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EXCLUSIVE CYCLIZATION AT SULFUR IN PHOTOLYSIS OF β-[(*o*-ARYLTHIO)PHENYL]VINYL BROMIDES

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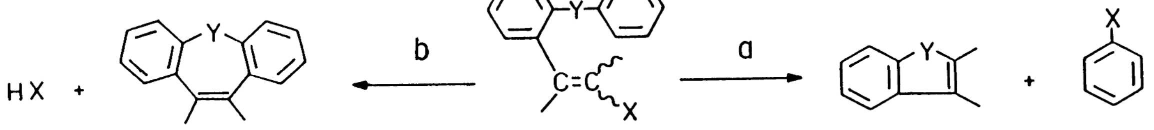
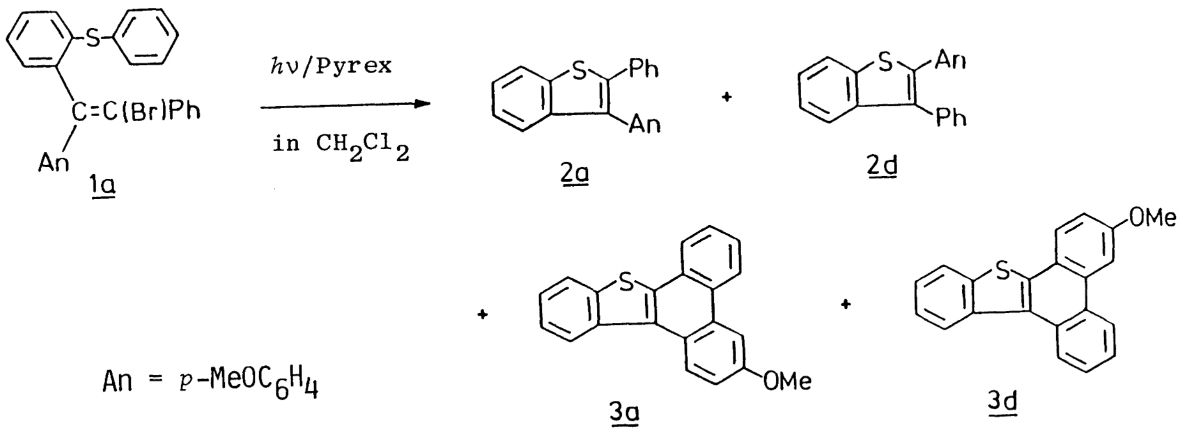
Photolysis of β-[(*o*-arylthio)phenyl]vinyl bromides, in contrast to the oxy-derivatives, resulted in exclusive cyclization at sulfur to give 1-benzothiophenes. The results were discussed by the nature of sulfur.

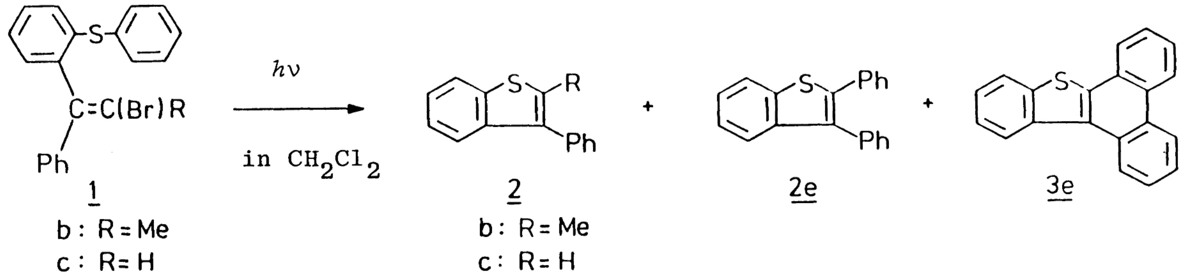
Intramolecular cyclization of vinyl cations is a convenient method for a direct synthesis of unsaturated cyclic compounds.1) In a previous paper,2) we reported that photolysis of β-[(*o*-aryloxy)phenyl]vinyl bromides afforded dibenz-[b,f]oxepins exclusively by cyclization at the aromatic ring of the aryloxyl group. In such vinyl halides possessing an *ortho*-arylhetero substituent, there are two likely modes of cyclization: (i) formation of 5-membered ring (path a) and (ii) formation of 7-membered ring (path b). When we examined the reaction of the thio-derivatives, β-[(*o*-arylthio)phenyl]vinyl bromides, in order to elucidate the factor determining the cyclization pathway, we found a remarkable difference in cyclization between the oxy- and thio-derivatives. Now we report an exclusive cyclization at a heteroatom (path a) from photolysis of β-[(*o*-arylthio)phenyl]vinyl bromides.



Irradiation of 1-phenyl-2-(*p*-methoxyphenyl)-2-[(*o*-phenylthio)phenyl]vinyl bromide (1a) (1 mmol) in dichloromethane (100 ml) was carried out under N_2 atmosphere at 10 °C for 2 h by use of a Pyrex-filtered high-pressure Hg lamp (100 W). The products isolated by column chromatography on alumina were 3-(*p*-methoxyphenyl)-2-phenyl-1-benzothiophene (2a)3) (30%), 2-(*p*-methoxyphenyl)-3-phenyl-1-benzothiophene (2d)3) (24%), 6-methoxyphenanthro[10,9-b][1]benzothiophene (3a)3) (8%), and 3-methoxyphenanthro[10,9-b][1]benzothiophene (3d)3) (8%), which can be divided into two types: (i) aryl-rearranged products 2d and 3d, and (ii) unrearranged ones 2a and 3a. Since no isomerization of 2a to 2d was observed under the photochemical conditions employed, the aryl rearrangement should take place across the double bond before cyclization. Such aryl rearrangements across the double bond are characteristic of vinyl cations.4) Therefore, it is reasonable to consider the intervention of vinyl cations 5 and 6 in this system and cyclization occurs in the vinyl cations 5 and 6.5)

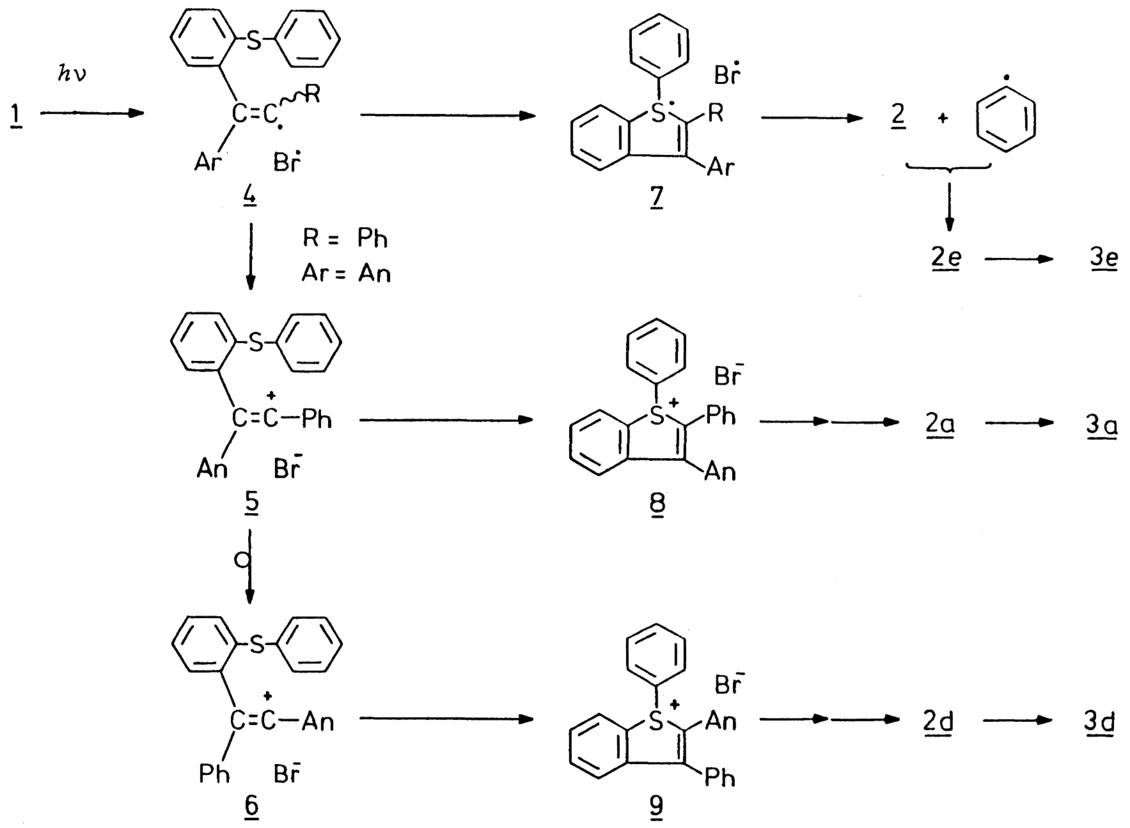


On the other hand, irradiation of 1-methyl-2-phenyl-2-[(*o*-phenylthio)phenyl]vinyl bromide (1b) without a Pyrex-filter for 2 h gave 2-methyl-3-phenyl-1-benzothiophene (2b)6) quantitatively. Similar irradiation of 2-phenyl-2-[(*o*-phenylthio)phenyl]vinyl bromide (1c) gave three kinds of products, 3-phenyl-1-benzothiophene (2c)7) (57%), 2,3-diphenyl-1-benzothiophene (2e)7) (12%), and phenanthro[9,10-b][1]benzothiophene (3e)9) (19%). Only in the photolysis of 1c,



recombination of phenyl radical and 2c took place to form 2e because of its steric preference and high reactivity of 2-position of 2c. The photolyses of 1b and 1c which have not afforded β-aryl rearranged products at all are reasonably explained by intramolecular cyclization of the resulting vinyl radical 4 from the following reasons. (i) 2-Arylvinyl radicals do not undergo 1,2-aryl rearrangement[10] which is observed necessarily in the cases of α-methyl and α-unsubstituted vinyl cation intermediates.[4] (ii) Sulfur atom can hold a valence expanded sulfranyl radical 7.[11] In addition, high reactivity of α-methyl and α-unsubstituted vinyl radicals 4 causes predominantly cyclization to sulfranyl radicals 7 before an electron transfer generating vinyl cations 5.

The above results reveal the dichotomy of the reaction pathway which strongly depends on α substituent: radical and ionic cyclization to 1-benzothiophenes 2. Both cases of vinyl radicals and vinyl cations, nevertheless, undergo cyclization at sulfur exclusively. This is attributed to the attracting nature of sulfur; (i) large size and close proximity to the reaction center, (ii) potential valence expansion, and (iii) high nucleophilicity to a cationic center.



References

1) T. Sonoda, M. Kawakami, T. Ikeda, S. Kobayashi, and H. Taniguchi, J. Chem. Soc., Chem. Commun., 1976, 612; T. Sonoda, S. Kobayashi, and H. Taniguchi, Bull. Chem. Soc. Jpn., 49, 2560 (1976); G. Capozzi, G. Melloni, and G. Modena, J. Chem. Soc., C, 1971, 3018; M. Hanack and R. Rieth, J. Chem. Soc., Chem. Commun., 1985, 1487, and references cited therein.

2) T. Kitamura, S. Kobayashi, and H. Taniguchi, Chem. Lett., 1984, 547.

3) 2a: mp 123-124 °C; NMR ($CDCl_3$) δ 3.83 (s, OMe) and 6.75-8.00 (m, ArH). 2d: mp 119-120 °C; NMR ($CDCl_3$) δ 3.75 (s, OMe) and 6.65-7.95 (m, ArH). 3a: mp 68-70 °C; NMR ($CDCl_3$) δ 3.91 (s, OMe) and 6.95-8.90 (m, ArH). 3d: mp 136-137 °C; NMR ($CDCl_3$) δ 3.97 (s, OMe) and 6.95-9.05 (m, ArH). These data were consistent with those of the authentic samples prepared independently.

4) P. J. Stang, Z. Rappoport, M. Hanack, and L. R. Subramanian, "Vinyl Cations," Academic Press, New York (1979).

5) The formation of 1-benzothiophenes 2 from the resulting sulfonium bromides 8 and 9 may proceed with the mechanism discussed in the photolysis of triarylsulfonium halides. See, J. W. Knapczyk and W. E. McEwen, J. Am. Chem. Soc., 91, 145 (1969); J. Org. Chem., 35, 2539 (1970).

6) T. S. Murthy and B. O. Tilak, J. Sci. Ind. Res. Sect. B, 19, 395 (1960); Chem. Abstr., 55, 11388c (1961).

7) O. Dann and M. Kobarudz, Chem. Ber., 91, 172 (1958).

8) G. Capozzi, G. Melloni, and G. Modena, J. Chem. Soc., C, 1970, 2621.

9) R. Wilputte and R. H. Martin, Bull. soc. chim. Belg., 65, 874 (1956); Chem. Abstr., 51, 6588h (1957).

10) Aryl rearrangement in 2-arylvinyl radicals has not been observed. See, J. K. Haynes, Jr., and J. A. Kampmeier, J. Org. Chem., 37, 4167 (1972).

11) P. Livant and J. C. Martin, J. Am. Chem. Soc., 98, 7851 (1976); W. Nakanishi, S. Koike, M. Inoue, Y. Ikeda, H. Iwamura, Y. Imahashi, H. Kihara, and M. Iwai, Tetrahedron Lett., 1977, 81; R. Leardini, G. F. Pedulli, A. Tundo, and G. Zanardi, J. Chem. Soc., Chem. Commun., 1985, 1390.

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