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Photolysis of β-(o-Methylthiophenyl)vinyl Bromides. A Versatile Synthesis of Benzo[b]thiophens

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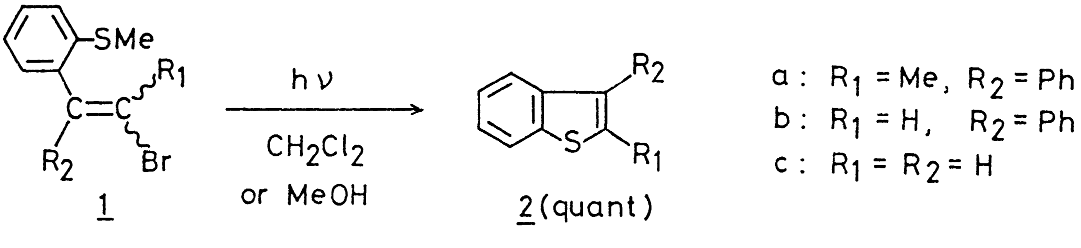
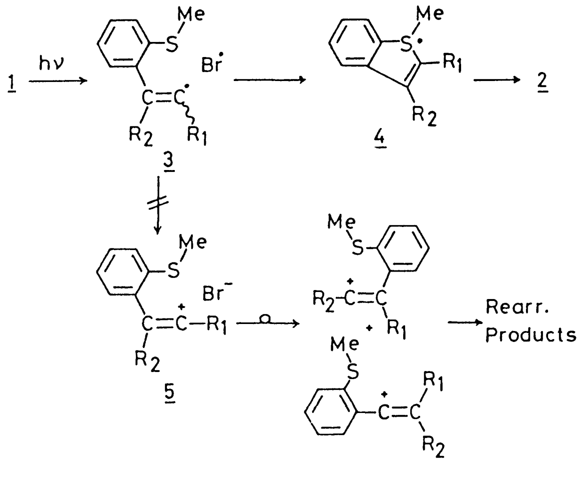
Exclusive cyclization in photolysis of β-(o-methylthiophenyl)-vinyl bromides to give benzo[b]thiophens is described.

Intramolecular cyclization is one of most useful methods for preparation of heterocyclic compounds.1) Previously we reported briefly photolysis of β,β-diarylvinyl bromides.2) In that communication, the vinyl bromide bearing ortho-methylthiophenyl group at the β position gave substituted benzo[b]thiophen, in contrast to other diarylvinyl bromides which underwent 1,2-aryl shift across the double bond to give tolans. We felt that the method might be useful for synthesis of benzo[b]thiophens and conducted photolysis of β-(o-methylthiophenyl)vinyl bromides. Now we report here that photolysis of β-(o-methylthiophenyl)vinyl bromides is useful for synthesis of benzo[b]thiophens.

The starting vinyl bromides 1 3) were easily prepared either by bromination of the corresponding olefins in carbon tetrachloride at 0 °C or by treating o-methylthiocinnamic acid dibromide with aqueous potassium acetate, in 50-90% yields. A methylene chloride solution of 2-bromo-1-(o-methylthiophenyl)-1-phenylpropene (1a) contained in a Quartz tube was irradiated by a high-pressure Hg lamp (100 W) at 20 °C under nitrogen atmosphere for 1.5 h. After evaporation of the solvent, ^{1}H NMR showed quantitative formation of 2-methyl-3-phenylbenzo[b]thiophen (2a),4) which was purified either by column chromatography on alumina or by Kugel Rohr distillation. Similar irradiation of 1a in methanol gave the same 2a as above quantitatively. Other examples of exclusive cyclization to benzo[b]thiophens 2b 5) and 2c 6) were obtained in photolysis of 1-bromo-2-(o-methylthiophenyl)-2-phenylethylene (1b) and 1-bromo-2-(o-methylthiophenyl)-ethylene (1c) in methylene chloride (quantitative yields by ^{1}H NMR or GC).





Previously we have discussed on photolysis of β-(o-methoxyphenyl)vinyl bromides where vinyl cations are generated from vinyl radicals and cyclize to benzofurans.$^{7)}$ When the α substituent is a hydrogen or a methyl group, β-aryl rearranged benzofurans are formed (50-85% of the products). In this study, no β-aryl rearrangement was observed.$^{8)}$ Therefore, it is considered that the cyclization to 2 occurs at the vinyl radical 3 before an electron transfer giving vinyl cation 5 because sulfur atom can hold a valence expanded sulphuranyl radical 4.$^{9)}$ Finally collapse of 4 leads to benzo[b]thiophen 2.

In summary, we have developed a simple and versatile method for preparation of benzo[b]thiophens from β-(o-methylthiophenyl)vinyl bromides. We expect this procedure to be of considerable synthetic utility.

References

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3) 1a (1:1 mixture of E and Z isomers) δ (CCl_4) 2.17 (s, Me), 2.25 (s, Me), 2.39 (s, 2MeS), 6.87-7.75 (m, ArH); 1b (3:2 mixture of E and Z isomers) δ (CCl_4) 2.24 (s, MeS), 2.27 (s, MeS), 6.47 (s, =CH), 6.84 (s, =CH), 7.03-7.41 (m, ArH); 1c δ (CCl_4) 2.30 (s, MeS), 6.40 (d, J = 13 Hz, =CH), 6.76-7.09 (m, ArH), 7.28 (d, J = 13 Hz, =CH).

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