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Aroyl Arenesulfonyl Peroxides. V. Mechanisms of the Reactions of Benzoyl *p*-Toluenesulfonyl Peroxide with Several Nucleophiles¹⁾

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Reactions of benzoyl *p*-toluenesulfonyl peroxide (BTP) with several nucleophiles were investigated. The reaction with triphenylphosphine gave benzoyl *p*-toluenesulfonate and triphenylphosphine oxide, that with diphenyl sulfide gave benzoyl *p*-toluenesulfonate and diphenyl sulfoxide, and that with *p*-tolylmagnesium bromide gave *p*-tolyl *p*-toluenesulfonate and benzoic acid. In the reaction of BTP[carbonyl-¹⁸O] with triphenylphosphine, 88% of carbonyl oxygen-18 was retained as the carbonyl oxygen of the benzoyl *p*-toluenesulfonate formed, whereas in the reaction of BTP[carbonyl-¹⁸O] with diphenyl sulfide only 58% of the label in the starting peroxide was found in the carbonyl oxygen of the benzoyl *p*-toluenesulfonate formed. In the reaction of BTP[sulfonyl-¹⁸O] with *p*-tolylmagnesium bromide, it was found that the two sulfonyl oxygens of BTP were completely retained in the two sulfonyl oxygens of the *p*-tolyl *p*-toluenesulfonate formed. Possible mechanisms of these reactions are discussed.

Benzoyl *p*-toluenesulfonyl peroxide (BTP) has been synthesized in our laboratories. Investigation on its decomposition under various conditions has revealed that the O-O bond of BTP tends to undergo heterolytic cleavage, and that the heterolysis is the main reaction unless some base is present in the medium for suppression of autocatalysis.²⁾

Diacyl and diaroyl peroxides are known to react with such nucleophiles as triphenylphosphine.³⁾ The re-

actions of BTP with various nucleophiles seem to be of great interest. Detailed investigation was carried out in order to determine which of the two peroxidic oxygen atoms is attacked and what products are formed from this unsymmetrical peroxide. The results are given in this paper.

Results and Discussion

When a carbon tetrachloride solution of triphenylphosphine or diphenyl sulfide was stirred into a carbon tetrachloride solution of benzoyl *p*-toluenesulfonyl peroxide (BTP) at 10°C, the mixture became turbid in five minutes, and fine needles precipitated. When such a mixture was heated at 30°C for 30 min, it became transparent again. The completion of the reaction was

1) Organic Sulfur Compounds. XXXI.

2) R. Hisada, H. Minato, and M. Kobayashi, This Bulletin, **44**, 2541 (1971).

3) a) L. Horner and W. Jurgeleit, *Ann. Chem.*, **591**, 138 (1955). b) M. A. Greenbaum, D. B. Denney, and A. K. Hoffmann, *J. Amer. Chem. Soc.*, **78**, 2563 (1956). c) D. B. Denney and M. A. Greenbaum, *ibid.*, **79**, 979 (1957).

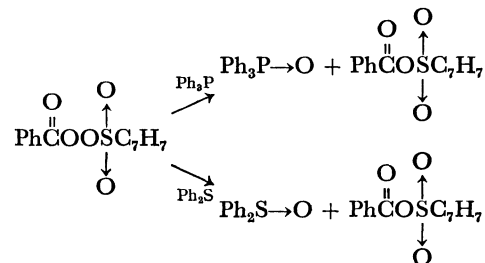
TABLE 1. REACTION PRODUCTS OF BTP WITH TRIPHENYLPHOSPHINE AND DIPHENYL SULFIDE (mol/100 mol of BTP)

Products	Nucleophiles	
	Ph ₃ P	Ph ₂ S
Ph ₃ PO	96	—
Ph ₂ SO	—	81
PhCO ₂ Ts ^{a)}	86 ^{b)}	98 ^{c)}
	98 ^{c)}	96 ^{c)}
PhCO ₂ H	11 ^{d)}	

- a) Determined by conversion into BzNHPh and TsOH or BzOH and TsOH on account of its instability.
 b) Determined as BzNHPh.
 c) Determined as TsOH.
 d) Probably formed by hydrolysis during the reaction with aniline.
 e) Determined as BzOH.

shown by disappearance of the infrared absorption of the peroxidic carbonyl group of BTP. The reaction was completed in about one hour with triphenylphos-

phine, but it took about 6 hr with diphenyl sulfide. The main product was identified to be benzoic *p*-toluenesulfonic anhydride, on the basis of a comparison of its infrared spectrum with that of an authentic sample prepared by the method of Karger and Mazur.⁴⁾ Since the anhydride is unstable toward hydrolysis, it was determined by converting it into BzNHPh and TsOH or BzOH and TsOH. The results are shown in Table 1. The reactions can be expressed as follows.



In order to investigate the detailed mechanism of these reactions, BTP [carbonyl-¹⁸O] was synthesized

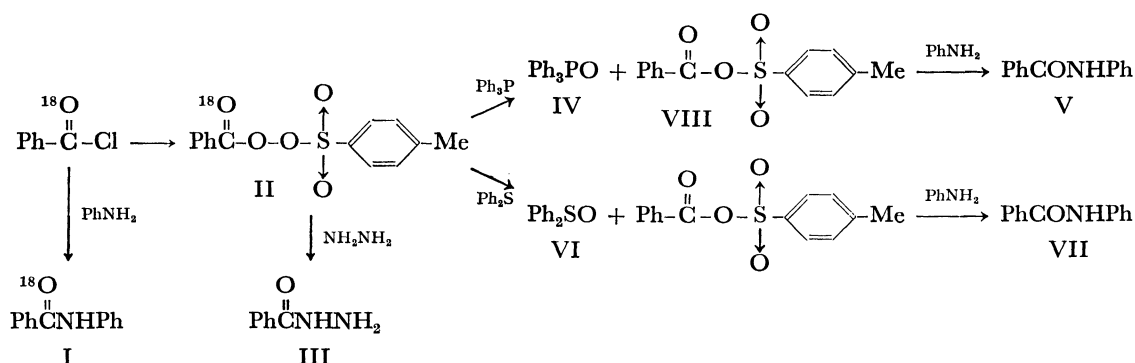


TABLE 2. EXCESS OXYGEN-18 ATOM % IN VARIOUS COMPOUNDS RELATED TO THE REACTIONS WITH TRIPHENYLPHOSPHINE AND WITH DIPHENYL SULFIDE^{a)}

	Nucleophile							
	Ph ₃ P				Ph ₂ S			
	Run 1		Run 2		Run 1		Run 2	
	Found	Calcd ^{b)}	Found	Calcd ^{b)}	Found	Calcd ^{b)}	Found	Calcd ^{b)}
¹⁸ O								
Ph ¹⁸ CNHPh (I)	1.28	(1.28)	1.20	(1.20)	1.28	(1.28)	1.20	(1.20)
Ph ¹⁸ COOTs (II)	0.27	0.26	0.24	0.24	0.27	0.26	0.24	0.24
Ph ¹⁸ CNHNH ₂ (III)	1.27	1.28	1.00	1.20	1.27	1.28	1.00	1.20
Ph ¹⁸ CNHPh (V or VII)	1.14	1.28	1.06	1.20	0.66	1.28	0.62	1.20
Ph ₃ PO (IV)	0.14	0	0.17	0	—	—	—	—
Ph ₂ SO (VI)	—	—	—	—	0.47	0	0.46	0
TsOH formed from Ph ¹⁸ COTs	(c)	0	0.01	0	(c)	0	0.04	0

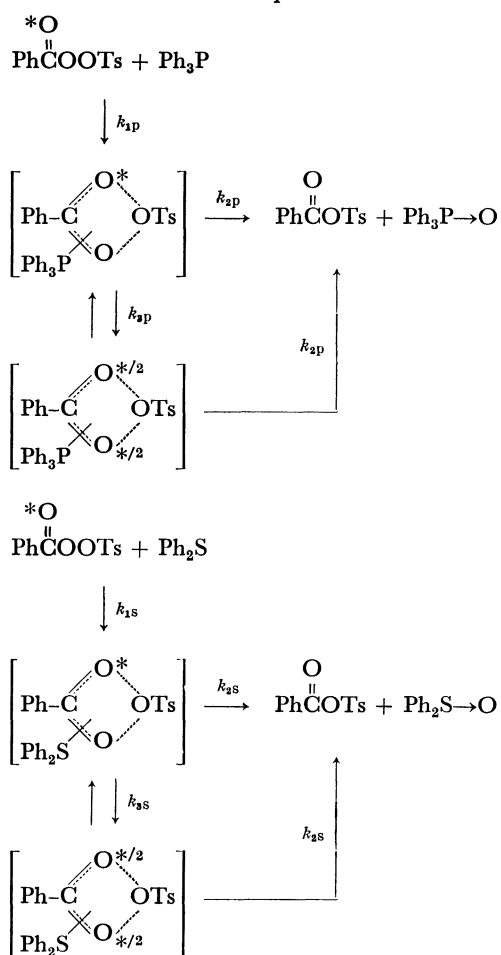
- a) Experimental error in two experiments for the same sample was within ± 0.02 excess atom %.
 b) Calculated on the assumption that the carbonyl oxygen of BTP becomes the carbonyl oxygen of the anhydride without scrambling.
 c) Not determined.

4) M. H. Karger and Y. Mazur, *J. Org. Chem.*, **36**, 528 (1971).

and the products of its reaction with triphenylphosphine and diphenyl sulfide were analyzed. The oxygen-18 contents of compounds (I)—(VIII) shown in the above scheme were determined. The results are shown in Table 2.

Benzanilide (V) formed from the anhydride obtained by the reaction with triphenylphosphine contains 88% of the excess oxygen-18 in the original BTP, whereas benzanilide (VII) formed from the anhydride obtained by the reaction with diphenyl sulfide contains only 58% of the excess oxygen-18 in the original BTP. This means that during the reaction with triphenylphosphine the carbonyl oxygen of the original BTP is retained as the carbonyl oxygen of the anhydride to a considerable extent, whereas the carbonyl oxygen of BTP is almost completely scrambled during the reaction with diphenyl sulfide.

These reactions can be expressed as follows.

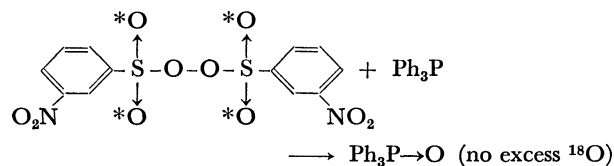


In this scheme, k_{1p} (or k_{1s}) is the rate of the complex formation between BTP and the nucleophile, k_{3p} (or k_{3s}) that of the oxygen scrambling in the complex, and k_{2p} (or k_{2s}) the rate of the formation of the final products from the complex. The exact nature of the complex has not been clarified as yet.

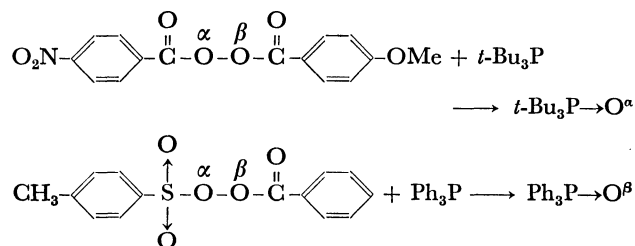
The results of ^{18}O analyses indicate that k_{2p} is greater than k_{3p} whereas k_{2s} is smaller than k_{3s} .

The fact that both triphenylphosphine oxide and diphenyl sulfoxide contain some excess oxygen-18 can be explained by the assumption that (a) the nucleophiles attack both the carbonyl and peroxidic oxygen

atoms, or (b) the nucleophiles attack the peroxidic oxygen atom and then some scrambling takes place before the anhydride is formed. Although the possibility (a) cannot be strictly excluded, it is less likely since both benzoyl peroxide^{3b)} and *m*-nitrobenzenesulfonyl peroxide⁵⁾ react with triphenylphosphine at their peroxidic oxygen atoms.



It is interesting to note that in the reactions of BTP with triphenylphosphine and diphenyl sulfide the peroxidic oxygen atom attacked is the one adjacent to the benzoyl group, and not the one adjacent to the more electron-withdrawing tosyl group. Denney and Greenbaum^{3c)} studied the reaction of *p*-nitrobenzoyl *p*'-methoxybenzoyl peroxide with tri-*t*-butylphosphine, and showed that the peroxidic oxygen atom adjacent to the more electron-withdrawing *p*-nitrobenzoyl group was attacked by tri-*t*-butylphosphine.



p-Tolylmagnesium bromide was chosen as another nucleophile and its reaction with BTP was investigated. When an ethereal solution of *p*-tolylmagnesium bromide was stirred into an ethereal solution of BTP under a nitrogen atmosphere at 3°C, white precipitates were formed immediately. The products were analyzed after stirring for 3 hr. Results: benzoic acid (91%), *p*-tolyl *p*-toluenesulfonate (41%) and *p*-toluenesulfonic acid (46%).

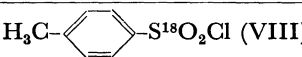
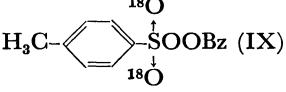
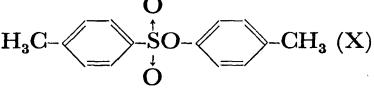
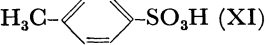
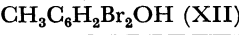
In order to study the mechanism of this reaction in detail, BTP [sulfonyl- ^{18}O] was synthesized and its reaction with *p*-tolylmagnesium bromide investigated. The distribution of the excess oxygen-18 in *p*-tolyl *p*-toluenesulfonate formed was determined by converting it into *p*-cresol and *p*-toluenesulfonic acid, according to the scheme (next page). The results are summarized in Table 3.

The data in Table 3 show that the sulfonyl oxygen of BTP is completely retained as the sulfonyl oxygen of *p*-tolyl *p*-toluenesulfonate within experimental error. This indicates that the following mechanism (next page) is plausible.

The reaction with the Grignard reagent is in contrast to the reactions with triphenylphosphine and diphenyl sulfide; and coordination between the basic carbonyl oxygen atom and the electrophilic magnesium atom takes place first, probably determining the course of the reaction. It is known that carbonyl oxygen atoms are much more basic than sulfonyl oxygen atoms.

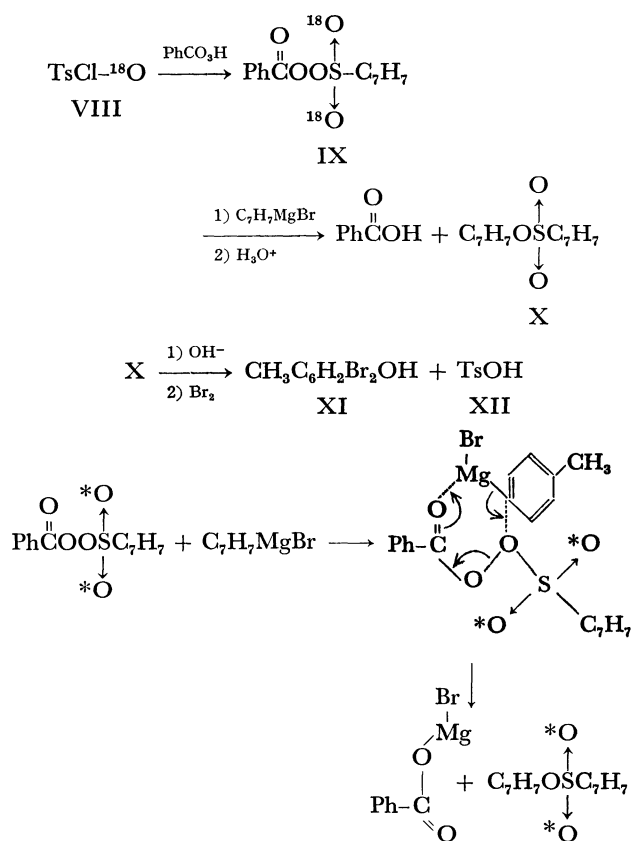
5) Y. Yokoyama, H. Wada, M. Kobayashi, and H. Minato, *This Bulletin*, **44**, 2479 (1971).

TABLE 3. EXCESS OXYGEN-18 ATOM % IN VARIOUS COMPOUNDS RELATED TO THE REACTION OF BTP[SULFONYL-¹⁸O] WITH *p*-TOLYLMAGNESIUM BROMIDE^{a)}

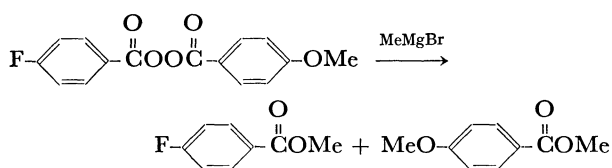
Compound	Run 1		Run 2	
	Found	Calcd ^{b)}	Found	Calcd ^{b)}
 (VIII)	0.46	(0.46)	0.91	(0.91)
 (IX)	0.20	0.18	0.37	0.36
 (X)	0.29	0.31	0.55	0.61
 (XI)	0.32	0.31	0.60	0.61
 (XII)	0.01	0	0.03	0

a) Experimental error in two experiments for the same sample was within ± 0.02 excess atom %.

b) Calculated on the assumption that the sulfonyl oxygen-18 is not equilibrated with the peroxidic oxygen.



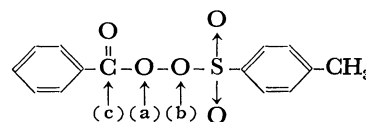
Ōkubo, Maruyama, and Ōsugi⁶⁾ studied the reactions of substituted benzoyl peroxides with Grignard reagents, and found that even *p*-fluorobenzoyl *p*'-methoxybenzoyl peroxide is attacked at both the peroxidic oxygens yielding two esters.



6) M. Ōkubo, K. Maruyama, and J. Ōsugi, *This Bulletin* **44**, 125 (1971).

When BTP is mixed with excess anhydrous hydrazine, its carbonyl carbon atom is attacked by the nucleophile, benzhydrazide being formed in 67% yield. Sodium methoxide reacts with BTP in a similar manner, producing methyl benzoate.

Thus, benzoyl *p*-toluenesulfonyl peroxide is attacked by nucleophiles at three different positions, *viz.*, a) the peroxidic oxygen atom adjacent to the benzoyl group (Ph_3P and Ph_2S), b) the peroxidic oxygen atom adjacent to the sulfonyl group (RMgBr) and c) the carbonyl carbon atom (N_2H_4 and NaOMe).



Experimental

Materials. Triphenylphosphine, extra pure grade of Wako Chemicals, was used without further purification. Diphenyl sulfide was prepared according to the procedure of Hartman, Smith and Dickey⁷⁾ and distilled under reduced pressure; the fraction boiling at 162–163°C/18 mmHg was collected and used. The preparation of BTP[carbonyl-¹⁸O] and BTP[sulfonyl-¹⁸O] was described in a previous paper.⁸⁾ *p*-Tolylmagnesium bromide was prepared according to the procedure of Lawesson and Yang.⁹⁾

Reaction of BTP[carbonyl-¹⁸O] with Triphenylphosphine. To 1.46 g (5 mmol) of BTP[carbonyl-¹⁸O] dissolved in 200 ml of carbon tetrachloride was added 1.44 g (5.5 mmol) of triphenylphosphine in 50 ml of carbon tetrachloride with stirring at 10°C. The reaction mixture was then warmed up to 30°C and allowed to stand for 15 hr. After 1.12 g (12 mmol) of freshly distilled aniline was added to the reaction mixture, it was refluxed for 30 min, washed successively with water, dilute hydrochloric acid and water, and then dried over anhydrous magnesium sulfate. Carbon tetrachloride

7) W. W. Hartman, L. A. Smith, and J. B. Dickey, "Organic Syntheses," Coll. Vol. II, p. 242.

8) R. Hisada, H. Minato, and M. Kobayashi, submitted to *This Bulletin*.

9) S. O. Lawesson and N. C. Yang, *J. Amer. Chem. Soc.*, **81**, 4230 (1959).

was evaporated under reduced pressure. The residue was chromatographed on active alumina (300 mesh).

Benzanilide (86% yield), mp 162–163°C (lit,¹⁰ 160–161°C) and triphenylphosphine oxide (96% yield), mp 153°C (lit,¹¹ 153.5°C) were obtained and recrystallized three times from a mixture of benzene and ether. They were subjected to the determination of ¹⁸O-contents, according to the method described previously.⁵ From the aqueous layer, benzoic acid was isolated and weighed (11% yield) and *p*-toluenesulfonic acid was weighed as its *S*-benzylisothiuronium salt (98% yield).

Reaction of BTP[carbonyl-¹⁸O] with Diphenyl Sulfide. To 1.46 g (5 mmol) of BTP[carbonyl-¹⁸O] dissolved in 200 ml of carbon tetrachloride was added 1.02 g (5.5 mmol) of diphenyl sulfide in 50 ml of carbon tetrachloride with stirring at 10°C. The mixture was treated in a manner similar to that for the reaction with triphenylphosphine.

Benzanilide and diphenyl sulfoxide obtained from the reaction mixture of BTP[carbonyl-¹⁸O]-diphenyl sulfide-aniline could not be completely separated from each other by elution chromatography. They were purified by repeated recrystallizations from a mixture of benzene and *n*-hexane; BzNHPh, mp 162°C, and Ph₂SO, mp 70°C (lit,¹² 70–71°C).

Since the yields could not be determined by this technique, unlabeled BTP was allowed to react with diphenyl sulfide, and benzoic *p*-toluenesulfonic anhydride produced was hydrolyzed to benzoic acid and *p*-toluenesulfonic acid; the former was weighed (98% yield), and the latter was converted into its *S*-benzylisothiuronium salt and weighed

(96% yield). Diphenyl sulfoxide and unreacted diphenyl sulfide were determined by gas chromatography (column: silicone oil SE 30, 1 m; 190°C; internal standard, *p*-tolyl benzoate), yield, 81% and 13%, respectively.

Reaction of BTP[sulfonyl-¹⁸O] and *p*-Tolylmagnesium Bromide. To 2.64 g (9 mmol) of BTP[sulfonyl-¹⁸O] in 100 ml of anhydrous ether was added 9 mmol of *p*-tolylmagnesium bromide in 50 ml of ether under a nitrogen atmosphere at 3°C with stirring. After the reaction mixture was allowed to stand at 3–5°C for 3 hr with stirring, water was added. The ethereal layer was separated from the aqueous layer, washed successively with a 10% sodium hydrogen carbonate solution and water, and dried over anhydrous magnesium sulfate. After the ether was removed under reduced pressure, the residue was chromatographed on silica gel (Wako Gel Q 22). *p*-Tolyl *p*-toluenesulfonate isolated (41% yield) was recrystallized three times from *n*-hexane, mp 69–69.5°C (lit,¹³ 69–70°C). The aqueous layer was acidified with hydrochloric acid and extracted with ether. After the combined extracts were dried over anhydrous magnesium sulfate, the solvent was evaporated and the benzoic acid isolated was weighed (91% yield). *p*-Toluenesulfonic acid was determined as its *S*-benzylisothiuronium salt (46% yield).

p-Tolyl *p*-toluenesulfonate was hydrolyzed to *p*-cresol and *p*-toluenesulfonic acid. *p*-Cresol was converted by bromine water into 2,6-dibromo-*p*-cresol, which was purified twice by sublimation, mp 48–49°C (lit,¹⁴ 49°C). *p*-Toluenesulfonic acid was obtained as *S*-benzylisothiuronium salt, and recrystallized three times from water, mp 180–181°C.

10) C. N. Webb, "Organic Syntheses," Coll. Vol. I, p. 82.

11) A. Michaelis and W. La Coste, *Ber.*, **18**, 2118 (1885).

12) O. Hinsberg, *ibid.*, **43**, 289 (1910).

13) F. Reverdin and P. Crépeux, *ibid.*, **35**, 1439 (1902).

14) C. Schall and C. Dralle, *ibid.*, **17**, 2528 (1884).