

Photochemistry of Vinyl Bromides: a Novel 1,2-Aryl Group Migration

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Summary Irradiation of 2,2-di-*p*-, *m*-, and *o*-anisylvinyl bromides (**1a—c**) gave mainly *p,p'*-, *m,m'*-, and *o,o'*-dimethoxytolans (**2a—c**) respectively, by a 1,2-shift of the anisyl groups.

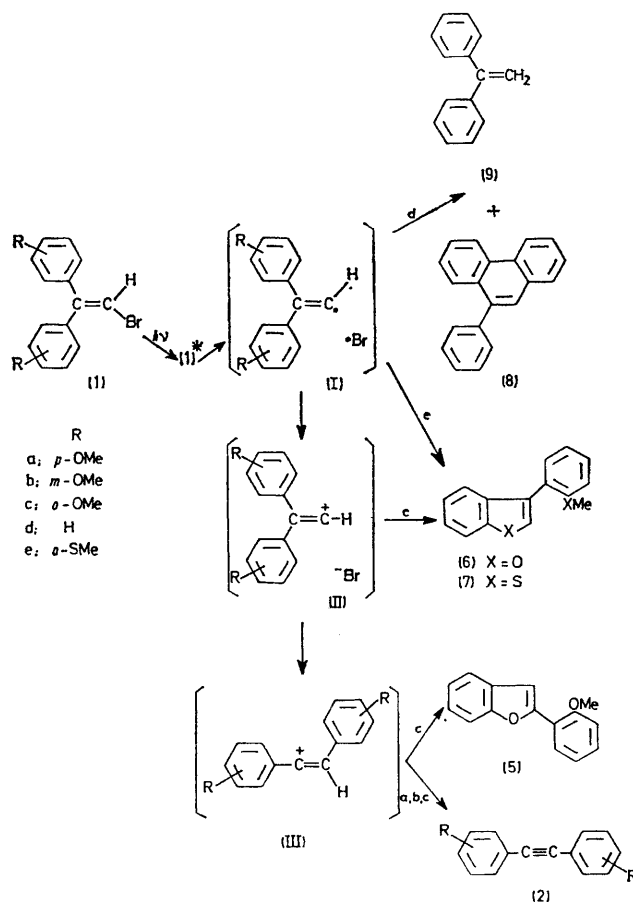
We report that a novel photochemical 1,2-anisyl group migration is observed on irradiation of 2,2-dianisylvinyl bromides (**1a—c**).

Irradiation of (**1a—d**) was carried out in benzene solution (5×10^{-2} M) with a 100 W high-pressure mercury lamp for 4 h under nitrogen atmosphere at 10 °C. The photoproducts of (**1a—c**) were mainly the corresponding tolans (**2a—c**) in yields of 53, 86, and 50%, respectively.†

Irradiation of (**1a**) gave 1,2-dibromo-1,2-di-*p*-anisylethylene (**3**) as a by-product (20%), but in the presence of zinc powder (10 mol equiv.) only (**2a**) was formed (67%). When acetic acid¹ was used as solvent instead of benzene, the 1,2-shift product (**2a**) was again formed, but in tetrahydrofuran a hydrogen abstraction compound, 1,1-di-*p*-anisylethylene (**4**), was the major product and (**2a**) was not detected.

In the case of (**1c**), 2- and 3-*o*-anisylbenzofurans (**5**) and (**6**) were also obtained (14 and 30%). The intramolecular cyclization to (**6**) is characteristic of (**1c**), and is analogous to that of 1-aryl-2,2-di-*o*-anisylvinyl bromides in both solvolysis and photolysis.² Similar selective cyclization to 3-*o*-thioanisylbenzothiophene (**7**) was observed when 2,2-di-*o*-thioanisylvinyl bromide (**1e**) was irradiated for only 2 h.

In contrast to (**1a—c**), irradiation of 2,2-diphenylvinyl bromide (**1d**) in benzene did not afford the corresponding tolan, but gave a mixture of 9-phenylphenanthrene (**8**) and 1,1-diphenylethylene (**9**) (40 and 13% respectively) as a result of a radical reaction *via* the intermediate (I). In the cases of (**1a—c**) the intermediate vinyl cation (II) could form through electron transfer in the electron-rich (I), followed by 1,2-anisyl migration to give the more stable intermediate (III).



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† All photoproducts were identified by comparison with authentic samples, and the conversions of (**1a—d**) were 85, 70, 84, and 75%, respectively. Besides (**2a—c**), 1,1-di-*p*-, *m*-, and *o*-anisylethylene were also detected by n.m.r. spectroscopy (trace, 8%, and trace, respectively).

¹ W. Tadros, A. B. Sakla, and Y. Akhooch, *J. Chem. Soc.*, 1956, 2701 [they found that exposure of (**1a**) in acetic acid to sunlight gave 1,1,4,4-tetra-*p*-anisylbutadiene].

² H. Taniguchi, unpublished results.