Photocyclisation of *o*-Methoxystilbenes to Phenanthrenes with Loss of the Methoxy-group

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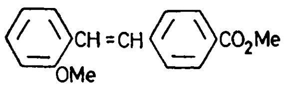
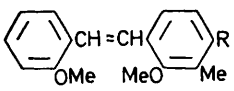
Summary *o*-Methoxystilbenes undergo photocyclisation under non-oxidative conditions to yield phenanthrenes by loss of the methoxy-group.

KANAOKA and ITOH recently reported that *o*-methoxybenzanilides undergo photocyclisation to phenanthridones with loss of methanol.[1] These authors suggested that this photocyclisation with expulsion of a methoxy-group may be characteristic of the anilide system. In contrast, our earlier work on the photocyclisation of *o*-methoxyphenyl phenyl ethers to dibenzofurans,[2] and our present work on *o*-methoxystilbenes demonstrates the generality of this reaction.

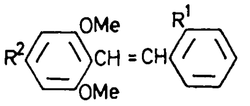
During our work on the synthesis of piloquinone[3] we observed that u.v. irradiation through Pyrex of cyclohexane solutions of the stilbenes (**1**)—(**3**) in presence of air and iodine gave appreciable yields of the phenanthrenes (**4**)—(**6**) as well as the expected products (**7**)—(**9**).



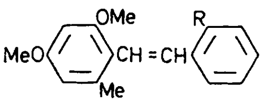
(1)



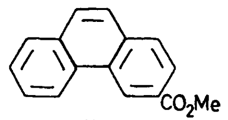
(2) R = CO_2Me
(3) R = CN



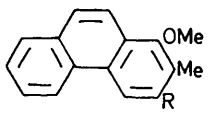
(10) $R^1 = R^2 = H$
(11) $R^1 = OMe, R^2 = H$
(12) $R^1 = H, R^2 = OMe$
(13) $R^1 = R^2 = OMe$



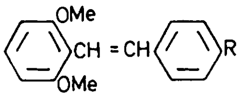
(14) R = H
(15) R = OMe



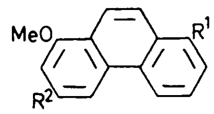
(4)



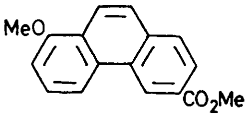
(5) R = CO_2Me
(6) R = CN



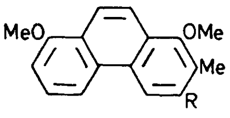
(16) R = Cl
(17) R = CO_2Me
(18) R = $CHMe_2$



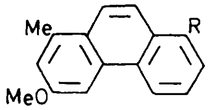
(19) $R^1 = R^2 = H$
(20) $R^1 = OMe, R^2 = H$
(21) $R^1 = H, R^2 = OMe$
(22) $R^1 = R^2 = OMe$



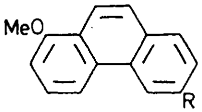
(7)



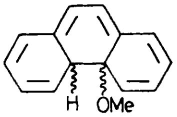
(8) R = CO_2Me
(9) R = CN



(23) R = H
(24) R = OMe



(25) R = Cl
(26) R = CO_2Me
(27) R = $CHMe_2$



(28)

Wood and Mallory[4] reported that u.v. irradiation of *o*-methoxystilbene under oxidative conditions gave a detectable amount of phenanthrene which however, could not be isolated, the major product (46%) being 1-methoxyphenanthrene. When we repeated this experiment by u.v. irradiation (30 h) of *o*-methoxystilbene in deoxygenated cyclohexane under nitrogen then the major product (58%) was phenanthrene.

TABLE

Substrate	Time of irradiation (h)	Product	Yield(%)
(10)	9	**(19)**	90
(11)	15	**(20)**	91
(12)	48	**(21)**	85
(13)	39	**(22)**	74[a]
(14)	55	**(23)**	38[a]
(15)	42·5	**(24)**	63[a]
(16)	11	**(25)**	56
(17)	46·5	**(26)**	48[a]
(18)	14	**(27)**	87

[a] Yield based on unrecovered starting material.

U.v. irradiation through silica of the stilbenes (**10**)—(**18**) in deoxygenated cyclohexane under nitrogen gave the phenanthrenes (**19**)—(**27**) respectively, generally in good yield (see Table). In the cases of stilbenes (**14**) and (**15**) ring closure occurred solely by elimination of a methoxy-group and none of the alternative products formed by elimination of a methyl group could be detected. In certain cases the cyclisation in low yield of *o*-methylstilbenes with expulsion of the methyl group had been reported.[5]

Since the reactions reported in the Table were observed under non-oxidative conditions a mechanism similar to that proposed by Kanaoka and Itoh,[1] in which loss of methanol from a dihydrophenanthrene intermediate (**28**) occurs, is indicated.

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[1] Y. Kanaoka and K. Itoh, *J.C.S. Chem. Comm.*, 1973, 647.
[2] J. A. Elix, D. P. H. Murphy, and M. V. Sargent, *Synthetic Comm.*, 1972, **2**, 427.
[3] T. M. Cresp, R. G. F. Giles, and M. V. Sargent, *J.C.S. Chem. Comm.*, 1974, 11.
[4] C. S. Wood and F. B. Mallory, *J. Org. Chem.*, 1964, **29**, 3373.
[5] See E. V. Blackburn, C. E. Loader, and C. J. Timmons, *J. Chem. Soc.* (*C*), 1970, 163.