensively studied thermal transformations of fluoro-substituted aryl-allyl ethers and has shown that reaction pathways could be importantly influenced by using appropriate reaction conditions.[8]

In our continuing interest in the effect of fluorine as substituent on phototransformations of organic molecules,[9] we found it worthwhile to study the photoreactions of fluorosubstituted aryl-prop-2-enyl ethers and thioethers.

RESULTS AND DISCUSSION

Irradiation (60 hr) of a cyclohexane solution of 1 mmol of pentafluorophenyl-prop-2-enyl ether at $\lambda = 253.7$ nm resulted in the formation of only one new product, which in its ^{19}F-NMR spectrum showed five multiplet signals: δ_F -145.8, -149.1, -150.2, -158.3, and -200.5, and five multiplet signals in its ^{1}H-NMR spectrum: δ_H 2.05, 2.7, 3.4, 4.35, 4.65. The product, isolated by preparative TLC, had the same molecular composition as the starting compound, but showed different fragmentations in its mass spectrum. On the basis of the spectroscopic data and spin–spin decoupling NMR experiments, we established that intramolecular [2+2] cycloaddition had occurred with the formation of 2,3,4,5,6 - pentafluoro - 1,8 - epoximethano bicyclo[4.2.0]octa-2,4-diene (**2**, Scheme 1).

Further, we studied the effect of the hetero atom on the course of phototransformation, and found that pentafluorophenyl-prop-2-enyl thioether (**1b**) reacted differently, with only C—S bond cleavage, which resulted in pentafluorothiophenol (**3**) and pentafluorophenyl-cyclohexyl thioether (**4**) formation.

In contrast to the behaviour of the above mentioned molecules (**1a** and **b**), tetrafluoro-pyridyl-prop-2-enyl ether proved to be photostable in cyclohexane solution under the same conditions.

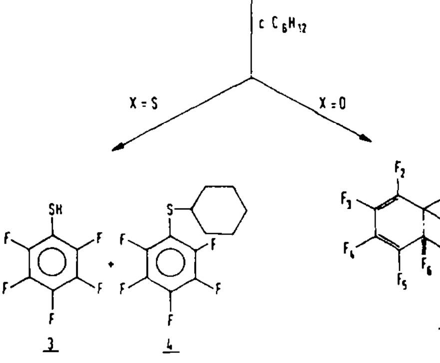
EXPERIMENTAL

Irradiations were carried out with a Rayonet Model 100 fitted with four RPR 253.7 nm lamps. IR spectra were recorded using a Perkin–Elmer 727B spectrometer and ^{1}H- and ^{19}F-NMR spectra by using a JEOL JNM PS 100 spectrometer, from $CDCl_3$ or CCl_4, with Me_4Si or $CClF_3$ as internal reference. Mass spectra and high-resolution measurements were taken on a CEC 21-100 spectrometer.

Materials. Pentafluorophenyl-prop-2-enyl ether, pentafluorophenyl-prop-2-enyl thioether, and tetrafluoro-4-pyridyl-prop-2-enyl ether were synthesized.[8] Cyclohexane was purified and distilled before use.

2,3,4,5,6 - *Pentafluoro* - 1,8 - *epoximethano bicyclo*[4.2.0]*octa*-2,4-*diene* (2)

1 mmol of **1a** was dissolved in 18 ml of cyclohexane, the soln was irradiated for 60 hr at $\lambda = 253.7$ nm, the solvent



Scheme 1.

evaporated *in vacuo* and the crude mixture (207 mg) analysed by ^{19}F-NMR spectroscopy. It contained, besides 44% of the starting material, 65% of product **2** which was isolated by preparative TLC (SiO_2; petroleum ether–$CHCl_3$ 9:1) as a white crystalline compound (68 mg (30.3%), m.p. 140–142°). NMR: δ_{F_5} −145.8 (ddd), δ_{F_4} −149.1 (dd), δ_{F_2} −150.2 (d), δ_{F_3} −158.3 (ddd), δ_{F_6} −200.5 (dddd), $\delta_{H_{10}}$ 4.65 (dd), 4.35 (d), δ_{H_8} 3.42 (m), δ_{H_7} 2.7 (dddd), 2.04 (ddd), $^3J_{F_6H_7} = {}^3J_{F_6H_7} = 24$ Hz, $^3J_{F_4F_5} = 18$ Hz, $^3J_{F_2F_3} = 15$ Hz, $^2J_{H_7H_7} = 14$ Hz, $^3J_{F_5F_6} = {}^3J_{H_7H_8} = {}^4J_{F_5H_7} = {}^2J_{H_{10}H_{10}} = 9$ Hz, $^1J_{H_7H_8} = 8$ Hz, $^3J_{F_5F_4} = 6$ Hz; MS: *m/e* calc for $C_9H_5F_5O$ 224.0260, found 224.0265, *m/e* (relative intensity) 225 ($M^+ + 1$, 9%), 224 (M^+, 91), 204 (24), 203 (67), 191 (15), 178 (35), 163 (48), 150 (24), 145 (13), 143 (13), 105 (22), 99 (17), 93 (17), 81 (17), 75 (15), 57 (15), 41 (100), 39 (26).

Irradiation of pentafluorophenyl-prop-2-enyl thioether (**1b**)

1 mmol of **1b** was dissolved in 18 ml of cyclohexane, the soln irradiated for 24 or 65 hr at $\lambda = 253.7$ nm, the solvent evaporated *in vacuo* and the crude mixture analysed by ^{19}F-NMR spectroscopy. In the case of 24 hr irradiation, it contained 72% of the starting material 17% of **3** and 11% of **4**, while the mixture obtained after 65 hr irradiation had 53% of **1b**, 35% of **3** and 12% of **4**. The structures of **3** and **4**, isolated by preparative GLC, were determined on the basis of their spectroscopic data and by comparison with the literature.

REFERENCES

[1] Presented in part: B. Šket, N. Zupančič and M. Zupan, *Xth IUPAC Symposium on Photochemistry*. Interlaken, 22–27 July (1984).

[2] D. Bryce-Smith, *Photochemistry*, Vols 1–13. The Chemical Society, Burlington House, London (1970–1983).

[3] D. Bryce-Smith and A. Gilbert, *Tetrahedron* **32**, 1309 (1976), **33**, 2459 (1977); G. Kaupp, *Angew. Chem.* **92**, 245 (1980); T. Wagner-Jauregg, *Synthesis* 165 (1980); 769 (1980); J. Cornelise and E. Havinga, *Chem. Rev.* **75**, 353 (1975).

[4] W. Adam, H. Fischer, H.-J. Hansen, H. Heimgartner, H. Schmid and H.-R. Waespe, *Angew. Chem.* **85**, 669 (1973).

[5] H.-R. Waespe, H. Heimgartner, H. Schmid, H.-J. Hansen, H. Paul and H. Fischer, *Helv. Chim. Acta* **61**, 401 (1978).

[6] A. Gilbert, *Pure Appl. Chem.* **52**, 2669 (1980).

[7] M. Zupan and B. Šket, *Isr. J. Chem.* **17**, 92 (1978).

[8] G. M. Brooke, *J. Fluorine Chem.* **22**, 483 (1983), and refs therein.

[9] Part XVII: B. Šket, N. Zupančič and M. Zupan, *Tetrahedron* **40**, 3795 (1984).