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Thermal Decomposition of Benzoyl *p*-Toluenesulfonyl Peroxide[1]

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Benzoyl *p*-toluenesulfonyl peroxide (BTP) was synthesized by addition of barium hydroxide and water to a mixture of *p*-toluenesulfonyl chloride and peroxybenzoic acid in dichloromethane at -15°C. Rates of decomposition of BTP in inert solvents increased rapidly as the decomposition proceeded. This autocatalysis was prevented and the reaction followed a first-order rate equation when magnesium oxide suspension was present in the medium for removal of *p*-toluenesulfonic acid produced by the decomposition. The products of decomposition were analyzed. When magnesium oxide suspension was present, main products were those ascribable to homolysis (biphenyl, 44 mol%, in benzene; chlorobenzene, 44 mol%, hexachloroethane, 27 mol%, in carbon tetrachloride), but products ascribable to ionic reactions were also present (phenyl *p*-toluenesulfonyl carbonate, 22—26 mol%).

Investigations in our laboratories revealed that *m*-nitrobenzenesulfonyl peroxide decomposed homolytically in chloroform, whereas its O–O bond was cleaved heterolytically in aromatic solvents.[2] Razuvaev, Likhterov, and Etlis studied the decomposition of acetyl cyclohexanesulfonyl peroxide in several solvents, and their products indicated that both homolytic and heterolytic reactions were taking place.[3] They also studied the decomposition of benzoyl alkanesulfonyl peroxide in benzene and carbon tetrachloride, and they found no products ascribable to homolytic cleavage of the O–O bond.[4]

Aroyl arenesulfonyl peroxides have not been reported in the literature. As an example of these unknown peroxides, synthesis of benzoyl *p*-toluenesulfonyl peroxide has been attempted in order to determine its properties and the nature of its decomposition under various conditions.

Results and Discussion

A literature survey revealed a paper describing an unsuccessful attempt for synthesis of benzoyl benzenesulfonyl peroxide. Kirmse and Horner mixed benzenesulfonyl chloride and sodium perbenzoate in 1:1 water-dioxane at 0°C, and the products were benzoyl peroxide, benzoic acid and carbon dioxide.[5]

After numerous attempts, it was found that addition of barium hydroxide and water to a mixture of *p*-

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[1] Organic Sulfur Compounds. Part XXVI.

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

[3] G. A. Razuvaev, V. R. Likhterov, and V. S. Etlis, *Zh. Obshch. Khim.*, **31**, 274 (1961); G. A. Razuvaev, L. M. Terman, V. R. Likhterov, and V. S. Etlis, *J. Polymer Soc.*, **52**, 123 (1961).

[4] G. A. Razuvaev, V. R. Likhterov, and V. S. Etlis, *Zh. Obshch. Khim.*, **32**, 2033 (1962); *Tetrahedron Lett.*, **1961**, 527.

[5] W. Kirmse and L. Horner, *Chem. Ber.*, **89**, 836 (1956).

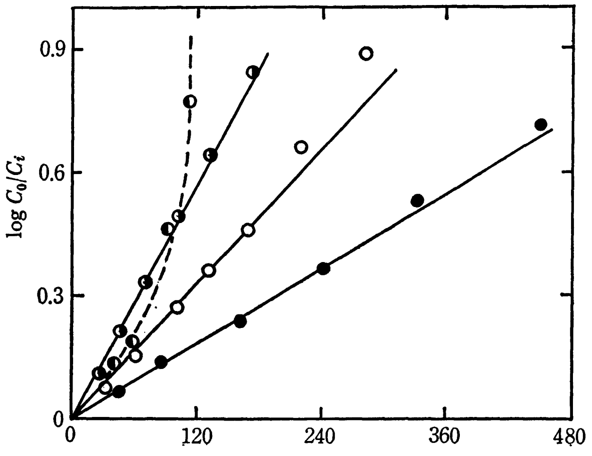


Fig. 1. Plots of $\log(C_0/C_i)$ vs. time for the decomposition of BTP in C_6H_6
● 40.0°C, ○ 45.0°C, ◑ 50.0°C, in the presence of MgO, ◐ 40.0°C, in the absence of MgO

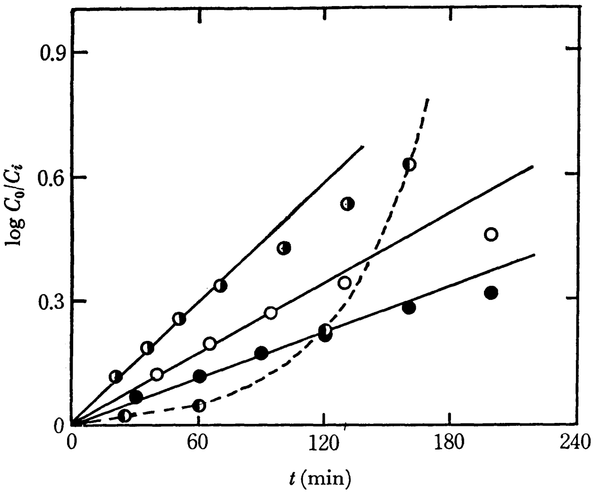


Fig. 2. Plots of $\log(C_0/C_i)$ vs. time for the decomposition of BTP in CCl_4
● 40.0°C, ○ 45.0°C, ◑ 50.0°C, in the presence of MgO, ◐ 40.0°C, in the absence of MgO

toluenesulfonyl chloride and peroxybenzoic acid in dichloromethane at −15°C resulted in the formation of benzoyl *p*-toluenesulfonyl peroxide (BTP).

When BTP was decomposed in benzene or carbon tetrachloride, the rate of decomposition increased rapidly with the progress of decomposition, as Figs. 1 and 2 show. When trifluoroacetic acid was added, the rate was very fast from the beginning, and the decomposition was complete in 3 hr at room temperature. These findings indicate that the decomposition of BTP is much accelerated by the *p*-toluenesulfonic acid produced by the decomposition. In order to investigate the possibility of the homolysis of BTP, such ionic autocatalysis must be prevented, and it was found that when powdery magnesium oxide was suspended in the medium the acceleration of rates was prevented and the decomposition followed a first-order rate equation till about two half-lives in benzene and one half-life in carbon tetrachloride. Rate constants and activation parameters are shown in Table 1 and Fig. 3.

Table 1. First-order rate constants for the decomposition of BTP

Temp. (°C)	in C_6H_6+ suspended MgO $k_1\times10^5$ (sec^{-1})	in CCl_4+ suspended MgO $k_1\times10^5$ (sec^{-1})
40.0	5.79	6.78
45.0	10.82	11.00
50.0	19.02	18.30
E_a (kcal/mol)	23.91	19.94
$\Delta S^{\pm}$ (e.u.)	−3.65	−16.06

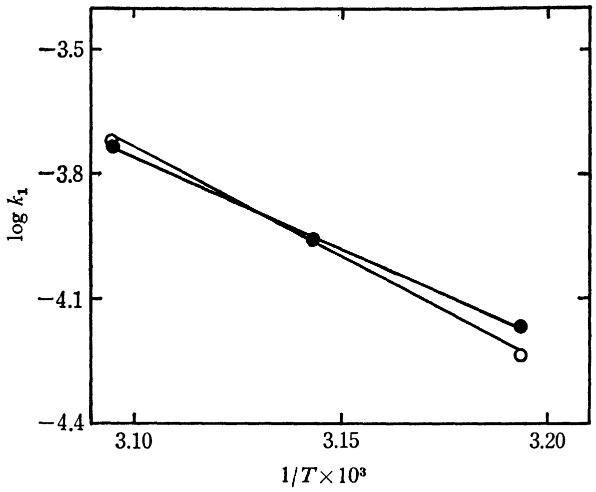


Fig. 3. Arrhenius plots for the decomposition of BTP
○ in C_6H_6+MgO, ● in CCl_4+MgO

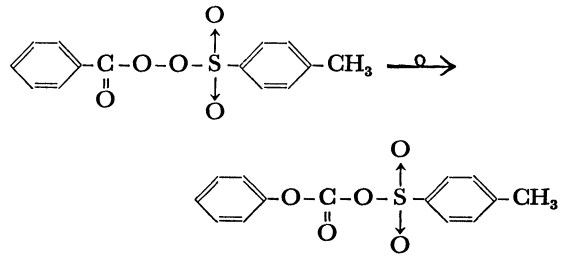
The products of decomposition of BTP in benzene or carbon tetrachloride in the presence and absence of suspended magnesium oxide and in benzene in the presence of trifluoroacetic acid were analyzed, and the results are summarized in Table 2.

Table 2. Decomposition products of BTP[a]

BTP (mmol)	5.0	5.0	5.0	5.0	5.0
Solvent (m*l*)	C_6H_6 50	C_6H_6 50	CCl_4 170	CCl_4 170	C_6H_6 75
Additives (mmol)	— 50	MgO 50	MgO 50	— 50	CF_3CO_2H 50
Products (mol/mol of BTP)					
Carbon dioxide		0.41	0.33	0.49	
Phenyl *p*-toluenesulfonyl carbonate	0.48	0.22	0.24	0.26	0.71
Biphenyl	0.01	0.44			0.005
Chlorobenzene			0.26	0.44	
Hexachloroethane			0.12	0.27	
Benzoic acid	0.23	0.10	0.33	0.09	0.15
p-Toluenesulfonic acid	0.33	0.57	0.57	0.33	0.10
Phenyl benzoate	0.04	0.08	0.01	0.02	0.01
p-Tolyl benzoate	trace	0.004	0.01	0.001	trace
Phenyl *p*-toluenesulfonate	trace	0.01	0.01	0.02	0.004
Chloride ion			0.05	>0.04	
Accounted for					
Phenyl (%)	76	84	86	85	88
p-Tolyl (%)	81	80	83	61	81

[a] Temperature, 45°C; Reaction time, 15 hr.

In the absence of suspended magnesium oxide, one of the major products was phenyl *p*-toluenesulfonyl carbonate formed by carboxy inversion process.



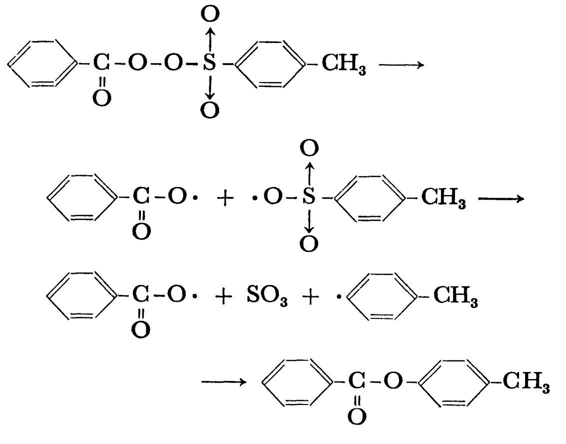
When trifluoroacetic acid was present, 71 mol% of BTP was converted to the mixed anhydride, and this finding shows that this rearrangement is accelerated by acid.

Even when suspended magnesium oxide was present in benzene or carbon tetrachloride to adsorb *p*-toluenesulfonic acid produced, about 22—26 mol% of BTP rearranged to the mixed anhydride. Therefore, the tendency for such rearrangement must be interpreted to be inherent in this peroxide rather than given by acid catalyst. The electron-withdrawing power of a *p*-toluenesulfonyloxy group is far greater than that of a benzoyloxy group, and even under the conditions which ensure the absence of acid in the medium the rearrangement proceeded at moderate rates at these temperatures.

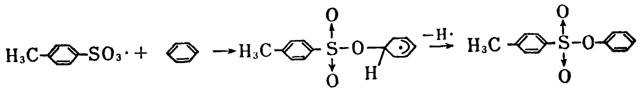
However, when magnesium oxide was added, the yield of biphenyl increased from 1 to 44 mol% in benzene, and the yields of chlorobenzene and hexachloroethane in the carbon tetrachloride increased from 26 to 44 mol% and from 12 to 27 mol%, respectively. These data show that magnesium oxide is effective in reducing heterolysis and promoting homolysis.

When BTP was decomposed in carbon tetrachloride in the presence of magnesium oxide, the yield of chlorobenzene was 44 mol% whereas that of hexachloroethane was 27 mol%; the latter corresponds to 54 mol % of trichloromethyl radical. Thus about 10 mol% trichloromethyl radical must be produced by abstraction of chlorine atom from carbon tetrachloride by radicals other than phenyl radicals. Therefore, benzoyloxy radical and/or *p*-toluenesulfonyloxy radical must abstract chlorine atom from carbon tetrachloride.

Formation of *p*-tolyl benzoate can be accounted for by the following recombination of radicals in cage.



Formation of phenyl *p*-toluenesulfonate can be explained by addition of *p*-toluenesulfonyloxy radical to benzene and subsequent hydrogen abstraction from the cyclohexadienyl radical or by geminate cage recombination of *p*-toluenesulfonyloxy radical with phenyl radical produced by fragmentation of benzoyloxy radical.



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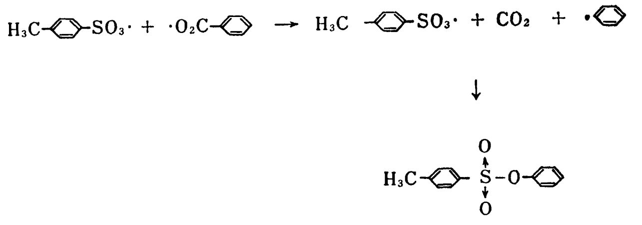
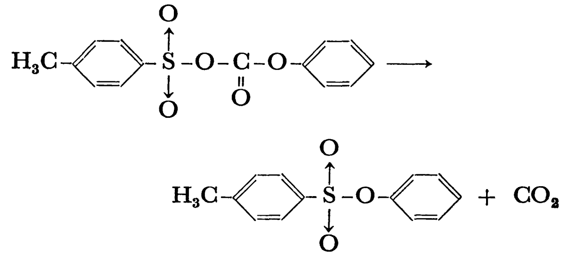
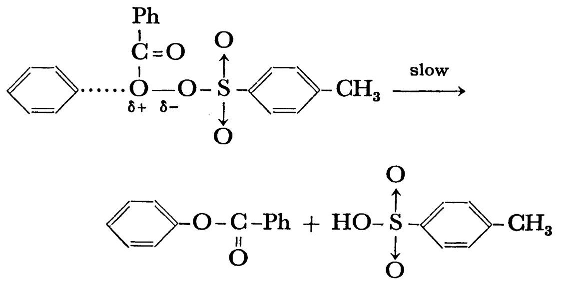


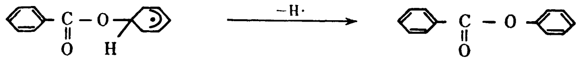
However, the fact that some sulfonate was formed even in the decomposition of BTP in the presence of trifluoroacetic acid indicates that at least part of the sulfonate arose from the mixed carbonate by an ionic path.



When *m*-nitrobenzenesulfonyl peroxide was decomposed in benzene, the main reaction products were *m*-nitrobenzenesulfonic acid and phenyl *m*-nitrobenzenesulfonate produced by electrophilic attack of a peroxidic oxygen atom on benzene.[6] If a similar reaction takes place with BTP, phenyl benzoate is the product expected in benzene. However, the yield of this ester in the absence of magnesium oxide was only 4 mol%, and this finding shows that positive character of the benzoyloxy oxygen of BTP is not large enough to accept nucleophilic attack of benzene readily.



When magnesium oxide was added, the yield of phenyl benzoate was doubled (8%), but the majority of this amount probably arose from attack of benzoyloxy radical on benzene.



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[6] R. L. Dannley and G. E. Corbet, *J. Org. Chem.*, **31**, 153 (1966).

Razuvaev, Likhterov, and Etlis[4] studied the decomposition of benzoyl ethanesulfonyl peroxide. They found that in benzene phenyl ethanesulfonyl carbonate was produced in 83 mol% yield and no biphenyl was found, whereas in carbon tetrachloride neither chlorobenzene nor hexachloroethane was formed. Therefore, BTP has greater tendency to undergo homolytic cleavage of the O–O bond than benzoyl ethanesulfonyl peroxide.

Experimental

Materials. Benzene was washed with concentrated sulfuric acid and water successively, dried over anhydrous calcium chloride and distilled at 80.0°C. Carbon tetrachloride was washed with a 10% sodium carbonate aqueous solution and water, dried over anhydrous calcium chloride, and distilled over phosphorus pentoxide. Boiling point was 76.7°C. *p*-Toluenesulfonyl chloride was recrystallized from *n*-hexane; mp 69—70°C. Peroxybenzoic acid was prepared according to Braun's method.[7] Magnesium oxide was used after heating in a crucible for 2 hr.

Preparation of Benzoyl p-*Toluenesulfonyl Peroxide (BTP).* A solution of 19.1 g of *p*-toluenesulfonyl chloride (0.1 mol) in 160 m*l* of dichloromethane was cooled to −15°C in a 500 m*l* three-necked flask equipped with a mechanical stirrer, an addition funnel, and a thermometer. A solution of 17.9 g of peroxybenzoic acid (0.13 mol) in 150 m*l* of dichloromethane was slowly added into the cooled and stirred solution. After the temperature of the mixture became below −15°C, 5 m*l* of water was slowly added and then 41.0 g of barium hydroxide (0.13 mol) was added in portions in 15 min. The temperature of the mixture should be kept below −12°C during the addition. After the addition was completed, the mixture was stirred at −12°C for 1.5 hr, and then washed with 10 *l* of ice water. The dichloromethane solution was dried over anhydrous magnesium sulfate, and the solvent was removed under reduced pressure. A brownish residue obtained was recrystallized from ether at −20°C, and 16.1 g of light yellowish crystals was obtained; yield, 52.8%. Recrystallization was repeated for two more times, and the crystals melting at 59.5°C were used for experiments. Iodometric analyses indicated the purity of 99.80%. The main infrared absorptions appeared at 1790, 1400, 1225, 1195 and 1180 cm^{-1} (in CCl_4). BTP was stable at −20°C, and no appreciable decomposition was observed when it was stored at −20°C for one month.

Found: C, 57.77; H, 3.85; S, 11.05%. Calcd for $C_{14}H_{12}O_5S$: C, 57.53; H, 4.14; S, 10.97%.

Kinetic Measurements. All the measurements were carried out under nitrogen atmosphere. A solution of 1.91 g of BTP (6.5 mmol) in 190 m*l* of benzene or carbon tetrachloride was deaerated by bubbling nitrogen for 30 min at 10°C. The solution was placed in a constant temperature bath, and after suitable intervals 15.0 m*l* aliquots of the solution were withdrawn and subjected to the iodometric analysis using a 0.05N sodium thiosulfate solution.[8]

When the runs were carried out in the presence of 2.62 g (65 mmol) of magnesium oxide suspension, 20.0 m*l* aliquots were withdrawn, the magnesium oxide was removed by a centrifuge, and 15.0 m*l* of the solution was subjected to the iodometric analysis.

Products of Decomposition of BTP. *(1) In Benzene*: A 0.1M solution of BTP in benzene was decomposed at 45.0±0.1°C for 15 hr. The reddish brown solution obtained was washed with water and then with a 10% sodium bicarbonate solution. The *p*-toluenesulfonic acid which dissolved into the water washings was titrated with bromothymolblue as the indicator. The sodium bicarbonate extracts were acidified by addition of hydrochloric acid, and the benzoic acid obtained was extracted with ether. The amount of benzoic acid was determined gravimetrically after evaporation of ethereal extracts. The benzene layer was dried over anhydrous magnesium sulfate, and then divided to three portions. One portion was used for determination of biphenyl and phenyl benzoate by vapor phase chromatography (Column: Apiezon L, 2 m; internal standard, dibenzyl). Another portion was used for determination of *p*-tolyl benzoate and phenyl *p*-toluenesulfonate by vapor phase chromatography after refluxing the solution with added aniline for 30 min, washing with water and then drying (Colum: Apiezon L, 2 m; internal standard, phenyl *p*-chlorobenzoate). The other portion was used for determination of phenyl *p*-toluenesulfonyl carbonate by elution chromatography after removal of benzene under reduced pressure (Wako Gel Q22 200 mesh; eluant, 1:2 *n*-hexane - benzene). The identities of biphenyl, phenyl benzoate, *p*-tolyl benzoate, and phenyl *p*-toluenesulfonate were established by comparison of the infrared spectra of these products, obtained by elution chromatography, with those of the authentic samples.

(2) In Carbon Tetrachloride: A 0.029M solution of BTP in carbon tetrachloride was decomposed at 45.0±0.1°C for 15 hr under nitrogen atmosphere. The carbon dioxide generated was absorbed in a 0.1N sodium hydroxide solution, which was titrated with a 0.2N sulfuric acid solution.[9] Then this solution was titrated for chloride ion by a 0.1N silver nitrate solution with potassium chromate as an indicator. The carbon tetrachloride solution was washed with water and a 10% sodium hydrogen carbonate solution, and then dried over anhydrous magnesium sulfate. The aqueous extracts were titrated by a 0.1N sodium hydroxide solution for *p*-toluenesulfonic acid and hydrogen chloride, and then titrated for chloride ion by a 0.1N silver nitrate solution with potassium chromate as the indicator. The $NaHCO_3$-extracts were acidified, and the benzoic acid separated was extracted with ether and determined gravimetrically. The carbon tetrachloride solution was divided into three portions. One portion was used for determination of chlorobenzene and hexachloroethane by vapor phase chromatography (Column, Silicone oil SE30, 2 m; internal standard, *p*-dichlorobenzene). Another portion was used for determination of ester by vapor phase chromatography after the treatment of the solution with aniline and then with water. The other portion was used for determination of phenyl *p*-toluenesulfonyl carbonate by elution chromatography.

(3) In Benzene and Carbon Tetrachloride with Suspended Magnesium Oxide: A 0.05M solution of BTP in benzene or a 0.029M solution of BTP in carbon tetrachloride containing suspended magnesium oxide was stirred with a mechanical stirrer under nitrogen for 15 hr at 45.0°C. Then magnesium oxide was dissolved by addition of dilute sulfuric acid, and the mixture was refluxed for 5 min. Carbon dioxide and hydrogen chloride expelled were titrated by the methods described above. (Expulsion of hydrogen chloride from the water-containing mixtures must be incomplete, and hence the actual amounts of hydrogen chloride produced were probably

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[7] G. Braun, "Organic Syntheses," Coll. Vol. I, p. 431 (1961).

[8] P. D. Bartlett and B. T. Storey, *J. Amer. Chem. Soc.*, **80**, 4954 (1958).

[9] K. Uneyama, W. Tagaki, I. Minamida, and S. Oae, *Tetrahedron*, **24**, 5271 (1968).

greater than the values obtained by titration.)

The mixture was separated into aqueous and organic layers, and both layers were analyzed by the methods described above. Since the amount of *p*-toluenesulfonic acid cannot be determined by acid-base titration, it was determined gravimetrically by converting it into its *S*-benzylisothiuronium salt as follows. The aqueous layer was made alkaline, and evaporated under reduced pressure. The sodium *p*-toluenesulfonate in the residue was dissolved by hot methanol, and the methanolic solution was evaporated under reduced pressure. Some water and hydrochloric acid was added, and *p*-toluenesulfonic acid was converted to its *S*-benzylisothiuronium salt.

(4) In Benzene Containing Trifluoroacetic Acid: After a 0.1 M solution of BTP in benzene and a benzene solution of trifluoroacetic acid were deaerated separately by nitrogen, they were mixed and stirred at room temperature. After 1 hr, the color of the solution was reddish brown. After 15 hr, the benzene solution was washed with water and then with a sodium hydrogen carbonate solution. The products of the reaction were analyzed according to the methods described above. The amount of *p*-toluenesulfonic acid was determined after it was converted into its *S*-benzylisothiuronium salt.

Synthesis of Phenyl p-*Toluenesulfonyl Carbonate.* To a solution of 11.8 g (0.04 mol) of anhydrous silver *p*-toluenesulfonate in 100 m*l* of acetonitrile, 6.4 g (0.04 mol) of phenyl chloroformate (94—95°C/41 mmHg) was added, and the mixture was refluxed for 18 hr. After the silver chloride was filtered, the acetonitrile was evaporated under reduced pressure. Recrystallization of the residue in 1:1 *n*-hexane-ether yielded 8.6 g of phenyl *p*-toluenesulfonyl carbonate (67%), mp 64—65°C.

Found: C, 57.83; H, 4.17; S, 10.97%. Calcd for $C_{14}H_{12}O_5S$; C, 57.53; H, 4.14; S, 10.97%. IR: 1795, 1395, 1230, 1180 cm^{-1} (KBr).

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