BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 45, 2902—2906 (1972)

Aroyl Arenesulfonyl Peroxides. VI. Benzoyloxylation and *p*-Toluenesulfonyloxylation of Aromatic Compounds with Benzoyl *p*-Toluenesulfonyl Peroxide[1]

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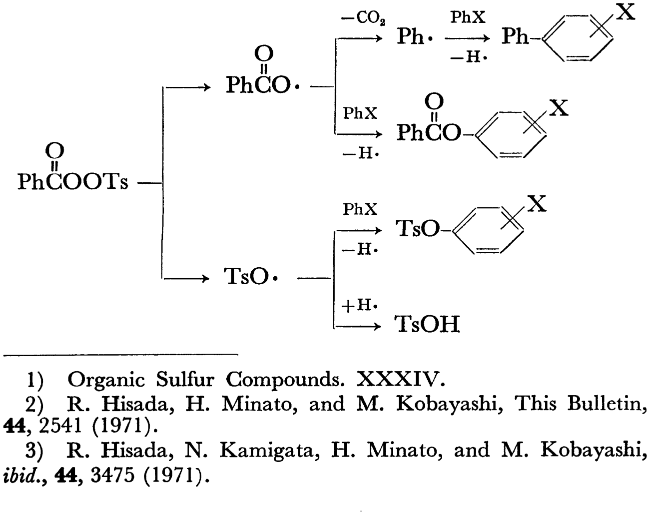
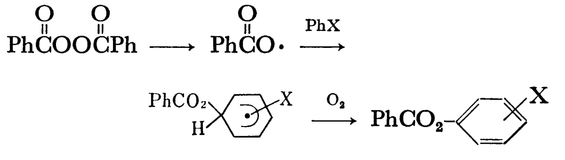
(Received March 18, 1972)

Benzoyl *p*-toluenesulfonyl peroxide (BTP) was decomposed in benzene, toluene, chlorobenzene, nitrobenzene, or anisole in a nitrogen or oxygen atmosphere. Yields of aryl benzoates and *p*-toluenesulfonates were always greater in an oxygen atmosphere than those in a nitrogen atmosphere, except those with nitrobenzene. The isomer distributions of these aryl benzoates and *p*-toluenesulfonates were determined. The rate of decomposition in anisole was considerably greater than those in other arenes. When BTP[carbonyl-^{18}O] was decomposed in anisole, the *o*- or *p*-anisyl benzoate formed was found to contain about equal amounts of oxygen-18 at both the carbonyl and phenoxy oxygens. On the basis of these findings the mechanisms of benzoyloxylation and *p*-toluenesulfonyloxylation were discussed.

A previous paper from our laboratories described that decomposition of benzoyl *p*-toluenesulfonyl peroxide (BTP) in benzene with suspended magnesium oxide under nitrogen yielded 44% diphenyl, 8% phenyl benzoate, and 1% phenyl *p*-toluenesulfonate.[2] It was proposed that under these conditions BTP decomposes homolytically, yielding phenyl radical and benzoyloxy radical, and *p*-toluenesulfonyloxy radical functions as an efficient hydrogen-abstractor.[3]



Benzoyloxylation of arenes with benzoyl peroxide (BPO) was studied by various groups.[4–7] Nakata, Tokumaru, and Simamura investigated the thermolysis and photolysis of BPO in arenes, and reported that the yields of aryl benzoates under oxygen are considerably greater than those under nitrogen.[4]



An investigation on the photolysis by use of BPO-[carbonyl-^{18}O] ascertained that this benzoyloxylation involves benzoyloxy free radical.[8]

BTP is a new reagent for benzoyloxylation, and a detailed investigation seems desirable. The decom-

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[1] Organic Sulfur Compounds. XXXIV.

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

[3] R. Hisada, N. Kamigata, H. Minato, and M. Kobayashi, *ibid.*, **44**, 3475 (1971).

[4] T. Nakata, K. Tokumaru, and O. Simamura, *Tetrahedron Lett.*, **1967**, 3303.

[5] P. Kovacic and his co-workers, *ibid.*, **1966**, 2689; *J. Org. Chem.*, **33**, 1950 (1968); *ibid.*, **35**, 2152 (1970).

[6] S. Hashimoto, W. Koike, and M. Yamamoto, This Bulletin, **42**, 2733 (1969).

[7] J. Bargon, *J. Amer. Chem. Soc.*, **93**, 4630 (1971).

[8] M. Kobayashi, H. Minato, and Y. Ogi, This Bulletin, **42**, 2737 (1969).

Table 1. Yields and isomer distributions of the products of phenylation, benzoyloxylation, and *p*-toluenesulfonyloxylation of PhX with BTP under nitrogen or oxygen[a]

X	N_2 or O_2	PhC_6H_4–X				$PhCO_2C_6H_4$–X				$TsOC_6H_4$–X			
		Yield (mol %)	Isomer distribution (%) *o*-	*m*-	*p*-	Yield (mol %)	Isomer distribution (%) *o*-	*m*-	*p*-	Yield (mol %)	Isomer distribution (%) *o*-	*m*-	*p*-
OMe[b]	N_2	4.2	Not detnd.			50.8	48	<1	52	1.3	36	<1	64
	O_2	4.2	Not detnd.			63.1	40	<1	60	2.4	37	<1	63
Me[c]	N_2	24.1	52	18	30	3.1	Not detnd.			3.5	53	21	26
	O_2	0.3	Not detnd.			34.5	55	32	13	5.3	54	18	28
H[c]	N_2	45.6				7.6				1.3			
	O_2	1.4				33.7				3.5			
Cl[c]	N_2	63.0	65	20	15	1.6	Not detnd.			0.9	12	32	56
	O_2	6.2	64	21	15	8.9	16	43	41	2.4	13	23	64
NO_2[c]	N_2	15.2	80	4	16	0				0			
	O_2	18.5	79	5	16	0				0			

a) These are the average values of two experiments. Errors in the isomer distributions are ±2%.
b) 25°C, 10 hr. c) 45°C, 15 hr.

position of BTP and BTP[carbonyl-^{18}O] in arenes with suspended magnesium oxide in oxygen atmosphere has been investigated under various conditions, and the results will be described in this paper.

Results and Discussion

In an oxygen atmosphere, BTP was decomposed in benzene, toluene, chlorobenzene, or nitrobenzene with suspended magnesium oxide for 15 hr at 45°C. Since BTP decomposes very rapidly in anisole, a dichloromethane solution of BTP was stirred into anisole containing suspended magnesium oxide under oxygen. Yields and isomer distributions of the products are shown in Table 1.

The yields of the products are much affected by the kinds of the atmosphere with the exceptions of the decompositions in nitrobenzene and anisole. Under nitrogen, the yields of phenylated products are greater than those of benzoyloxylated products, whereas under oxygen the yields of benzoyloxylated products are greater than those of phenylated products. Since the isomer distributions of aryl benzoates are similar in both atmospheres, the mechanism must be the same. The yields of aryl benzoates decrease in the order of anisole, toluene, benzene, chlorobenzene, and nitrobenzene, and the yield in nitrobenzene is zero. These results are in agreement with those of Nakata *et al.*[4] The increases in the yields of the esters are more extensive in toluene, benzene, and chlorobenzene than those in anisole.

In nitrobenzene, BTP gave no nitrophenyl benzoate, and phenyl *p*-toluenesulfonyl carbonate was formed in 52—60% yield. This suggests that the main reaction in nitrobenzene is the carboxy-inversion even though magnesium oxide was suspended in the medium. A previous paper described that, when magnesium oxide was absent, the main reaction of BTP in benzene was the carboxy inversion.[2] It is reasonable that the ionic carboxy inversion process takes place more easily in polar solvents such as nitrobenzene. Even when BTP undergoes homolysis to some extent, both radicals produced ($PhCO_2\cdot$ and $TsO\cdot$) are strongly electrophilic and not likely to attack the electron-deficient nitrobenzene.

It is possible that aryl benzoates are produced by the attack of benzoyloxy cation. However, this possibility is rejected by the findings that 1) much substituted diphenyls are produced, 2) in nitrobenzene the main products are *ortho* and *para* nitrodiphenyls which must be formed by the attack of phenyl free radical, not by phenyl cation, and 3) the yields of aryl benzoates are much greater under oxygen because of abstraction of hydrogen from the substituted cyclohexadienyl radicals by oxygen.

Except nitrobenzene, all the arenes are *p*-toluenesulfonyloxylated although the yields are not so great. The yields under oxygen are greater than those under nitrogen (1.5—2.7 times), but the mechanism must be similar since the isomer distributions do not differ.

Dannley and his co-workers reported that the reactions between *m*-nitrobenzenesulfonyl peroxide and arenes are ionic, and electrophilic attack of the peroxidic oxygen on arenes results in the formation of aryl *m*-nitrobenzenesulfonates.[9,10] In the reactions of BTP with toluene and chlorobenzene, considerable amounts of *meta* substituted products were found. It is concluded that these aryl *p*-toluenesulfonates arise, not from electrophilic attack of the *p*-toluenesulfonyloxy oxygen, but from attack of *p*-toluenesulfonyloxy radical, on the basis of the findings that 1) free radical phenylation and benzoyloxylation take place simultaneously, 2) yields of aryl benzoates and *p*-toluenesulfonates are greater under oxygen, and 3) considerable *meta*-substitution takes place with toluene and chlorobenzene. The decomposition of BTP in arenes is the first example which clearly indicates the attack of a sulfonyloxy radical on an aromatic ring.

The mechanism of the substitutions of an arene is expressed as follows.

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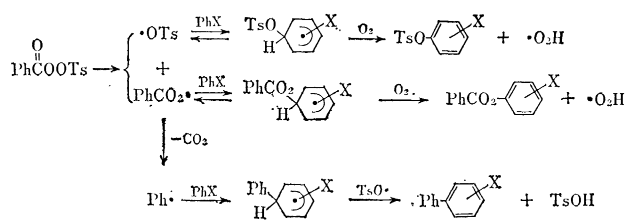
[9] R. L. Dannley and G. E. Corbett, *J. Org. Chem.*, **31**, 153 (1966).

[10] R. L. Dannley, J. E. Gagen, and O. J. Stewart, *ibid.*, **35**, 3076 (1970).



Additions of p-toluenesulfonyloxy and benzoyloxy radicals on an arene are reversible. When abstraction of a hydrogen atom from the cyclohexadienyl radicals is slow (under nitrogen), p-toluenesulfonyloxy and benzoyloxy radicals are reformed; the latter further decomposes to carbon dioxide and phenyl radical.

The decomposition of BTP in anisole is quite different from the decompositions in other solvents; 1) the rate of decomposition was much faster, 2) even under nitrogen the yields of benzoates were very large (that is, very little decarboxylation of benzoyloxy radical occurs) and the yields under oxygen are only slightly greater, and 3) no carboxy inversion product (phenyl p-toluenesulfonyl carbonate, PTC) was found. Therefore, attack of free benzoyloxy radical on anisole does not appear to be the reaction which is taking place in an anisole solution of BTP.

It is conceivable that the electron-rich anisole nucleus attacks the electron-deficient O–O bond of BTP, and thus the rate is faster and the yields of benzoates are greater. In order to check this possibility, BTP-[carbonyl-^{18}O] was synthesized and decomposed in anisole in the presence and absence of suspended magnesium oxide. Even in the absence of magnesium oxide, anisyl benzoates were formed in 40 mol% yield (o:m:p =41:<1: 59%) and PTC was formed only in 10 mol% yield. The compounds I—VII shown in the following scheme were converted to carbon dioxide,[11] which was then analyzed by use of a mass spectrometer. The results are shown in Table 2.

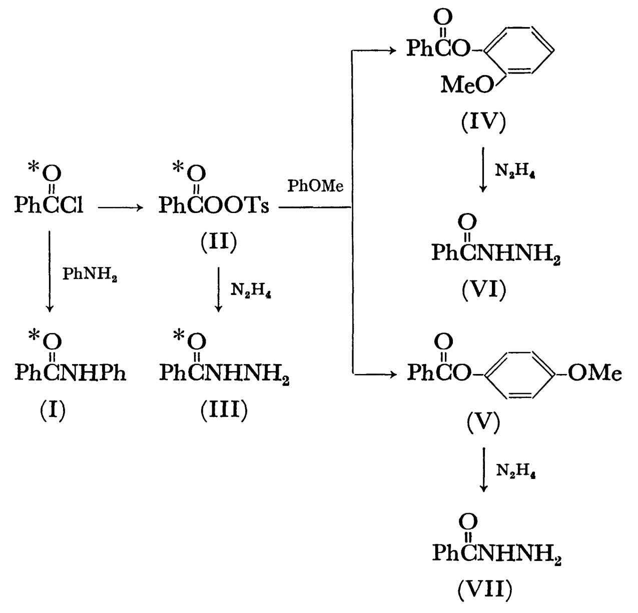


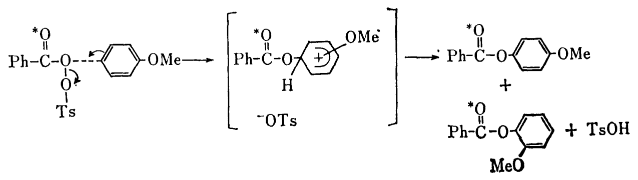
TABLE 2. ^{18}O ANALYSES IN THE BENZOYLOXYLATION OF ANISOLE WITH BTP [CARBONYL-^{18}O] IN THE PRESENCE AND ABSENCE OF MAGNESIUM OXIDE[a)]

Compound	Excess atom %		
	Found (with MgO)	Found (without MgO)	Calcd[b)]
BzNHPh (I)	1.20	1.20	(1.20)
BzOOTs (II)	0.23	0.24	0.24
BzN_2H_3 (III)	1.00	1.00	1.20
$BzOC_6H_4OMe$-o (IV)	0.42	0.41	0.40
$BzOC_6H_4OMe$-p (V)	0.39	0.37	0.40
BzN_2H_3 (VI)	0.53	0.61	0.60
BzN_2H_3 (VII)	0.51	0.71	0.60

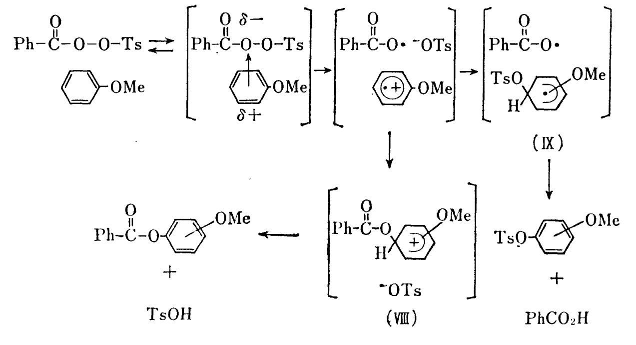
a) Experimental error in two measurements with the same sample was ±0.02 excess atom %.

b) Calculated on the assumption that the carbonyl oxygen is completely equilibrated with the ester oxygen.

It is clear that within experimental error the carbonyl oxygen of BTP is completely equilibrated between the carbonyl and phenoxy oxygens in anisyl benzoates (IV) and (V). These results are similar to those of the photochemical benzoyloxylation of benzene with BPO[8)] and $CuCl_2$-catalyzed benzoyloxylation of p-xylene with BPO.[12)] The results of the ^{18}O study reject the possibility of the electrophilic (S_N2 type) attack of the benzoyloxy oxygen on anisole.



Since the rate of decomposition of BTP in anisole is much greater than those in other solvents, some sort of interaction between BTP and anisole must exist. On the basis of all the results obtained so far, the following scheme seems to represent what is taking place in an anisole solution of BTP.



A charge-transfer complex is formed by donation of π-electrons of anisole to the antibonding orbital of the O–O bond of BTP, and the O–O bond scission is much accelerated by this electron donation. A related example is the enhancement of the homolysis rates of

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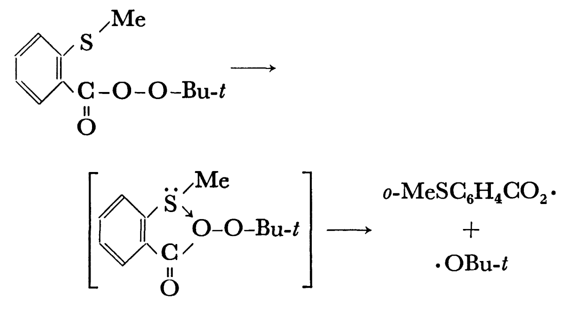
[11)] D. Rittenberg and L. Ponticorvo, *Int. J. Appl. Radiat. Isotopes*, **1**, 208 (1956).

[12)] C. G. Reid and P. Kovacic, *J. Org. Chem.*, **34**, 3308 (1969).

ortho substituted perbenzoates.[13]



$$\frac{k_{o\text{-MeS}}}{k_H} = 1 \times 10^4$$

The C. T. complex formed from BTP and anisole dissociates to give a trio of benzoyloxy radical, *p*-toluenesulfonate anion and anisole radical cation in cage. A one-electron transfer reaction of this kind is observed in the reaction of BPO with dimethylaniline.[14] Two processes are possible from the trio of benzoyloxy radical, *p*-toluenesulfonate anion and anisole radical cation; benzoyloxy radical and anisole radical cation may combine to form a benzenium ion (VIII), or *p*-toluenesulfonate anion and anisole radical cation may combine to form a cyclohexadienyl radical (IX).

When BTP was photolyzed in benzene under oxygen or nitrogen with a high pressure mercury lamp at 9°C for 5 hr, the results were similar to those shown in Table 1; under oxygen the yield of diphenyl is lower and the yields of phenyl benzoate and *p*-toluenesulfonate are greater. The results of the photolyses also support the hypothesis that benzoyloxylation and *p*-toluenesulfonyloxylation of arenes proceed by the free radical mechanism.

Experimental

Materials. Benzene and substituted benzenes were purified by the procedures described previously.[15] BTP and BTP[carbonyl-^{18}O] were prepared by the method described in the previous papers.[2,16]

Decomposition of BTP in Benzene, Toluene, Chlorobenzene, or Nitrobenzene with Suspended Magnesium Oxide under Nitrogen or Oxygen. A solution of BTP (4 mmol) in benzene, toluene, chlorobenzene, or nitrobenzene (50 m*l*) with suspended magnesium oxide (40 mmol) was stirred with a mechanical stirrer for 15 hr at 45°C. Throughout the reaction nitrogen or oxygen was bubbled in the reaction mixture. After the completion of the decomposition the internal standard samples for gas chromatographic analyses of the products were added to the mixture. After the magnesium oxide was filtered off, the filtrate was washed successively with a sodium hydrogen carbonate solution and water, and dried over anhydrous magnesium sulfate. It was concentrated under reduced pressure, and subjected to gas chromatographic analyses.

Decomposition of BTP in Anisole with Suspended Magnesium Oxide under Nitrogen or Oxygen. Nitrogen (or oxygen) was bubbled through a solution of BTP (4 mmol) in dichloromethane (10 m*l*) for 15 min. Nitrogen (or oxygen) was also bubbled through anisole (50 m*l*) with suspended magnesium oxide (40 mmol). Then, the BTP solution was added drop by drop with stirring into the anisole, and the mixture was stirred for 10 hr at 25°C with bubbling of nitrogen (or oxygen). The work-up procedure was the same as described above.

Gas Chromatography. The amounts of substituted diphenyls, aryl benzoates, and aryl *p*-toluenesulfonates produced were determined by a Hitachi Gas Chromatograph K-53, on the basis of the comparison with authentic samples. The columns and the internal standard samples used are described in Table 3.

Table 3. Conditions used for gas chromatographic analyses

Products (*o*, *m*, and *p* isomers)	Internal standards	Column[a]	Column length (m)	Temp (°C)
Ph_2	$(PhCH_2)_2$	(A)	1	190
$PhCO_2Ph$; TsOPh	*p*-$ClC_6H_4CO_2Ph$	(A)	1	210
PhC_6H_4OMe; $PhCO_2C_6H_4OMe$	*m*-$NO_2C_6H_4Ph$	(A)	3	210
$TsOC_6H_4OMe$	*p*-$MeOC_6H_4O_2CPh$	(B)	2	220
$PhC_6H_4CH_3$; $PhCO_2C_6H_4CH_3$	*β*-MeO-Naphthalene $PhCO_2Ph$	(A)	3	190
$TsOC_6H_4CH_3$	*p*-$ClC_6H_4O_2CPh$	(B)	2	220
PhC_6H_4Cl	$(PhCH_2)_2$	(A)	5	190
$PhCO_2C_6H_4Cl$	*m*-$CH_3C_6H_4O_2CPh$	(A)	2	230
		(B)	5	225
$TsOC_6H_4Cl$	*p*-$MeOC_6H_4OTs$	(A)	2	230
		(B)	3	235
$PhC_6H_4NO_2$	$(PhCH_2)_2$	(A)	2	190
$PhCO_2C_6H_4NO_2$	*m*-$MeOC_6H_4OTs$	(C)	3	200
$TsOC_6H_4NO_2$	*m*-$MeOC_6H_4OTs$	(C)	3	220

a) Column: (A), 10% Apiezon L on Chromosorb W. (B), 10% Silicone DC 550 on Chromosorb W. (C), 10% Silicone SE 30 on Chromosorb W.

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13) W. G. Bentrude and J. C. Martin, *J. Amer. Chem. Soc.*, **84**, 1561 (1962).

14) C. Walling, "Free Radicals in Solution," John Wiley & Sons, Inc., New York, N. Y. (1957), pp. 590—595, and the references cited therein.

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

16) R. Hisada, H. Minato, and M. Kobayashi, *ibid.*, **45**, 2814 (1972).

Decomposition of BTP[carbonyl-^{18}O] in Anisole in the Presence or Absence of Suspended Magnesium Oxide under Nitrogen. A solution of BTP[carbonyl-^{18}O] (12 mmol) in anisole (150 m*l*) was decomposed in the presence or absence of magnesium oxide (120 mmol), and the reaction mixture was washed successively with a sodium hydrogen carbonate solution and water, and dried over anhydrous magnesium sulfate. After the anisole was evaporated under reduced pressure, the residue was chromatographed on silica gel (Wako Gel Q 22). Phenyl *p*-toluenesulfonyl carbonate (in the absence of magnesium oxide), *o*- and *p*-anisyl benzoates and *o*- and *p*-anisyl *p*-toluenesulfonates were isolated, and identified by comparison of their infrared spectra with those of authentic samples. *o*-Anisyl and *p*-anisyl benzoates were recrystallized three times from *n*-hexane; mp 57—58°C (lit,[17] 58—59°C) and mp 86—87°C (lit,[18] 87.5—88.5°C), respectively.

Reaction of o-*Anisyl or* p-*Anisyl Benzoate with Anhydrous Hydrazine.* A mixture of *o*- or *p*-anisyl benzoate (*ca.* 300 mg) and anhydrous hydrazine (300 mg) in benzene (10 m*l*) was refluxed for 3 hr. After the benzene and unchanged hydrazine were evaporated under reduced pressure, the benzhydrazide produced were recrystallized three times from ether; mp 111—112°C (from *o*-anisyl benzoate) and mp 112°C (from *p*-anisyl benzoate) (lit,[19] 112.5°C).

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17) G. Cilento, *J. Org. Chem.*, **24**, 413 (1959).
18) G. Cilento, *J. Amer. Chem. Soc.*, **75**, 3748 (1953).
19) R. Stolle, *J. Prakt. Chem.*, **69**, 145 (1904).