

Aroyl Arenesulfonyl Peroxides IV. The Mechanism of Carboxy-inversion of Benzoyl *p*-Toluenesulfonyl Peroxide¹⁾

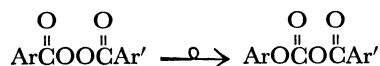
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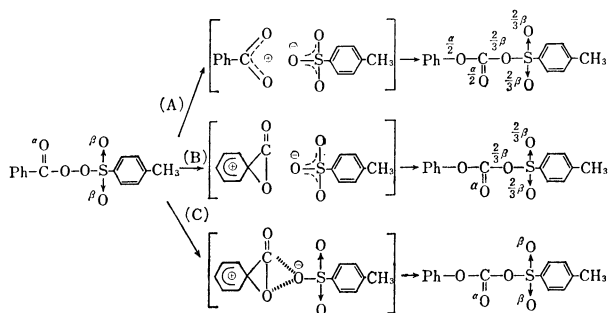
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Benzoyl *p*-toluenesulfonyl peroxide (BTP) with ¹⁸O-labeled carbonyl oxygen and ¹⁸O-labeled sulfonyl oxygen were prepared. They were decomposed in benzene in the presence or in the absence of trifluoroacetic acid, and the phenyl *p*-toluenesulfonyl carbonate (PTC)-¹⁸O produced was isolated and analyzed. It was found that the carbonyl oxygen-18 of BTP was retained as the carbonyl oxygen of PTC, whereas the sulfonyl oxygen-18 of BTP was equilibrated with the peroxidic oxygen. The mechanism of the carboxy-inversion was discussed.

The thermal decompositions of symmetrical and asymmetrical acyl (aroyl) peroxides *via* the carboxy-inversion process are well documented.²⁾ It is known that the asymmetrical acyl (aroyl) peroxides rearrange to the corresponding anhydrides more readily than symmetrical peroxides. Therefore, the acyl sulfonyl



peroxides are expected to rearrange to the mixed anhydrides more easily than the diacyl peroxides. Razuvaev, Likhterov, and Etlis³⁾ reported that the decomposition of benzoyl alkanesulfonyl peroxides in benzene gave phenyl alkanesulfonyl carbonates in 83% yield. In the previous papers^{4,5)} from our laboratories, we have reported that benzoyl *p*-toluenesulfonyl peroxide (BTP) and *p*-chlorobenzoyl *p*-toluenesulfonyl peroxide rearrange to phenyl *p*-toluenesulfonyl carbonate (PTC) (48% yield), and *p*-chlorophenyl *p*-toluenesulfonyl carbonate (42% yield), respectively. Plausible mechanisms for this rearrangement are the followings.

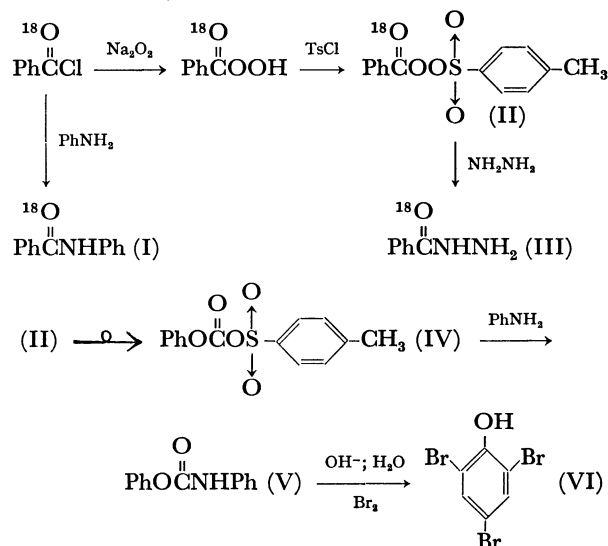


In order to establish the mechanism, the rearrangement of BTP to PTC has been investigated by the ¹⁸O-labeling technique, and the results will be described in this paper.

Results and Discussion

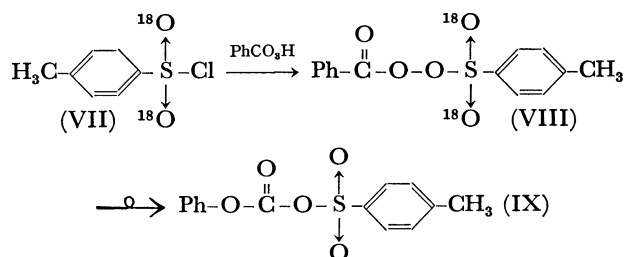
BTP[carbonyl-¹⁸O] and BTP[sulfonyl-¹⁸O] were pre-

pared and decomposed in benzene either in the presence or in the absence of trifluoroacetic acid. Yields of the carboxy-inversion product, PTC, were 43—48% in benzene and 67—71% in benzene-trifluoroacetic acid. The PTC produced from the decomposition of BTP-[carbonyl-¹⁸O] was converted, by the reaction with aniline, to phenyl phenylcarbamate and *p*-toluenesulfonic acid. The phenyl phenylcarbamate obtained was hydrolyzed to phenol, which was then converted into 2,4,6-tribromophenol. The ¹⁸O-contents of compounds I—VI in the following scheme were determined.



The results obtained are summarized in Table 1. Table 1 shows that practically all the carbonyl oxygen-18 of BTP is retained in the carbonyl oxygen of PTC, and that the rearrangement of BTP to PTC does not go through a state in which the carbonyl oxygen and the peroxidic oxygen of BTP are scrambled.

From *p*-toluenesulfonyl chloride-¹⁸O the BTP[sulfonyl-¹⁸O] was prepared, and the oxygen-18 contents of VII—XIII were determined.



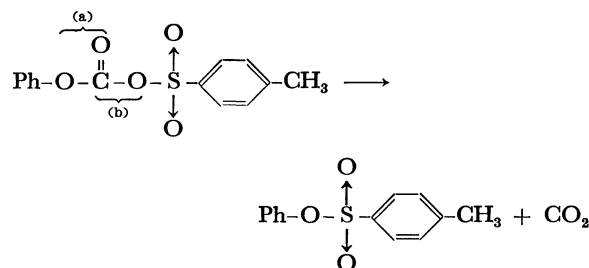
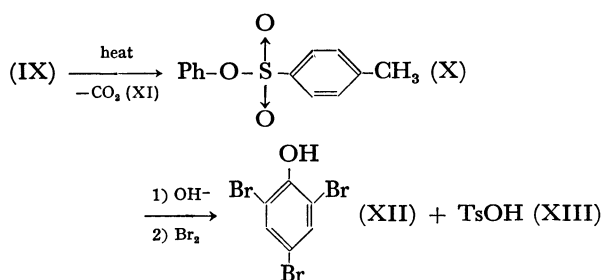
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TABLE 1. THE ^{18}O -CONTENTS IN BTP [CARBONYL- ^{18}O] AND RELATED COMPOUNDS^{a)} (excess atom % oxygen-18)

Sample	Run 1			Run 2	
	Found ^{b)}	Found ^{c)}	Calcd ^{d)}	Found ^{b)}	Calcd ^{d)}
^{18}O PhC(=O)NPh (I)	1.20	1.20	(1.20)	1.26	(1.26)
^{18}O PhC(=O)OOTs (II)	0.24	0.25	0.24	0.25	0.25
^{18}O PhC(=O)NHNH ₂ (III)	1.00	1.00	1.20	1.18	1.26
PhOC(=O)OTs (IV)	0.24	0.25	0.24	0.28	0.25
PhOC(=O)NPh (V)	0.67	0.65	0.60	—	—
Br ₃ C ₆ H ₂ OH (VI)	0.07	0.01	0	0.06	0

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

b) In benzene-trifluoroacetic acid. c) In benzene. d) Calculated on the assumption that the carbonyl oxygen is not equilibrated with the peroxidic oxygen.



In order to determine the distribution of oxygen-18 in the sulfonyl oxygen and the ether oxygen in IX, one has to find some reactions with which these two kinds of oxygen can be distinguished. Reactions of IX with hydrazine or sodium methoxide were attempted, but they did not attack the sulfonyl sulfur atom. The method which met the requirements was the pyrolysis of neat IX at 230°C.

However, the mechanism of the pyrolysis of IX must be established. There are two possible modes of decarboxylation from IX. If the pyrolysis occurs according to process (a), the carbon dioxide evolved should contain no oxygen-18 regardless of whether or not the sulfonyl oxygen and the peroxidic oxygen of VIII were scrambled during the rearrangement.

The results of the ^{18}O analyses of VII—XIII are

TABLE 2. THE ^{18}O -CONTENTS IN BTP[SULFONYL- ^{18}O] AND RELATED COMPOUNDS^{a)} (excess atom % oxygen-18)

		Run 1		Run 2	
		Found	Calcd ^{b)}	Found	Calcd ^{b)}
TsCl- ^{18}O	(VII)	0.81	(0.81)	0.76	(0.76)
PhC(=O)OOS(=O) ₂ -C ₆ H ₄ -CH ₃	(VIII)	0.33	0.32	0.29	0.30
PhOC(=O)OS(=O) ₂ -C ₆ H ₄ -CH ₃	(IX)	0.33	0.32	0.29	0.30
PhOS(=O) ₂ -C ₆ H ₄ -CH ₃	(X)	0.37	0.36	0.32	0.34
CO ₂	(XI)	0.32	0.27	0.27	0.25
Br ₃ C ₆ H ₂ OH	(XII)	0.03	0	0.04	0
H ₃ C-C ₆ H ₃ (SO ₃ H)	(XIII)	0.36	0.36	0.35	0.34

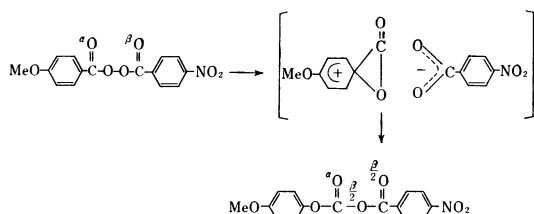
a) Experimental error in two measurements for the same sample was ± 0.02 excess atom %.

b) Calculated on the assumption that two sulfonyl oxygens are completely equilibrated with one peroxidic oxygen.

shown in Table 2. Since the carbon dioxide contains excess oxygen-18, process (a) is rejected, and thus it has been established that the thermal decarboxylation of arenesulfonyl aryl carbonates occurs according to process (b).

Since the hydrolysis of aryl arenesulfonates proceeds with S-O cleavage instead of C-O cleavage, no excess ^{18}O -incorporation in XII indicates that no excess ^{18}O in the phenoxy oxygen in IX and X. The ^{18}O -contents in IX, X, and XI show that during the rearrangement of VIII to IX two sulfonyl oxygens and one peroxidic oxygen of VIII are completely scrambled.

These findings reject mechanism (A), and probably mechanism (C) as well. It is possible that the sulfonyl oxygen-18 atoms are completely retained during the carboxy-inversion process and then, prior to the decarboxylation, completely scrambled when the mixed anhydride was heated up to 230°C. However, the decarboxylation proceeds with the S-O bond cleavage, whereas the scrambling requires the C-O bond cleavage. It seems less likely that both the C-O bond and the S-O bond of the mixed anhydride are cleaved upon heating. Therefore, the rearrangement of aryl arenesulfonyl peroxides to aryl arenesulfonyl carbonates probably proceeds through a state similar to that shown in mechanism (B). Mechanism (B) is similar to the mechanism proposed for the rearrangement of *p*-methoxybenzoyl *p*'-nitrobenzoyl peroxide.^{6,7}



Experimental

Preparation of Peroxybenzoic Acid[carbonyl- ^{18}O]. Benzoyl chloride [carbonyl- ^{18}O] was prepared according to the method of Denney and Denney.⁷ Peroxybenzoic acid[carbonyl- ^{18}O] was prepared according to the procedure of Vilkas⁸ by use of benzoyl chloride[carbonyl- ^{18}O] and sodium peroxide with some modification. Peroxybenzoic acid[carbonyl- ^{18}O] was extracted from the aqueous layer with dichloromethane, and the dichloromethane solution was used for preparation of BTP[carbonyl- ^{18}O].

Preparation of BTP[carbonyl- ^{18}O] or BTP[sulfonyl- ^{18}O]. BTP[carbonyl- ^{18}O] or BTP[sulfonyl- ^{18}O] was prepared, according to the method used for the preparation of the unlabeled BTP,³ by using peroxybenzoic acid[carbonyl- ^{18}O] and *p*-toluenesulfonyl chloride, or peroxybenzoic acid and *p*-toluenesulfonyl chloride [sulfonyl- ^{18}O], respectively.

Decomposition of BTP[carbonyl- ^{18}O] or BTP[sulfonyl- ^{18}O]. A solution of 4.39 g (15 mmol) of BTP[carbonyl- ^{18}O] in 150 ml of benzene, or 2.64 g (9 mmol) of BTP[sulfonyl- ^{18}O] in 120 ml of benzene in the presence of trifluoroacetic acid (5 mol/mol BTP) was decomposed under the conditions described previously.⁴ Phenyl *p*-toluenesulfonyl carbonate

(PTC) was isolated by elution chromatography on a silica gel column (Wako Gel Q 22), and then recrystallized from ether; mp 64–65°C.

Reaction of PTC with Aniline. To 1.33 g (4.6 mmol) of PTC dissolved in 30 ml of dichloromethane was added 0.93 g (10 mmol) of freshly distilled aniline. The reaction mixture was refluxed for 30 min, washed with water, dilute hydrochloric acid and water, successively, and dried over anhydrous magnesium sulfate. Solvent was evaporated under reduced pressure and phenyl phenylcarbamate obtained was recrystallized from carbon tetrachloride; yield, 850 mg (87%); recrystallized three times from carbon tetrachloride; mp 124–125°C (lit,⁹ 126°C).

Hydrolysis of Phenyl Phenylcarbamate. A mixture of phenyl phenylcarbamate (626 mg), sodium (850 mg), water (15 ml) and ethanol (10 ml) was refluxed for 2 hr. The ethanol was evaporated under reduced pressure, and then water and ether were added to the residue. The aqueous layer was washed with ether twice, and neutralized with hydrochloric acid. Phenol isolated was converted by bromine water into 2,4,6-tribromophenol; 850 mg (88%); purified by sublimation twice, mp 94–95°C (lit,¹⁰ 95°C).

Pyrolysis of PTC. In a vessel connected with a gas buret, 1.00 g of PTC was placed. After the atmosphere was replaced with nitrogen, the vessel was heated gradually to 230°C and kept at this temperature until about 60 ml of carbon dioxide was evolved. The brownish reaction mixture obtained was dissolved in benzene, washed with water, and dried over anhydrous magnesium sulfate. After the benzene was removed under reduced pressure, the residue was chromatographed on a silica gel column. Phenyl *p*-toluenesulfonate isolated (223 mg, 26.5%) was twice recrystallized from *n*-hexane, mp 95°C (lit,¹¹ 95–96°C).

Hydrolysis of Phenyl *p*-Toluenesulfonate. A mixture of phenyl *p*-toluenesulfonate (172 mg), sodium hydroxide (276 mg), dioxane (3 ml) and water (4 ml) was sealed in an ampoule and heated at 94°C for 100 hr. After dioxane was removed under reduced pressure, water was added to the mixture. The aqueous layer was acidified with hydrochloric acid and the phenol formed was extracted with ether. *p*-Toluenesulfonic acid remaining in the aqueous layer was converted to its *S*-benzylisothiuronium salt (235 mg, 91%) which was recrystallized three times from water, mp 180–181°C (lit,¹² 181–182°C). Phenol obtained from the ether layer was converted to 2,4,6-tribromophenol; 171 mg (75%); purified by sublimation, mp 94–95°C.

Reaction of BTP[carbonyl- ^{18}O] with Anhydrous Hydrazine. A solution of 0.90 g of BTP[carbonyl- ^{18}O] in 25 ml of anhydrous benzene was added drop by drop to a mixture of 1.0 g of anhydrous hydrazine and 5 ml of benzene at 2°C with stirring. After the addition was over, benzene and unreacted hydrazine were removed under reduced pressure. Benzhydrazide produced (250 mg, 61%) was recrystallized three times from ether, mp 112.5–113°C (lit,¹³ 112.5°C).

Determination of Oxygen-18 Contents. All the samples were converted to carbon dioxide according to the method of Rittenberg and Ponticorvo¹⁴ for determination of the ^{18}O -contents. The ^{18}O -contents were determined by use of a Hitachi RMU-6E Type Mass Spectrometer.

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