Influence of Substituent Groups on Nuclear Reactivity in Formation of Substituted Biphenyls through Reactions of Aromatic Diazo and Cognate Compounds with Aromatic Liquids. IV[1]. *The Methyl Group*

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In a paper, which has very recently become available, Hey, Pengilly and Williams[2] reported partial rate factors for the phenylation of toluene by phenyl radicals generated from benzoyl peroxide at 80°. This prompts us to publish the results of our study which we have been carrying out on a similar subject. Our experimental methods were different from those of the British workers in that our source of the phenyl radical was N-nitrosoacetanilide and that the competition between toluene and benzene for the radical generated was investigated.

N-Nitrosoacetanilide (6.7 g., 40.8 millimoles) was dissolved in a mixture of 225 cc. of benzene and 271 cc. of toluene (both 2.55 moles) at 21°; the decomposition of the nitroso compound set in immediately evolving nitrogen. After a few days, when the reaction had been completed, the reaction mixture was washed successively with aqueous sodium hydrogen carbonate, 10% sodium hydroxide, dilute hydrochloric acid and water. The solvent was then removed from the solution dried with calcium chloride by distillation through a Vigreux column 30 cm. in length. The residue was subjected to steam distillation, and the distillate, combined with the residue from the redistillation of the solvent recovered mentioned above, was fractionally distilled under reduced pressure, giving a small amount of toluene and then a fraction (I, 1.891 g.) boiling at 122–135° at 20 mmHg which consisted of biphenyl and methylbiphenyls. The residue (30 mg.) was almost pure *p*-methylbiphenyl, m.p. 46–48°. The fore- and after-runs of fraction I, which were combined together, amounted to 0.326 g. (fraction II). The compositions of fractions I and

II as determined by infra-red spectrophotometry were found to be as follows:

Fraction	Methylbiphenyls (%)			Biphenyl (%)
	o	*m*	*p*	
I	51	9.2	4.1	37
II	31	25	15	28

Thus, the total quantities of *o*-, *m*- and *p*-methylbiphenyls and biphenyl itself amounted to 1.053, 0.255, 0.156 and 0.782 g., respectively; and consequently the ratio of the isomeric methylbiphenyls was $o:m:p=72:17.4:10.6$[3]. From these data, the relative reactivities of the ortho, meta and para positions of toluene are calculated to be 3.7, 0.9 and 1.1, respectively, the reactivity of one nuclear position of benzene itself being taken as unity. These values are to be compared with those found by Hey and his collaborators, i.e., 4.1, 1.0 and 1.4. The general agreement between the two sets of values is of interest in view of the difference in experimental methods.

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1) Part III, O. Simamura and T. Migita, This Bulletin, 27, 228 (1954).

2) D. H. Hey, B. W. Pengilly and G. H. Williams, *J. Chem. Soc.*, **1955**, 6.

3) Note added in proof—After the submission of this communication two papers by R.L. Dannley and B. Zaremsky *J. Am. Cnem. Soc.*, 77, 1588 (1955), and by C.S. Rondestvedt and H.S. Blanchard, ibid., 1769, came to our attention. The former reported the isomer composition of methylbiphenyls obtained by phenylation of toluene by the decomposition of benzoyl peroxide to be $o:m:p=65:19:16$; and the latter gave very similar values, $o:m:p=62:20:18$, for phenylation by nitrosoacetanilide.

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