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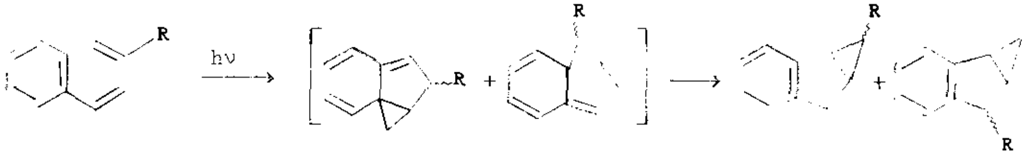
PHOTOCHEMISTRY of β-(2-FURYL) SUBSTITUTED o-DIVINYLBENZENES

Marija Šindler-Kulyk*[1], Lidija Špoljarić[1], and Željko Marinić[2]

[1] Organic Chemistry Department, Faculty of Technology, University of Zagreb, Marulićev trg 20, 41000 Zagreb, Yugoslavia
[2] Rugjer Boškovic Institute, Zagreb, Yugoslavia

Abstract - Irradiation of the benzene solution of 1-(2-vinylphenyl)-2-(2-furyl)ethenes (7) resulted in the formation of furo[3,2-b]-6,7-benzobicyclo[3.2.1]octa-2,6-dienes (10) as the main product. The structure of the products was determined by spectroscopic data.

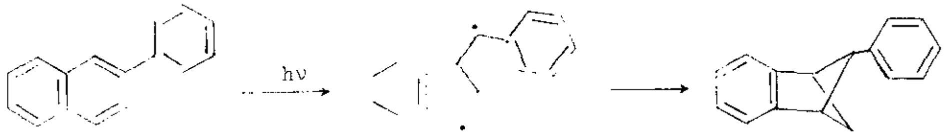
Intramolecular photochemical cycloadditions of o-divinylbenzene (1) and its derivatives containing alkyl and/or aryl substituents at any of the double bond positions have been reported previously[1-6]. It was shown that the parent compound (1)[1] and its alkyl derivatives (2)[2] gave benzobicyclo[3.1.0]-hexenes (3) by a photo Diels-Alder reaction followed by vinylcyclopropane-cyclopentene rearrangement.



1, R= H
2, R=alkyl

3, R=H,alkyl

Contrary to o-divinylbenzene (1), the β-phenyl substituted derivative (R=C_6H_5), 2-vinylstilbene (4), and derivatives of 4 which do not possess substituents at sterically interfering positions gave a [2+2]cycloadduct, benzobicyclo[2.1.1]-hex-2-ene (6) or its derivatives via a radical mechanism[3-6].

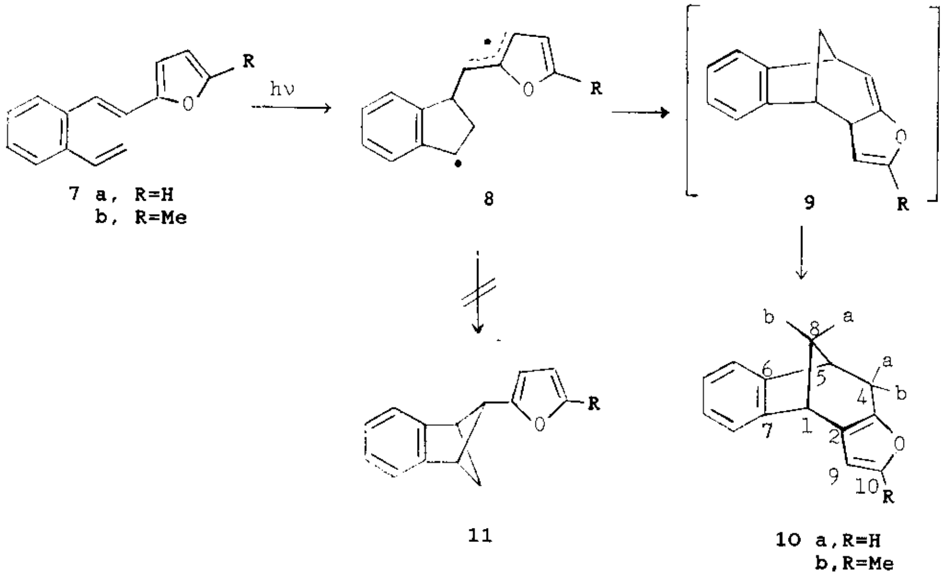


4

5

6

It is also known that heterocyclic compounds possess more or less aromatic properties depending on the heteroatom and that their photochemical properties are different from those of the corresponding phenyl derivative[7]. Therefore the previous study of photochemical cycloaddition reactions[3] has now been extended to 1-(2-vinylphenyl)-2-(2-furyl)ethenes (7)[8]. This molecule may be regarded as a furyl analogue of 2-vinylstilbene or as a system in which one vinyl group (of 1) is extended by the furyl group into a hexatrienyl group.



7 a, R=H
b, R=Me

8

9

11

10 a, R=H
b, R=Me

Direct irradiation of the benzene solution of 7a ($c=10^{-2}$) in Rayonet at 300 nm for 20 hrs in a quartz tube or for 80 hrs in a Pyrex tube gave a cycloadduct in more than 90% yield. The product was isolated and purified by column chromatography. From the nmr spectrum it was evident that the product could not be 11 by the absence of the characteristic pattern of all benzobicyclo[2.1.1]derivatives[3]. The ^{1}H nmr spectrum of the product was, however, in full accord with furo[3,2-b]-6,7-benzobicyclo[3.2.1]octa-2,6-diene (10a). The ^{1}H nmr spectrum of 10a exhibits a six-proton pattern between δ 2 and 4 ppm which could be, using decoupling techniques, completely analysed: a doublet at δ 3.78 (J=4.5 Hz) is assigned to H-1, a double triplet at 3.57 (J=0.98; 5.0 Hz) to H-5, a double doublet at 3.11 (J=5.0; 16 Hz) and 2.58 (J=0.98; 16 Hz) to H-4a and H-4b, two triplets at 2.39 (J=5.0; 4.5; 10 Hz) to H-8a and a doublet at 2.01 (J=10 Hz) to H-8b. Furthermore in the aromatic pattern of the spectrum there is a multiplet of 5 protons (4 aromatic and H-10 of the furyl group). The furyl proton H-9 absorbs at δ 6.30 ppm (J=1,95 Hz). The nmr spectrum of the product 10b (R=Me) showed a very similar pattern to product 10a (R=H) except for H-9 which appeared as a narrow quartet at δ 5.83 (J=1 Hz) and for appearance of the methyl group as a doublet at 2.16 (J=1 Hz). In the off-resonance decoupled ^{13}C nmr spectrum the existence of two triplets (δ 43.0 and 30.9, C-4 and C-8) and two doublets (δ 40.4 and 39.3, C-1 and C-5) is an undoubtable evidence for the referred structure of the photoproduct 10a. After shorter irradiation time (several hours) only traces of photoproduct 10 were found besides a cis-trans mixture enriched on cis-isomer of the starting material 7. At longer irradiation times, besides 10 as a main product, minor amounts of other products are formed. Becouse the results from both, 7a and 7b, are simlar it can be concluded that the methyl substituent at the 5 position of the furan ring does not influence the photoreactivity of compound 7. In comparison to the mechanism of the formation of 6 from 4 the formation of the biradical 8 seems appropriate. Ring closure under formation of 9 is preferred to 11, obviously for steric reasons. By a photochemically allowed superfacial 1,3-H shift[9] 9 is transformed into the final product 10.

EXPERIMENTAL

The ^{1}H and ^{13}C nmr spectra were recorded on a JEOL FX-90 Q instrument in deuteriochloroform using tetramethylsilane as an internal standard. Mass spectral data were obtained on a Varian MAT CH-7 (70 eV) instrument. UV spectra were determined on Perkin-Elmer double beam spectrophotometer 124. Purification by column chromatography was accomplished on silica gel (Merck 0.05-0.2 mm) by eluting with petroleum ether. Melting points are uncorrected. Irradiations were performed in a Rayonet reactor, fitted with 300 nm lamps.

Irradiation of 1-(2-vinylphenyl)-2-(2-furyl)ethenes (7a and 7b)[8]

A degassed benzene solution (10^{-2}mol) of 7a-b under nitrogen was irradiated for 20-80 h at 300 nm in a quarz tube. Solvent was removed in vacuo and the residue was column chromatographed to give in the first fractions the unreacted starting materials followed by bicyclo products 10a-b (20-90% yield) and some unidentified products. Physical and analytical data of the isolated photoproducts are given below :

Furo[3,2-b]-6,7-benzobicyclo[3.2.1]octa-2,6-diene (10 a): mp 58-59° C; m/z:196 (M^+,100%); ^{1}H nmr ($CDCl_3$,TMS): 6.90-7.30(m,5H), 6.30(d,1H,J=1.95Hz), 3.78 (d, 1H, J=4.5Hz), 3.57(dt,1H,J=0.98, 5Hz), 3.11(dd,1H,J=5, 16Hz), 2.58(dd,1H,J=16, 0.98Hz), 2.39(dt,1H,J=5, 4.5, 10Hz), 2.01(d,1H,J=10Hz); ^{13}C nmr ($CDCl_3$,TMS)

151.9(s), 146.7(s), 144.8(s), 140.1(d), 126.4(d), 126.1(d), 124.3(s), 123.8(d), 120.5(d), 108.7(d), 43.0(t), 40.4(d), 39.3(d), 30.9(t); uv(λ_{max},EtOH):218(5570), 229(5490), 261(2010), 268(1300), 275(1260).

2-Methylfuro[3,2-b]-6,7-benzobicyclo[3.2.1]octa-2,6-diene (10 b): mp 56-57°C; m/z:210(M$^+$,100%); ^{1}H nmr (CDCl$_3$,TMS): 7.00-7.30(m,4H), 5.80(q,1H,J=1Hz), 2.16 (d,3H,J=1Hz), 3.70(d,1H,J=4Hz), 3.58(dt,1H,J=1, 5Hz), 3.10(dd,1H,J=5, 17Hz), 2.55(dd,1H,J=17, 1Hz), 2.39(dt broad,1H,J=4, 5, 10Hz), 2.03(d,1H,J=10Hz); ^{13}C nmr (CDCl$_3$,TMS): 151.9(s), 149.4(s), 144.7(s), 144.2(s), 126.2(d), 125.8(d), 125.0(s), 123.6(d), 120.2(d), 104.2(d), 42.9(t), 40.3(d), 39.2(d), 30.7(t), 13.4(q); uv ($_{max}$, EtOH): 206(6850), 230(5760), 261(1350), 268(1580), 275(1420); Anal.Calcd for $C_{15}H_{14}O$: C, 85.68; H, 6.71. Found: C, 85.87, H, 6.88.

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REFERENCES

1. M.Pomerantz, J.Am.Chem.Soc., 1967, 89, 694; J.Meinwald and R.H. Mazzocchi, ibid., 1967, 89, 696.
2. J.Meinwald and D.Seeley, Tetrahedron Lett., 1970, 3739; L.Ulrich, H.J. Hansen, and H.Schmid, Helv. Chim. Acta, 1970, 53, 1323; H.Heimgartner, L.Ulrich, H.J. Hansen, and H.Schmid, ibid., 1971, 54, 2313.
3. M.Sindler-Kulyk and W.H.Laarhoven, J.Am.Chem.Soc., 1976, 98,1052; ibid., 1978, 100, 3819; Recl.Trav.Chim.Pays-Bas, 1979, 98, 187; ibid., 1979, 98, 452.
4. P.M.op den Brouw and W.H.Laarhoven, J.Chem.Soc.,Perkin Trans. II, 1983, 1015; ibid., 1982, 795; Recl.Trav.Chim.Pays-Bas, 1982, 101, 58; J.Org.Chem., 1982, 47, 1546.
5. P.M.op den Brouw, P.de Zeeuw, and W.H.Laarhoven, J.Photochem., 1984, 27, 327.
6. W.H.Laarhoven and Th.J.H.M.Cuppen, J.Photochem., 1986, 32, 105.
7. "Photochemistry of Heterocyclic Compounds", edited by O.Buchardt,John Wiley & Sons, Inc., New York, 1976.
8. The synthesis of β-heteroaryl-substituted o-divinylbenzenes will be published elsewhere.
9. U.Chiacchio, A.Compagnini, R.Grimaldi, G.Purrello, and A.Padwa, J.Chem.Soc. Perkin Trans I, 1983, 915.

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