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Aroyl Arenesulfonyl Peroxides. II.[1] Phenylation with Phenyl Radical Generated from Benzoyl *p*-Toluenesulfonyl Peroxide

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We previously reported that spontaneous decomposition of benzoyl *p*-toluenesulfonyl peroxide (BPT) in benzene gave phenyl *p*-toluenesulfonyl carbonate (yield, 48 mol%), *p*-toluenesulfonic acid (33 mol%), benzoic acid (23 mol%), and biphenyl (1 mol%), and that in the presence of magnesium oxide 44 mol% of biphenyl and 22 mol% of phenyl *p*-toluenesulfonyl carbonate together with *p*-toluenesulfonic acid (57 mol%) and benzoic acid (10 mol%) were produced.[1] It was suggested that the biphenyl obtained was produced by the attack of phenyl radical on benzene. In order to ascertain whether or not the intermediate is phenyl radical, the orientation and the partial rate factors for phenylation with BTP in substituted benzenes were determined. The results will be described in this paper.

Experimental

Materials. Purification of benzene and substituted benzenes[2] and preparations of BTP[1] and the authentic samples of substituted biphenyls[2] have been described previously.

Magnesium oxide was used after heating in a crusible for 2 hr.

Decomposition of BTP. Into a mixture of 300 mmol each of a substituted benzene and benzene (or chlorobenzene), 5 mmol of BTP and 50 mmol of magnesium oxide were added at 10°C. After nitrogen gas was bubbled through the mixture for 20 min, the reaction flask was placed and stirred in a constant-temperature bath at 45.0°C. After 15 hr the reaction mixture was washed with a 5% sodium hydroxide solution to remove acidic products, washed with water, and dried over anhydrous magnesium sulfate. The amounts of the substituted biphenyl isomers were determined gas-chromatographically by the method described previously.[2]

Results and Discussion

The spontaneous decomposition of BTP in benzene was not a simple homolysis, and acid-catalyzed rearrangement to phenyl *p*-toluenesulfonyl carbonate always took place. A detailed study on the mechanism of this rearrangement is being carried out, and the results will be published soon.

When magnesium oxide was suspended in benzene for adsorption of *p*-toluenesulfonic acid produced, the rearrangement was suppressed considerably. In order to check the effect of magnesium oxide on yields of products, decomposition of benzoyl peroxide in benzene

Table 1. Orientations and partial rate factors for phenylation at 45.0°C

PhX	Orientation (%)			Partial rate factors			
	o-	*m*-	*p*-	k_o/k	k_m/k	k_p/k	k_x/k_H
PhOMe	62.3	26.7	11.0	4.75	2.03	1.65	2.53
PhEt	58.0	28.9	13.1	2.28	1.14	1.03	1.31
PhCl	64.6	19.9	15.5	3.92	1.21	1.88	2.02
$PhNO_2$	64.6	9.5	25.9	10.8	1.58	8.66	5.58

a) These data are the average values of two experiments. Errors for orientations are usually 3% except that for *m*-methoxy (6%). Errors for partial rate factors are usually 2% except those for *m*-methoxy (7%) and *p*-methoxy (9%).

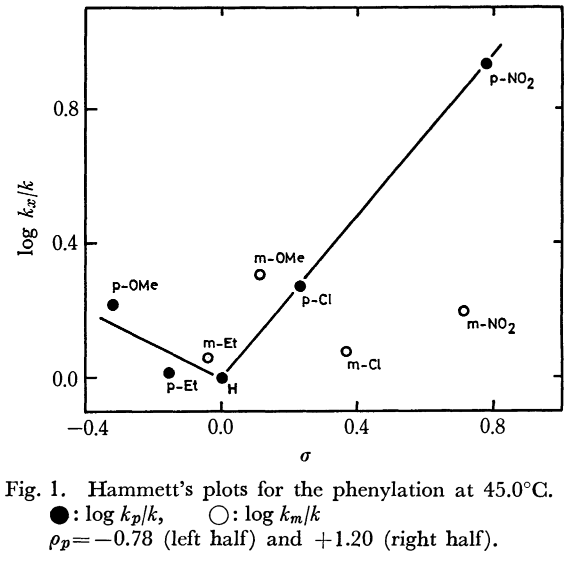
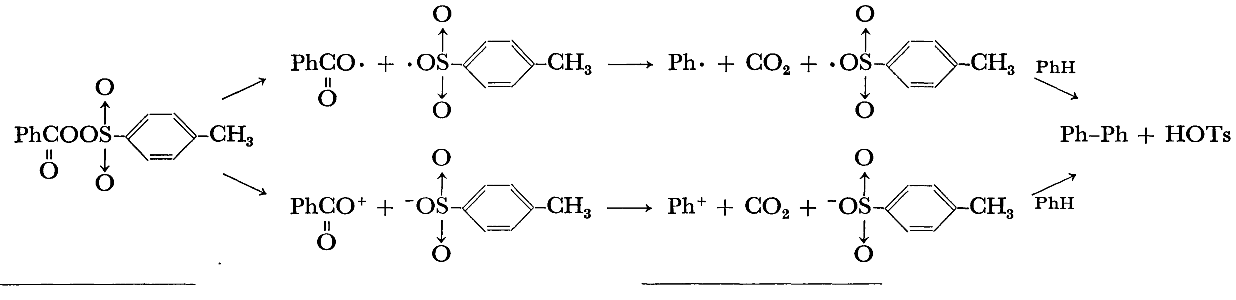


Fig. 1. Hammett's plots for the phenylation at 45.0°C.
●: log k_p/k, ○: log k_m/k
$\rho_p = -0.78$ (left half) and $+1.20$ (right half).



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[1] For the previous paper in this series, see R. Hisada, H. Minato, and M. Kobayashi, This Bulletin, **44**, 2541 (1971).

[2] M. Kobayashi, H. Minato, E. Yamada, and N. Kobori, *ibid.*, **43**, 215 (1970).

in the presence and in the absence of magnesium oxide was studied. Yields of biphenyl, benzoic acid, and phenyl benzoate were the same within experimental error.

The main products of the decomposition of BTP in benzene in the presence of magnesium oxide were biphenyl and *p*-toluenesulfonic acid in addition to the rearranged product, phenyl *p*-toluenesulfonyl carbonate.[1] Biphenyl and *p*-toluenesulfonic acid could arise *via* either phenyl radical or phenyl cation according to the scheme shown above.

The orientations and the partial rate factors for phenylation of substituted benzenes are shown in Table 1. Figure 1 is the Hammett plots of the partial rate factors of *meta* and *para* positions. V-shaped straight lines could be drawn for *para* positions with $\rho=-0.78$ and $+1.20$. Similar results were obtained by the phenylation with phenyl radical produced from benzoyl peroxide ($\rho_p=-1.42$ and $+1.15$ at 80°C)[3] or *N*-nitrosoacetanilide ($\rho_p=-0.39$ and $+1.27$ at 20°C).[4] Both the orientations and the partial rate factors obtained with BTP were quite different from those for phenylation with phenyl cation.[2,5] These data prove that biphenyls are produced by the attack of phenyl radical.

The partial rate factors for *meta* phenylations are not too different from unity except that for the *m*-methoxy position. Experiments were repeated, but the abnormality was reproduced within experimental error. It is possible that nucleophilic anisole and electrophilic BTP have some kind of weak interaction.

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3) G. H. Williams, "Homolytic Aromatic Substitution," Pergamon Press, Oxford (1960), pp. 68—73.

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

5) M. Kobayashi, H. Minato, and N. Kobori, This Bulletin, **43**, 219 (1970).