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Studies of Organo Sulfur Compounds. II. The Preparation and Reactions of Benzoyl Benzenethiosulfonates

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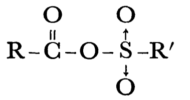
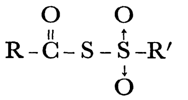
Some mixed sulfonic thiocarboxylic anhydrides (II, R, R′: Aryl) were obtained from the reactions of potassium substituted-thiobenzoate with benzene- or *p*-toluenesulfonyl chlorides. The reactions of benzoyl benzenethiosulfonate were examined in comparison with those of the corresponding mixed sulfonic carboxylic anhydrides.

Although a few reports[1–8] have been recorded on the mixed sulfonic carboxylic anhydride (I), there have been no reports for the mixed sulfonic thiocarboxylic anhydride (II). In this paper an attempt at the syntheses and reactions of mixed sulfonic carboxylic anhydride (II) will be described.



$$R\text{-}\overset{\overset{O}{\|}}{C}\text{-}O\text{-}\underset{\underset{O}{\downarrow}}{\overset{\overset{O}{\uparrow}}{S}}\text{-}R'$$

I

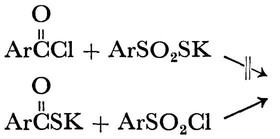


$$R\text{-}\overset{\overset{O}{\|}}{C}\text{-}S\text{-}\underset{\underset{O}{\downarrow}}{\overset{\overset{O}{\uparrow}}{S}}\text{-}R'$$

II

R, R′: Alkyl, Aryl

The reaction of benzoyl chloride with potassium *p*-toluenethiosulfonate gave no benzoyl *p*-toluenethiosulfonate. However, it was found that the reactions of potassium substituted thiobenzoate with benzene- or *p*-toluenesulfonyl chloride gave the corresponding aroyl benzenethiosulfonate (Eq. (1)). We attempted to react the mixed sulfonic thiocarboxylic anhydride thus obtained with several reagents (*cf.* Chart 1).



$$\begin{aligned}&Ar\overset{\overset{O}{\|}}{C}Cl + ArSO_2SK \not\searrow \\ &\qquad\qquad\qquad\qquad II \qquad (1)\\ &Ar\overset{\overset{O}{\|}}{C}SK + ArSO_2Cl \nearrow\end{aligned}$$

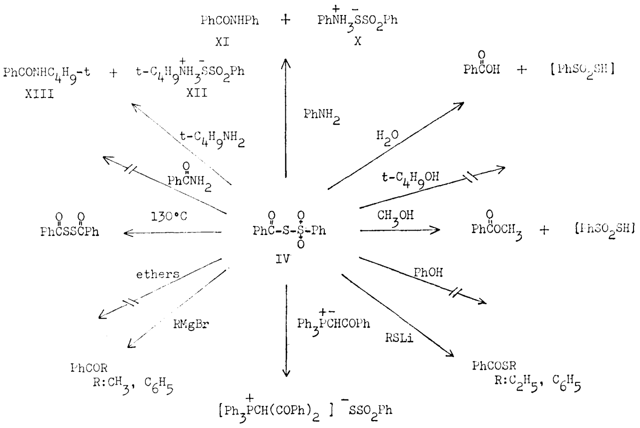


Chart 1. Reactions of benzoyl benzenethiosulfonate.

Results and Discussion

Potassium thiobenzoate and an equimolar amount of benzenesulfonyl chloride in dry acetonitrile (or THF) reacted exothermically. From the reaction mixture, benzoyl benzenethiosulfonate (IV), dibenzoyl disulfide (V), potassium benzenesulfonate (VI), benzoic anhydride, and potassium chloride were isolated in 31, 40, 20, trace, and 65% yields (based on the potassium thiobenzoate used) respectively. The structure IV was confirmed by the result of elemental analyses and by the IR spectrum. On the other hand, V and VI were identified by elemental analyses and by comparisons of the IR spectra with those of authentic samples. By an

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1) A. Fahlberg, *Chem. Ber.*, **22**, 757 (1889).

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5) H. Böhme and K. H. Meyer-Dulheuer, *Justus Liebigs, Ann. Chem.*, **688**, 78 (1965).

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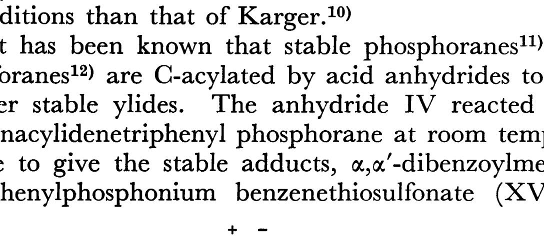
8) M. H. Karger and Y. M. Mazur, *J. Org. Chem.*, **36**, 528 (1971).

analogous treatment of potassium thiobenzoate with *p*-toluenesulfonyl chloride, and of potassium *p*-methylthiobenzoate with benzenesulfonyl chloride, *p*-methylbenzoyl benzenethiosulfonate (IX) and benzoyl *p*-toluenethiosulfonate (XI) were obtained in 22.9 and 20.5% yields respectively.

The thiosulfonates were a slightly yellow oil or a semi-solid which could not be crystallized and which showed a strong carbonyl absorption band at 1690 cm^{-1}. They were fairly stable under anhydrous conditions below 130°C,[9] but were hydrolyzed by moisture when the THF solution was stood in air at room temperature; the absorption at 1690 cm^{-1} disappeared completely after 6 hr. Furthermore, the addition of a few drops of water to IV, IX, and XI accelerated their decomposition.

One of the most interesting reactivities of these anhydrides is their ability as acylating reagents. Benzoyl benzenethiosulfonate (VI) reacted with aniline exothermally in ether to give benzanilide (VIII) and anilinium benzenethiosulfonate (VIII) quantitatively. Furthermore, the reaction of IV with *n*-, or *t*-butylamine gave *N*-*n*(or *t*)-butylbenzamide (XVI or XIII), and *n*(or *t*)-butylammonium benzenethiosulfonate (XV or XIII) in good yields, respectively. However in contrast to benzoyl benzenesulfonate,[3] it did not react with phenol, *t*-butyl alcohol and benzamide. Recently, Karger and Mazur[10] have reported the powerful acylating ability of mixed sulfonic carboxylic anhydrides or the basis of their facile cleavage of ethers (*n*-butyl ether, benzyl ether, THF, *etc*). However, the reactions of IV with propylene oxide, tetrahydrofuran, tetrahydropyran, 1,4-dioxane, dibenzyl ether, and di-*n*-butyl ether did not occur even under more severe conditions than that of Karger.[10]

It has been known that stable phosphoranes[11] and sulforanes[12] are C-acylated by acid anhydrides to give other stable ylides. The anhydride IV reacted with phenacylidenetriphenyl phosphorane at room temperature to give the stable adducts, α,α′-dibenzoylmethyltriphenylphosphonium benzenethiosulfonate (XVIII),

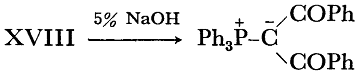


$$\mathrm{PhCOSSO_2Ph} + \mathrm{Ph_3\overset{+}{P}\text{-}\overset{-}{C}HCOPh} \xrightarrow[\mathrm{CH_2Cl_2}]{\mathrm{rt}} \left[\mathrm{Ph_3\overset{+}{P}\text{-}CH}\begin{matrix}\mathrm{COPh}\\ \mathrm{COPh}\end{matrix}\right]\overset{-}{\mathrm{SSO_2Ph}} \qquad (2)$$

IV

XVIII

in a 56% yield (Eq. (2)). The XVIII structure was confirmed by elemental analyses by the IR spectrum, which a strong new peak at 1670 cm^{-1} due to carbonyl stretching, and the formation of α,α′-dibenzoylmethyltriphenyl phosphorane (XIX) through a reaction with 5% aqueous sodium hydroxide (Eq. (3)):



$$\mathrm{XVIII} \xrightarrow{5\%\ \mathrm{NaOH}} \mathrm{Ph_3\overset{+}{P}\text{-}\overset{-}{C}}\begin{matrix}\mathrm{COPh}\\ \mathrm{COPh}\end{matrix} \qquad (3)$$

XIX

Moreover, the anhydride (IV) in petroleum ether reacted exothermally with methyl- and phenylmagnesium bromide to give acetophenone (41%), and benzophenone (46%) respectively. In addition, the treatment of the anhydrides (IV) with lithium ethane- and benzenethiolate gave 52% of *S*-ethyl thiobenzoate and 33% of *S*-phenyl thiobenzoate.

Experimental

All the melting points are uncorrected. The IR spectra were measured on a JASCO Grating Infra-red spectrophotometer IR–G.

Materials. Benzene- and *p*-toluenesulfonyl chloride were purified by distillation before use. The potassium substituted thiobenzoate was prepared according to the directions in the literature.[13] The phenacylidenetriphenyl phosphorane was prepared according to the procedure of Ramirez and Dershowitz;[14] mp 185.2—186.5°C. The solvents were rigorously dried and distilled before use.

Reactions and the manipulations of the samples were carried out under dry nitrogen.

Benzoyl Benzenethiosulfonate (IV). A suspended solution of potassium thiobenzoate (8.4 g, 0.05 mol) in acetonitrile (100 ml) was added to a solution of benzenesulfonyl chloride (8.4 g, 0.05 mol) in acetonitrile (50 ml), after which the mixture was stirred for 5 hr at room temperature. After the acetonitrile had been evaporated from the organic layer, the residue was washed with two 20 ml portions of dichloromethane.

The concentration of the washings and subsequent chromatographic separation on silica gel [*n*-hexane–ether (9.5: 0.5)] under dark conditions gave 6.3 g (30.6%) of IV from the second effluent, which showed one spot on thin-layer chromatography. IR (neat): ν C=O 1690 cm^{-1}, ν SO_2 1382 (asym) and 1180 (sym) cm^{-1}, Found: C, 56.01; H, 3.42; S, 22.60%. Calcd for $C_{13}H_{10}O_3S_2$: C, 56.11; H, 3.30; S, 22.90%. An effluent insoluble in the dichloromethane insoluble parts were recrystallized from benzene–*n*-hexane to give 3.6 g of dibenzoyl disulfide (V) as colorless crystals. The melting point, the result of sulfur analysis, and the IR spectrum coincided exactly with those of an authentic sample obtained by the reaction of potassium thiobenzoate with iodine. Mp 134—135°C, IR (KBr): ν C=O 1700 and 1680 cm^{-1}, Found: S, 25.70% (Calcd for $C_{14}H_{10}O_2S_2$: S, 26.06%). On the other hand, the acetonitrile insoluble parts (solid) was extracted with five 30 ml portions of hot methanol. The subsequent evaporation of the methanol from the extracts left 4 g (25% based on the benzenesulfonyl chloride used) of potassium benzenesulfonate (VI). The results of elemental analyses and the spectrum were identical with those of an authentic sample prepared from benzenesulfonic acid and potassium hydroxide. IR (KBr): ν SO_2 1200 and 1190 cm^{-1}. Found: C, 35.62; H, 2.63; S, 14.49% (Calcd for $C_6H_5O_3SK$: C, 35.58; H, 2.50; S, 14.24%). The methanol insoluble part contains 95% KCl, as determined by Standard Volhard potentiometric titration (65%, based on the potassium thio-

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[9] Heating of IV in glass ampoule at 150°C for 3 hr under nitrogen atmosphere gave a 63% of dibenzoyl disulfide together with intractable oil.

[10] M. H. Karger and Y. M. Mazur, *J. Org. Chem.*, **36**, 532 (1971).

[11] P. A. Chopard, R. J. G. Searle, and F. H. Devitt, *ibid.*, **30**, 1015 (1965).

[12] a) H. Nozaki, M. Takaku, and K. Kondo, *Tetrahedron*, **22**, 2145 (1966). b) A. W. Johnson, and R. T. Amel, *J. Org. Chem.*, **34**, 1240 (1969).

[13] P. Noble and D. S. Tarbell, "Organic Syntheses" Coll. Vol. IV, p. 924.

[14] F. Ramirez and S. Dershowitz, *J. Org. Chem.*, **22**, 41 (1957).

benzoate used).

p-Methylbenzoyl Benzenethiosulfonate (VII). Yield, 22.9%: IR (neat) ν C=O 1691 cm^{-1}, ν SO$_2$ 1388 (asym) and 1190 (sym) cm^{-1}. Found: C, 57.44; H, 4.01; S, 21.74%. Calcd for $C_{14}H_{12}O_3S_2$: C, 57.39; H, 4.19; S, 21.90%.

Benzoyl p-Toluenethiosulfonate (VIII). Yield 20.5%: IR (neat) ν C=O 1691 cm^{-1}, ν SO$_2$ 1385 (asym) and 1197 (sym) cm^{-1}. Found: C, 57.50; H, 4.20; S, 21.98%. Calcd for $C_{14}H_{12}O_3S_2$: C, 57.39; H, 4.19; S, 21.90%.

Reaction of the Anhydride IV with Methanol. A methanol solution (20 ml) of IV (1.08 g, 0.04 mol) was refluxed for 10 hr. After the evaporation of the excess methanol from the reaction mixture, vacuum distillation of the residue gave 0.3 g (41% based on the IV used) of methyl benzoate (IX): bp 55°C/0.04 mmHg. The IR spectrum was identical with that of an authentic sample. The treatment of the distillation residue with 4 ml of aqueous 5% potassium hydroxide, the evaporation of the water from the reaction mixture, and subsequent recrystallization of the evaporation residue from methanol gave 0.3 g (96%) of potassium benzenesulfonate, which was identified by a comparison of the IR spectrum with that of an authentic sample.

Reaction of Benzoyl Benzenethiosulfonate (IV) with Aniline. When a solution of 0.4 g (0.04 mol) of aniline in 2 ml of ether was added to a solution of 0.56 g (0.002 mol) of IV in 10 ml of ether, the reaction began immediately and gave the precipitates. After the reaction mixture had been stirred at room temperature for 10 min, the insoluble parts were filtered out and washed four times with 3 ml portions of hot ether to give 0.45 g (50.5% based on the IV used) of anilinium benzenethiosulfonate (X), mp 171—172°C. IR (KBr): ν-NH$_3$ 3100 cm^{-1} (strong, broad absorption), 1540 cm^{-1}, ν SO$_2$ 1160 and 1038 cm^{-1}. Found: C, 54.12; H, 4.80; N, 5.11; S, 23.94%. Calcd for $C_{12}H_{13}NO_2S_2$: C, 54.14; H, 4.89; N, 4.89; S, 24.00%. The structure X was comfirmed by elemental analyses and by the IR spectrum. From the ether soluble parts, a 1.3 g portion of benzanilide (XI, mp 162.5—163.5°C) was obtained. The mp and IR spectrum were identical with those of the commercially obtained compound.

Reaction of the Anhydride IV with t-Butylamine. A solution of 0.29 g (0.04 mol) of *t*-butylamine in 2 ml of ether was added to a solution of 0.56 g (0.002 mol) of IV in 10 ml of ether and the mixture was stirred at room temperature for 15 min. The precipitates were filtered, washed four times with 3 ml portions of ether, and recrystallized from ethanol to give 0.37 g (79%, based on the IV used) of *t*-butylammonium benzenethiosulfonate (XII) as colorless crystals. Mp 196—197°C, IR (KBr): ν-NH$_3$ 3100 cm^{-1} (strong, broad absorption), ν SO$_2$ 1185 and 1050 cm^{-1}. Found: C, 50.93; H, 7.03; N, 5.48; S, 26.84%. Calcd for $C_{10}H_{17}NO_2S_2$: C, 50.84; H, 7.20; N, 5.51; S, 27.12%. The XII structure was comfirmed by elemental analyses and by the IR spectrum. From the ether-soluble parts, 0.29 g (81%, based on the IV used) of *N-t*-butylbenzamide (XIII) was obtained. Mp 128—129°C, IR (KBr), ν NH 3300 cm^{-1}, ν C=O 1630 cm^{-1}. The mp and the IR spectrum were identical with those of an authentic sample prepared from benzoyl chloride and *t*-butylamine.

Reaction of the Anhydride IV with n-Butylamine. An analogous treatment of IV (0.002 mol) with *n*-butylamine (0.004 mol) gave 0.32 g (68%, based on the IV used) of *n*-butylammonium benzenethiosulfonate (XV) and 0.3 g (78%, based on the IV used) of *N-n*-butylbenzamide (XVI). XV: mp 168—170°C, IR (KBr), ν-NH$_3$ 3100 cm^{-1} (strong-broad absorption), ν SO$_2$ 1170 and 1040 cm^{-1}. Found: C, 50.62; H, 7.12; N, 5.44; S, 27.03%. Calcd for $C_{10}H_{17}NO_2S_2$: C, 50.48; H, 7.20; N, 5.51; S, 27.12%. XVI: mp 69—71°C, IR (KBr), ν NH 3300 cm^{-1}, ν C=O 1630 cm^{-1}. The mp and the IR spectrum were identical with that of an authentic sample prepared from benzoyl chloride and *n*-butylamine.

Reaction of the Anhydride IV with Phenol. A mixture of IV (0.52 g, 0.002 mol) and phenol (0.18 g, 0.002 mol) was heated in a glass ampoule at 100°C for 20 hr. Phenol (0.17 g, 92%) was subsequently recovered from the mixture by distillation.

Reaction of Anhydride IV with Benzamide. A solution of benzamide (0.94 g, 0.008 mol) and IV (1.04 g, 0.004 mol) in ether (30 ml) was refluxed for 24 hr. The subsequent concentration of the reaction mixture gave 0.88 g of colorless crystals; was 94% of the recovered benzamide. The mp and the IR spectrum of the crystal consisted with those of benzamide obtained commercially.

Hydrolysis of the Anhydride IV. A benzene-solution (20 ml) of IV (1.05 g, 0.004 mol) was stirred for 6 hr at room temperature. After the evaporation of the solvent from the reaction mixture, the extraction of the residue with small portions of hot water and the cooling of the extracts gave 0.3 g of benzoic acid (XVII); mp 121—123°C.

On the other hand, the treatment of the hot water insoluble parts with 5 ml of aqueous potassium hydroxide gave 0.6 g of potassium *p*-toluenesulfonate.

Reaction of the Anhydride IV with Phenacylidenetriphenyl Phosphorane. A solution of 1.52 g (0.004 mol) of phenacylidenetriphenyl phosphorane and 1.05 g (0.004 mol) of IV dissolved in 10 ml of dichloromethane (1.05 g, 0.004 mol) was stirred for 12 hr at room temperature. After the subsequent concentration of the reaction mixture, the residue was crystallized from a small portion of acetone, subsequent recrystallization from dichloromethane–acetone containing minimum amount of *n*-hexane gave 1.5 g (56%) of α,α'-dibenzoylphenacyltriphenylphosphonium benzenethiosulfonate (XVIII) as slightly yellow crystals; mp 245—247°C, IR (KBr): ν C=O 1670 cm^{-1}. Found: C, 71.53; H, 4.74; P, 4.60; S, 9.61%. Calcd for $C_{39}H_{31}O_4PS_2$: C, 71.69; H, 4.71; P, 4.58; S, 9.60%.

Treatment of α,α'-Dibenzoylmethyl Triphenylphosphonium Benzenethiosulfonate (XVIII) with Base. The treatment of XVIII (1.3 g, 0.02 mol) with an aqueous 5% sodium hydroxide solution according to the usual method gave 0.86 g (85%) of α,α'-dibenzoylmethyl triphenylphosphorane (XIX), which was identified by a comparison of the mp and the IR spectrum with those of an authentic sample prepared according to the literature;[14] mp 191—193°C, IR (KBr) ν C=O 1520 cm^{-1}.

The Reaction of the Anhydride IV with Grignard Reagents.

a) Methylmagnesium Bromide: An ether solution of methylmagnesium bromide (0.01 mol) was added to an equimolar amount (2.8 g) of IV in the same solvent (10 ml) at 0°C, and the mixture was stirred at room temperature for 30 min. After the removal of the insoluble parts from the reaction mixture by filtration, the vacuum evaporation of the solvent from the filtrate and the distillation of the residue gave 0.49 g of acetophenone, bp 201—202°C (lit,[15] 202°C), IR (neat) ν C=O 1680 cm^{-1}. The boiling point and the IR spectrum coincided with those of an authentic sample which had been obtained commercially.

b) Phenylmagnesium Bromide. The similar treatment of the anhydride IV with phenylmagnesium bromide gave 0.83 g of benzophenone, bp 99°C/0.2 mmHg (lit,[16] 108°C/1 mmHg), IR (CCl$_4$) ν C=O 1664 cm^{-1}. The IR spectrum was quite similar to that of an authentic sample.

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[15] "The Merck Index" 7 ed. Merck and Co. INC. p. 9 (1960).

[16] *ibid.*, p. 134 (1960).

Treatment of the Anhydride IV with Thiolates. *a) Lithium Ethanethiolate*: An ether solution of IV (2.78 g, 0.01 mol) was slowly added to a petroleum ether solution of lithium ethanethiolate (0.01 mol), which had been prepared from *n*-butyllithium and ethanethiol, at 0°C, and the mixture was stirred at room temperature for 1 hr. After filtrating the insoluble parts had been filtered from the reaction mixture, the evaporation of the solvent and vacuum distillation gave 0.85 g of *S*-ethyl thiobenzoate. Bp 79—80°C/2 mmHg (lit,[17] 83—84°C/2.5 mmHg). IR (neat) ν C=O 1669 cm^{-1}. The IR spectrum was identical with that of an authentic sample prepared from benzoyl chloride and lithium ethanethiolate.

b) Lithium Benzenethiolate: A similar treatment of IV (0.01 mol) with lithium benzenethiolate (0.01 mol) in petroleum ether gave *S*-phenyl thiobenzoate (0.69 g), mp 55—58°C (lit,[18] 56°C), IR (KBr) ν C=O 1685 cm^{-1}. The IR spectral data was quite similar to that of an authentic sample prepared from benzoyl chloride and lithium benzenethiolate in petroleum ether.

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