A Remark on the Unsuitable Use of Nitrobenzene as a Standard Substrate for Homolytic Aromatic Substitution

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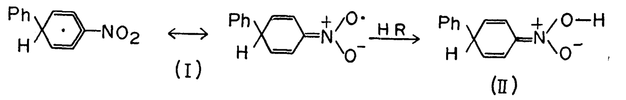
(Received August 2, 1971)

In homolytic aromatic substitution,1) reactivities of various aromatic substrates are often determined relative to nitrobenzene1a,1b,2) or benzene3) as a standard substrate. We now wish to report that the apparent reactivity of nitrobenzene towards phenyl radicals appreciably changes in the presence of substances carrying transferrable hydrogen atoms such as toluene, ethylbenzene or cyclohexane, showing that nitrobenzene cannot be generally used as a standard substrate for homolytic substitution.

In a mixture of substrates, either phenylhydrazine was treated with nickel peroxide at room temperature4) or benzoyl peroxide was decomposed at 80°C under nitrogen to generate phenyl radicals and the resulting biaryls were determined by gas chromatography. Whereas the reaction employing phenylhydrazine in nitrobenzene or in toluene gave *o*-, *m*-, and *p*-nitrobiphenyl in a distribution of 58, 7, and 35% or *o*-, *m*-, and *p*-methylbiphenyl in 68, 19, and 13%, respectively,4) the reaction in a mixture of nitrobenzene and toluene led to a variation in distribution of *o*-, *m*-, and *p*-nitrobiphenyl to 73, 9, and 18% without affecting the distribution of methylbiphenyl isomers. The apparent relative reactivity of toluene to nitrobenzene, $k_{\mathrm{PhMe}}/k_{\mathrm{PhNO_2}}$, is 0.69. This is higher than the expected value of 0.33 estimated from the ratio of the reactivities, relative to benzene,3) of toluene ($k_{\mathrm{PhMe}}/k_{\mathrm{PhH}}$, 1.68) and nitrobenzene ($k_{\mathrm{PhNO_2}}/k_{\mathrm{PhH}}$, 5.02). The use of benzoyl peroxide as a phenylating source similarly changed the reactivity of nitrobenzene. The value of $k_{\mathrm{PhMe}}/k_{\mathrm{PhNO_2}}$ is 1.1, distribution of *o*-, *m*-, and *p*-nitrobiphenyl being 71, 11, and 18%, respectively, and that of *o*-, *m*-, and *p*-methylbiphenyl, 63, 22, and 15%, respectively. Likewise, the reactivity of nitrobenzene changed in its mixture with ethylbenzene or cyclohexane.5)

In order to determine the apparent reactivity, relative to benzene, of nitrobenzene in the presence of toluene, phenylation employing phenylhydrazine was carried out in a ternary mixture of nitrobenzene, toluene, and benzene to show, for nitrobenzene, $k_{\mathrm{PhNO_2}}/k_{\mathrm{PhH}}$ to be 2.1_1 and partial rate factors, f_o, f_m, and f_p to be 5.1_6, 0.30, and 1.7_5, respectively, and, for toluene, $k_{\mathrm{PhMe}}/k_{\mathrm{PhH}}$, f_o, f_m, and f_p to be 1.5_3, 3.0_4, 0.86, and 1.3_6, respectively. On the other hand, phenylation of a binary mixture of nitrobenzene or toluene with benzene was reported to give, concerning nitrobenzene, 5.02, 9.32, 1.16, and 9.05 for $k_{\mathrm{PhNO_2}}/k_{\mathrm{PhH}}$, f_o, f_m, and f_p and, concerning toluene, 1.68, 3.30, 1.09, and 1.27 for $k_{\mathrm{PhMe}}/k_{\mathrm{PhH}}$, f_o, f_m, and f_p, respectively.3,6) These results clearly indicate that the presence of toluene, without variation of its reactivity, lowered the apparent reactivity of nitrobenzene, the depression of the partial rate factor of which was the most remarkable for para-position of the nitro group and the least for the ortho-position.

The anomalous behaviour of nitrobenzene could be understood by assuming that nitrophenylcyclohexadienyl radicals resulting from the addition of phenyl radicals to nitrobenzene would, at the expense of transferring their hydrogen atoms to give nitrobiphenyl, abstract hydrogen atoms from a hydrogen donor on their nitro group, as proposed for photo-excited nitrobenzene.7) Then a precursory radical of *p*-nitrobiphenyl (I) would undergo abstraction to give II more easily than an isomeric radical precursory of *o*-nitrobiphenyl, in which the reactive center might be sterically hindered by the adjacent phenyl group, leading to higher reduction in the yield of *p*-nitrobiphenyl than *o*-isomer. The resulting compound, II or its isomer, subsequently might undergo either dehydration to give nitroso compound which can scavange free radicals8) without finally producing nitrobiphenyl, or dehydrogenation to nitrobiphenyl or other reactions.



(I) (II)

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1) As a general reference for homolytic aromatic substitution, see, for example: a) G. H. Williams, "Homolytic Aromatic Substitution," Pergamon Press, Oxford (1960). b) D. H. Hey, in G. H. Williams, ed., "Advances in Free-radical Chemistry," Vol. II, Logos Press, London (1967), p. 47. c) O. Simamura, T. Migita, N. Inamoto, and K. Tokumaru, "Yuriki Hanno," Tokyo Kagaku Dozin, Tokyo (1969), Chapter 11.

2) For example, D. H. Hey, S. Orman, and G. H. Williams, *J. Chem. Soc.*, **1961**, 565.

3) R. Ito, T. Migita, N. Morikawa, and O. Simamura, *Tetrahedron*, **21**, 955 (1965).

4) H. Ohta and K. Tokumaru, This Bulletin, in press.

5) It is to be noticed that decomposition of benzoyl peroxide in a mixture of equal volumes of nitrobenzene and cyclohexane gave cyclohexanol (3% based on the peroxide) and cyclohexanone (1%), both of which were not formed from decomposition in cyclohexane carried out alone in a degassed ampoule. It is also worth mentioning that Prof. T. Migita and his coworkers showed that decomposition of *t*-butyl peroxide in a mixture of toluene and nitrobenzene gave benzoic acid and *t*-butanol in a remarkable yield (private communication).

6) Phenylation using phenylhydrazine and nickel peroxide was found to give similar values to those obtained from phenylation using *N*-nitrosoacetanilide at 20°C.3)

7) J. W. Weller and G. A. Hamilton, *Chem. Commun.*, **1970**, 1390.

8) G. R. Chalfont, D. H. Hey, K. S. Y. Liang, and M. J. Perkins, *J. Chem. Soc.*, *B*, **1971**, 233.