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FORMATION OF DIBENZ[b,f]OXEPINS FROM β-(*o*-ARYLOXYPHENYL)VINYL BROMIDES

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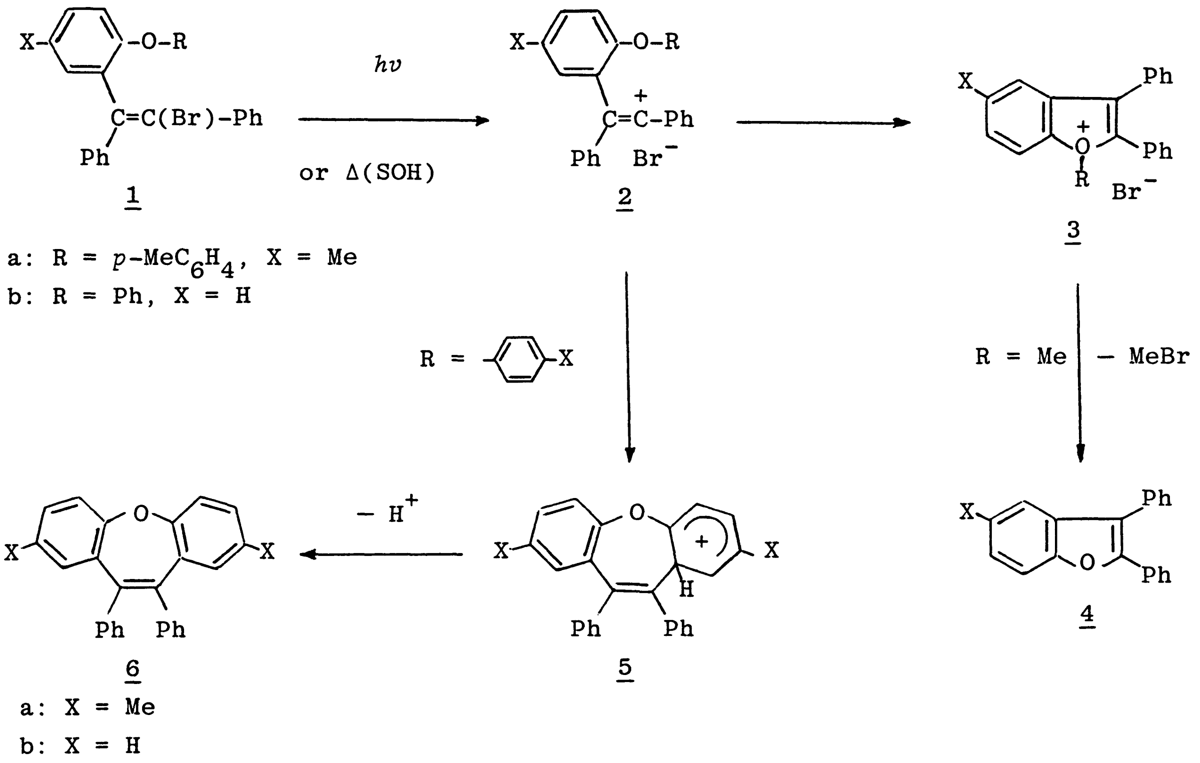
Photolysis of β-(*o*-aryloxyphenyl)vinyl bromides in methylene chloride as well as solvolysis in 60% EtOH gave dibenz[b,f]oxepins exclusively by a new type of intramolecular cyclization of vinyl cations.

Recent intensive studies on solvolysis and photolysis of vinyl halides made clear the intervention of vinyl cations.¹⁾ When the β aryl group of the vinyl halide 1 has methoxyl group at the ortho position (R = Me), vinyl cation 2 is exclusively trapped by the methoxyl group, followed by release of methyl group to produce benzofuran derivative 4.²⁾ When the reaction was extended to aryloxy-substituted vinyl halide (1, R = Ar), both photolysis and solvolysis of the vinyl bromide 1 (R = Ar) resulted in exclusive formation of the dibenz[b,f]oxepin 6. We describe here these reactions, hoping that these reactions are useful for a new synthetic method of the oxepins.



Irradiation of β-(*o*-aryloxyphenyl)vinyl bromide 1a (0.26 mmol) in methylene chloride (7 ml) containing pyridine (0.03 ml) was carried out by use of a Pyrex-filtered high-pressure mercury lamp (400 W) for 2 h at 15 °C under nitrogen atmosphere. Evaporation of the solvent gave white crystals, mp 184-185 °C, and were confirmed as 2,8-dimethyl-10,11-diphenyldibenz[b,f]oxepin (6a) by the analytical data,3) showing that 2a was formed quantitatively. Similar irradiation of 1b gave 10,11-diphenyldibenz[b,f]oxepin (6b),3) mp 208-209 °C, quantitatively. These results indicate that photolysis of β-(*o*-aryloxyphenyl)vinyl bromides 1 (R = Ar) leads to exclusive intramolecular cyclization to give dibenz[b,f]oxepins 2.

Solvolysis of 1a was conducted. A solution of 60% EtOH (15 ml) containing 1a (0.30 mmol) and sodium hydroxide (3.0 mmol) was heated in a sealed tube at 160 °C for 48 h. Workup of the reaction mixture afforded 6a as the sole product accompanied with the starting material (conversion 45%).

It is well established that vinyl cations are generated under the solvolytic conditions employed above.1) Therefore, the following mechanism involving vinyl cation 2 is proposed with respect to the formation of dibenz[b,f]oxepin 6. The vinyl cation 24) can attack the oxygen atom or the ortho position of the aryloxyl group. The latter intramolecular electrophilic substitution should be preferred by activation of the aryloxyl group and a steric demand. Conversely, even if the onium ion 3 was formed similarly to the case of β-(*o*-methoxyphenyl)vinyl bromides,2) the difficulty of dearylation would not cause the benzofuran formation. In connection with photolysis of β-(*o*-methoxyphenyl)vinyl bromides,2) it is presumed that vinyl cation 2 is also involved in this photochemical formation of dibenz[b,f]-oxepin 6.

Consequently, the new type of the intramolecular cyclization of vinyl cation 2 to afford dibenz[b,f]oxepin 6 will be applicapable for synthesis of dibenz[b,f]-oxepin derivatives because of the high selectivity and easy operation. Further investigation on the scope is now in progress.

References

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3) 6a: ^{1}H-NMR δ($CDCl_3$) 2.13 (s, Me) and 6.80-7.25 (m, ArH); ^{13}C-NMR δ($CDCl_3$) 20.81, 120.14, 126.23, 127.40, 130.03, 130.52, 130.81, 132.42, 133.78, 139.49, 141.68, and 156.79; MS m/e (rel %) 375 (M^{+}+1, 31), 374 (M^{+}, 100), and 297 (M^{+}-Ph, 32). 6b: ^{1}H-NMR δ($CDCl_3$) 6.90-7.41 (m, ArH); ^{13}C-NMR δ($CDCl_3$) 120.72, 124.62, 126.47, 127.59, 129.49, 130.66, 130.76, 133.00, 139.68, 141.73, and 158.74; MS m/e (rel %) 347 (M^{+}+1, 14), 346 (M^{+}, 50), 269 (M^{+}-Ph, 100), and 258 (61).

4) For formation of vinyl cations by photolysis of vinyl halides: T. Suzuki, T. Sonoda, S. Kobayashi, and H. Taniguchi, J. Chem. Soc., Chem. Commun., 1976, 180; S. A. McNeely and P. J. Kropp, J. Am. Chem. Soc., 98, 4319 (1976); B. Sket and M. Zupan, J. Chem. Soc., Perkin Trans. 1, 1979, 752; S. Kobayashi, T. Kitamura, H. Taniguchi, and W. Schnabel, Chem. Lett., 1983, 1117 and references cited therein.

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