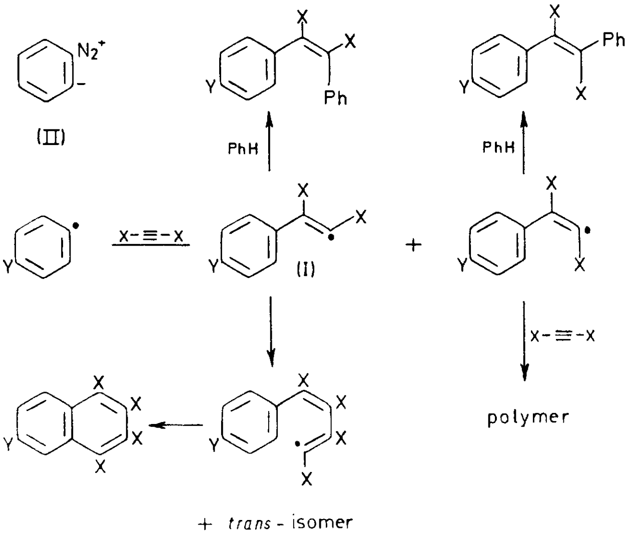
A New Aromatic Annelation Process: Reaction of Aryl Radicals with Dimethyl Acetylenedicarboxylate

By B. D. BAIGRIE, J. I. G. CADOGAN,* J. COOK, and J. T. SHARP
(*Department of Chemistry, University of Edinburgh, West Mains Road, Edinburgh* EH9 3JJ)

Summary An easily effected aromatic annelation is described, involving reaction of an aryl radical with two molecules of dimethyl acetylenedicarboxylate to give 1,2,3,4-tetramethoxycarbonylnaphthalenes.



SCHEME. X = CO_2Me, Y = H, Br, Me.

AROMATIC annelation reactions are rare. We now report a simple method whereby aryl radicals, generated from diaroyl peroxides, in the presence of dimethyl acetylenedicarboxylate give the corresponding 1,2,3,4-tetramethoxycarbonylnaphthalenes.† Thus, the reaction of dibenzoyl peroxide (1 mol) with dimethyl acetylenedicarboxylate (10 mol) at 80° gave 1,2,3,4-tetramethoxycarbonylnapthalene (0·5 mol/mol peroxide). Similarly *p*-methyl- and *p*-bromo-benzoyl peroxides gave 6-methyl- and 6-bromo-1,2,3,4-tetramethoxycarbonylnaphthalenes, but in lower yields (0·2 mol/mol peroxide). We present evidence here that the reaction proceeds as in the Scheme *via* addition of an aryl radical to the acetylene followed by further addition of the first formed substituted styryl radical to another molecule of the acetylene with subsequent cyclisation. It follows that aryl radicals are involved because different sources of phenyl radicals (*N*-nitrosoacetanilide or acetanilide–pentyl nitrite) also give 1,2,3,4-tetramethoxycarbonylnaphthalene. Further, dilution of the reaction mixture by benzene leads, not only to the naphthalene derivative, but to a mixture (15%) of dimethyl 1,2-diphenyl-maleate and -fumarate, indicating interception by benzene of the first formed 1,2-dimethoxycarbonylstyryl radical (I), in both its *cis* and *trans* forms. In this connection it is noteworthy that the yield of 1,2,3,4-tetramethoxycarbonylnaphthalene (0·5 mol) from the experiment in neat dimethyl acetylenedicarboxylate is that theoretically possible assuming equal chance of formation of *cis*- and *trans*-styryl or phenylbutadienyl radicals in each step of the reaction. The concept of radical participation is also supported by the observation that *m*-bromobenzoyl peroxide gives a mixture (0·2 mol/mol peroxide) of 5- and 6-bromo-1,2,3,4-tetramethoxycarbonylnaphthalene in the ratio of 2·7: 1, showing that intramolecular attack takes place more readily *ortho* rather than *para* to the bromo-substituent, it being well known that radical substitution in bromobenzene occurs more readily in the *o*-rather than the *p*-position.[1] The evidence now obtained in favour of

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† All compounds had correct analyses, mass and/or n.m.r. spectroscopic data.

radical participation rules out the possibility, tentatively advanced previously,[2] of reaction of a polar intermediate (II) with dimethyl acetylenedicarboxylate.

This novel reaction of aryl radicals with dimethylacetylenedicarboxylate, proceeding *via* intramolecular cyclisation appears to be capable of considerable extension, now being evaluated, *via* the use of heterocyclic, polycyclic, and other aryl radicals and/or other acetylenic derivatives.

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[1] G. H. Williams, 'Homolytic Aromatic Substitution,' Pergamon Press, Oxford, 1961.

[2] J. I. G. Cadogan, *Accounts Chem. Res.*, 1971, **4**, 186.