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Phenylation with Phenyl Radical Generated from Phenylazotriphenylmethane

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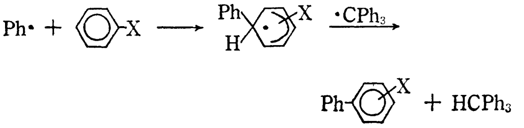
Phenylazotriphenylmethane was decomposed in substituted benzenes, and orientations and partial rate factors for phenylation were determined.

Phenylazotriphenylmethane (PAT) decomposes on heating with evolution of nitrogen to yield phenyl radical and triphenylmethyl radical.[1] Though many investigations have been performed on the reactions of phenyl radicals produced from PAT,[2] no systematic ones on the orientations and the partial rate factors for phenylation by means of PAT have been reported except for a few reports involving limited numbers of substrates.[3] It has long been known that substituted biphenyls are produced when phenyl radical is generated in substituted benzenes,[4] but the details of the mechanism of this homolytic substitution have not been completely clarified yet. Although the absence of kinetic hydrogen isotope effect has been reported for phenylation with *N*-nitrosoacetanilide in contrast with the phenylation by benzoyl peroxide, it has recently been found that kinetic hydrogen isotope effect is observable in the phenylation with phenyl radical produced from benzenediazonium tetrafluoroborate-sodium nitrite, and the importance of the role of a hydrogen abstractor has been pointed out.[5] In view of these findings, it seemed highly desirable to carry out a systematic investigation on phenylation with PAT and to determine whether or not orientations and partial rate factors are different from those of other phenyl radical sources due to the difference in hydrogen abstractors. Such investigation has been performed, and the results will be described in this paper.

$$\text{Ph-N=N-CPh}_3 \rightarrow \text{Ph}\cdot + \text{N}_2 + \cdot\text{CPh}_3$$



Experimental

Benzene and substituted benzenes were purified by the methods described in a previous paper.[6] Ethylbenzene was purified by distillation, bp 131—134°C. The purity of all the aromatic solvents were checked by a Hitachi Gas Chromatograph K53.

Phenylazotriphenylmethane was prepared by the bromine-water oxidation of phenylhydrazotriphenylmethane,[7] which was synthesized from the reaction between phenylhydrazine and triphenylmethyl chloride[8] in ether. Crude PAT was recrystallized from benzene-ethanol, mp 111—112°C (decomp.).

Authentic samples of substituted biphenyls were prepared by the methods described previously.[6]

Results and Discussion

Phenylazotriphenylmethane (PAT) was dissolved in a large excess of a substituted benzene ($PhNO_2$, PhCN, PhCl, PhEt and PhOMe), and the PAT solution was allowed to decompose at 60°C under nitrogen atmosphere. Evolution of nitrogen was almost quantitative and followed a first-order rate equation. The rate constants were about 4.2×10^{-4} sec at 60°C.

Formation of triphenylmethane was almost quantitative, and the total yields of substituted biphenyl isomers were about 50%. The amounts of substituted biphenyl isomers were determined by a Hitachi Gas Chromatograph K53 by use of calibration curves. The orientations and the partial rate factors for phenylation of substituted benzenes by PAT are summarized in Table 1. The partial

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[1] H. Wieland, E. Popper and H. Seefried, *Ber.*, **55**, 1816 (1922).

[2] W. A. Pryor, J. T. Echols, Jr., and K. Smith, *J. Amer. Chem. Soc.*, **88**, 1189 (1966); M. Harada, R. Ito, T. Migita and O. Simamura, *Kogyo Kagaku Zasshi*, **69**, **607**, 962 (1966).

[3] Chlorobiphenyls (*o*, 58%; *m*, 28%; *p*, 14%) were obtained from the decomposition of PAT in chlorobenzene at 45°C. R. Huisgen and R. Grashey, *Ann. Chem.*, 46 (1957).

[4] D. H. Hey, *J. Chem. Soc.*, **1934**, 1966.

[5] M. Kobayashi, H. Minato, N. Kobori and E. Yamada, submitted to this Bulletin.

[6] M. Kobayashi, H. Minato, E. Yamada and N. Kobori, This Bulletin, **43**, 215 (1970).

[7] M. Gomberg and H. W. Berger, *Ber.*, **36**, 1088 (1903).

[8] C. R. Hauser and B. E. Hudson, Jr., "Organic Syntheses," Coll. Vol. 3, p. 842 (1955).

Table 1. ORIENTATIONS AND PARTIAL RATE FACTORS FOR PHENYLATION AT 60°C

PhX	Orientations (%)			Partial rate factors			
	o-	*m*-	*p*-	k_o/k	k_m/k	k_p/k	k_x/k_H
PhOMe	69	21	10	4.2	1.4	2.6	2.3
PhEt	49	35	16	1.7	1.5	1.3	1.4
PhCl	59	24	17	3.8	1.5	2.2	2.1
PhCN	69	9	22	6.9	1.0	4.6	3.4
$PhNO_2$	79	7	14	9.2	1.1	6.0	4.4

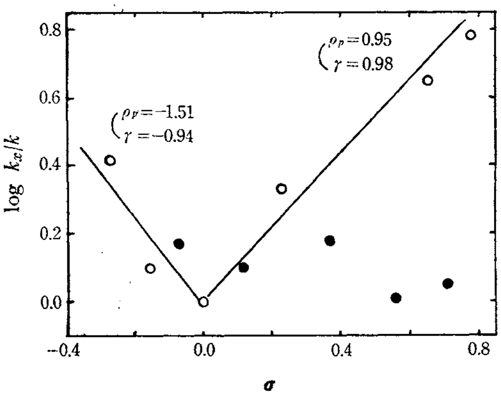
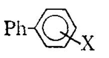


Fig. 1. Hammett plots for phenylation.
—●—: log k_m/k —○—: log k_p/k

rate factors were determined by means of competitive phenylation in a mixture of a substituted benzene and benzene or chlorobenzene as the standard according to the following equation.

$$\mathrm{Ph}\cdot + \mathrm{PhH} \xrightarrow{k_H} \mathrm{PhPh}$$

$$\mathrm{Ph}\cdot + \mathrm{PhX} \xrightarrow{k_x}$$



$$\frac{1}{k_x}\cdot\frac{[\mathrm{PhC_6H_4X}]}{[\mathrm{PhX}]_0} = \frac{1}{k_H}\cdot\frac{[\mathrm{PhPh}]}{[\mathrm{PhH}]_0}$$

where $k_H = 6k$

$k_x = 2k_o + 2k_m + k_p$

$[PhX]_0$ and $[PhH]_0$ are the initial concentrations of the aromatic solvents.

When the partial rate factors of meta or para positions were plotted *versus* Hammett's σ values, two straight lines of V-shape were obtained as shown in Fig. 1. The ρ value was −1.51 (correlation coefficient, γ=0.94) for *p*-substituents of negative σ values and 0.95 (γ=0.98) for *p*-substituents of positive σ values. Similar V-shape lines were obtained when the partial rate factors of para positions for phenylations with benzoyl peroxide (80°C)[9] or *N*-nitrosoacetanilide (20°C)[10] were plotted *versus* σ values. The ρ_p values obtained for *p*-substituents of negative and positive σ values were −1.42 and 1.14 for benzoyl peroxide at 80°C and −0.39 and 1.27 for *N*-nitrosoacetanilide at 20°C, respectively. The ρ values for PAT and benzoyl peroxide are in fairly good agreement, but the ρ values for *N*-nitrosoacetanilide are quite different from those for PAT and benzoyl peroxide especially with respect to the electron-releasing *p*-substituents. Such difference in the ρ values is probably not ascribable to the difference in temperature. The difference in hydrogen abstractors, the difference in solvents and some other factors are probably responsible for such difference in the partial rate factors. This interesting problem has been currently investigated in our laboratories.

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9) G. H. Williams "Homolytic Aromatic Substitution," Pergamon Press, Oxford (1960), pp. 68, 73; The value for OMe was taken from C. S. Rondestvedt, Jr., and H. S. Blanchard, *J. Org. Chem.*, **21**, 229 (1956).

10) R. Ito, T. Migita, N. Morikawa and O. Simamura, *Tetrahedron*, **21**, 955 (1965). The value for Me was used instead of the value for Et.