

Intramolecular Arylation

By MARCELLO TIECCO

(Istituto di Chimica Organica e di Chimica Industriale, Bologna, Italy)

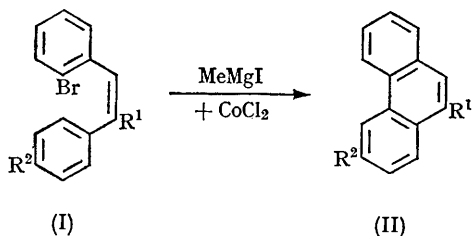
THE transition-metal halide-catalyzed reaction of Grignard reagents with organic halides was discovered by Kharasch and his collaborators.¹

In a recent investigation² in which methylmagnesium iodide, cobaltous chloride, and phenyl halides were allowed to react in the presence of

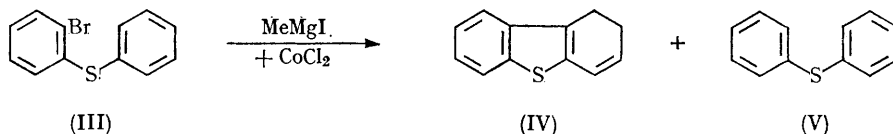
¹ M. S. Kharasch and E. K. Fields, *J. Amer. Chem. Soc.*, 1941, **63**, 2316.

² D. I. Davies, D. H. Hey, and M. Tiecco, *J. Chem. Soc.*, in the press.

aromatic solvents, products formed by substitution in the solvent by phenyl radicals derived from the phenyl halides were obtained. This method has now been successfully applied to intramolecular arylation. Thus, the addition of an ethereal



- (A) $R^1 = R^2 = H$ (B) $R^1 = H, R^2 = Me$
 (C) $R^1 = H, R^2 = OMe$ (D) $R^1 = Ph, R^2 = H$



solution of methylmagnesium iodide to a suspension of cobaltous chloride in an ethereal solution of 2-bromo-*cis*-stilbene³ (IA) afforded phenanthrene

(IIA) in 75% yield. Similarly 2-bromo-4'-methyl-*cis*-stilbene b.p. 151—152°/3mm. (IB) and 2-bromo-4'-methoxy-*cis*-stilbene b.p. 146—147°/3mm. (IC) gave respectively 3-methylphenanthrene (IIB) and 3-methoxyphenanthrene (IIC) in yields of 78 and 85%. 1,1-Diphenyl-2-*o*-bromophenylethylene m.p. 60—62° (ID) afforded 9-phenylphenanthrene (IID) in 75% yield.

The reaction with phenyl *o*-bromophenyl sulphide (III) as halide gave dibenzothiophen (IV) in 10% yield, but the major product (60%) was diphenyl sulphide (V) resulting from the dehalogenation of (III). All products were identified by a comparison with authentic specimens^{4,5,6} and their picrates.^{5,6,7}

The reactions are interpreted as proceeding *via* the homolytic fission of the carbon-halogen bond to give a free radical which can then react in an intramolecular substitution reaction. The

generality of this reaction is being further investigated.

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³ D. F. deTar and L. A. Carpino, *J. Amer. Chem. Soc.*, 1956, **78**, 475.

⁴ C. S. Wood and F. B. Mallory, *J. Org. Chem.*, 1964, **29**, 3373.

⁵ R. Pschorr, *Ber.*, 1901, **34**, 3998.

⁶ K. Bradsher and A. K. Schneider, *J. Amer. Chem. Soc.*, 1938, **60**, 2960.

⁷ R. D. Haworth, *J. Chem. Soc.*, 1932, 1125.