BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 45, 2930—2932 (1972)

The Preparation of Acyl Alkoxycarbonyl Sulfides and the Related Compounds

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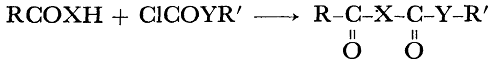
(Received November 19, 1971)

A number of mixed carboxylic carbonic anhydrides (**1**) were prepared by the reaction of carboxylic acid and chloroformate in a series of studies by Tarbell.[1] *p*-Nitrobenzoic thiolcarbonic anhydrides (**3**), the sulfur analogue of the mixed anhydride, were prepared from *p*-nitrobenzoic acid and thiolchloroformate more recently.[2] In the present paper, the preparation of another types of sulfur analogues of the mixed anhydride such as acyl alkoxycarbonyl sulfides (**2**) and acyl alkylthiocarbonyl sulfides (**4**) is described.[3]



$$\mathrm{RCOXH + ClCOYR' \longrightarrow R\text{-}\underset{\displaystyle O}{\underset{\|}{C}}\text{-}X\text{-}\underset{\displaystyle O}{\underset{\|}{C}}\text{-}Y\text{-}R'}$$

1: X=O, Y=O **3**: X=O, Y=S
2: X=S, Y=O **4**: X=S, Y=S

First, acyl alkoxycarbonyl sulfides (**2a**—**f**) were pre-

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[1] D. S. Tarbell and J. A. Price, *J. Org. Chem.*, **21**, 144 (1956), and the later papers.

[2] D. S. Tarbell and T. Parasaran, *ibid.*, **29**, 2471 (1964); L. Wei and D. S. Tarbell, *ibid.*, **33**, 1884 (1968).

[3] During the course of the present work, H. Yoshida, T. Ogata, and S. Inokawa reported the synthesis of **4** starting from tetramethylammonium dithiolcarbonate [This Bulletin, **44**, 1949 (1971)] and H. Böhme and H. P. Steudel reported the synthesis of **2** starting from potassium *O*-alkyl thiolcarbonate [*Ann.*, **730**, 121 (1969)].

Table 1. Acyl alkoxycarbonyl sulfides; RCOSCOOR′

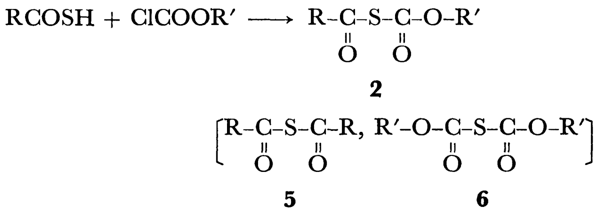
Compound	R	R′	Bp (°C/mmHg)	Yield (%)	Found (%) C	Found (%) H	Found (%) S	Calcd (%) C	Calcd (%) H	Calcd (%) S
2a	CH_3	CH_3	60—61/6	23	35.37	4.50	23.44	35.81	4.51	23.90
2b	CH_3	C_2H_5	63—65/5	23	41.07	5.55	21.20	40.53	5.44	21.64
2c	CH_3	n-C_3H_7	52—53/1	26	44.95	6.23	20.11	44.43	6.21	19.77
2d	CH_3	i-C_4H_9	66.5—67/1.5	24	47.81	6.81	18.03	47.71	6.86	18.19
2e	C_2H_5	n-C_3H_7	63.5—64.5/1.5	30	47.95	6.79	17.92	47.71	6.86	18.19
2f	C_2H_5	i-C_4H_9	65—66/1	13	50.90	7.41	16.68	50.50	7.42	16.85

Table 2. Diacyl sulfides and bis(alkoxycarbonyl)sulfides

Diacyl sulfides, $(RCO)_2S$				Bis(alkoxycarbonyl)sulfides, $(R'OCO)_2S$						
Compound	R	Bp (°C/mmHg)	Yield[a] (%)	Compound	R′	Bp (°C/mmHg)	Yield[a] (%)	Found (Calcd) C(%)	Found (Calcd) H(%)	Found (Calcd) S(%)
5a	CH_3	38—39.5/5 (lit, 63/20)	45	**6a**	CH_3	79.5/7 (mp 34—35)	35	31.72 (32.00)	4.29 (4.03)	21.10 (21.35)
5b			45	**6b**	C_2H_5	87—88/4.5 (lit, 118/22)	47	40.75 (40.44)	5.71 (5.66)	18.01 (17.99)
5c			27	**6c**	n-C_3H_7	87—88/1.5	22	46.64 (46.59)	6.60 (6.84)	15.68 (15.55)
5d			39	**6d**	i-C_4H_9		21			
5e	C_2H_5	54—55/3	36	**6e**	n-C_3H_7		23			
5f			66	**6f**	i-C_4H_9	87—93/1	52	51.48 (51.26)	7.49 (7.74)	13.72 (13.68)

[a] Calculated based on the assumption that these compounds were formed by the decomposition of **2** according to the following reaction; 2 RCOSCOOR′ ⟶ $(RCO)_2S+(R'OCO)_2S$, [*Ann.*,**730**, 121 (1969)].

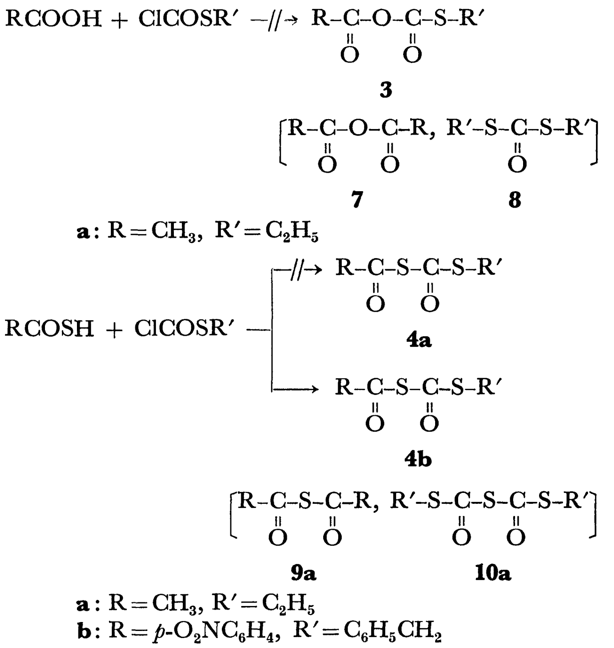
pared from thiocarboxylic acid and alkyl chloroformate in THF at −50°C in the presence of triethylenediamine (Table 1). In the preparation, diacyl sulfides (**5a**—**f**) and bis(alkoxycarbonyl)sulfides (**6a**—**f**) were isolated as by-products (Table 2). The NMR spectra and the analytical values were in accord with the expected structure for **2a**—**f** and **6a**—**f** (Tables 1 and 2) and the IR spectra of **2a**—**f** showed the double peaks (about 1780 and 1720 cm^{-1}) in the carbonyl region which resemble closely the typical anhydride absorption. Butyryl methoxycarbonyl sulfide (**2g**) and butyryl ethoxycarbonyl sulfide (**2h**) were not isolated because the boiling point was very close to those of the by-products. When triethylamine was used in the reaction instead of triethylenediamine, **2** was not obtained but **5** and **6** were formed. *p*-Nitrobenzoyl benzyloxycarbonyl sulfide (**2i**) was obtained as pale yellow crystals by a similar procedure, accompanied by no bis(*p*-nitrobenzoyl)sulfide (**5i**) or bis(benzyloxycarbonyl)sulfide (**6i**) as by-products.



$$RCOSH + ClCOOR' \longrightarrow R\text{-}\underset{O}{\underset{\|}{C}}\text{-}S\text{-}\underset{O}{\underset{\|}{C}}\text{-}O\text{-}R' \quad \mathbf{2}$$

$$\left[R\text{-}\underset{O}{\underset{\|}{C}}\text{-}S\text{-}\underset{O}{\underset{\|}{C}}\text{-}R,\ R'\text{-}O\text{-}\underset{O}{\underset{\|}{C}}\text{-}S\text{-}\underset{O}{\underset{\|}{C}}\text{-}O\text{-}R'\right] \quad \mathbf{5} \quad \mathbf{6}$$

a: $R=CH_3$, $R'=CH_3$ **e**: $R=C_2H_5$, $R'=n\text{-}C_3H_7$
b: $R=CH_3$, $R'=C_2H_5$ **f**: $R=C_2H_5$, $R'=i\text{-}C_4H_9$
c: $R=CH_3$, $R'=n\text{-}C_3H_7$ **i**: $R=p\text{-}O_2NC_6H_4$,
d: $R=CH_3$, $R'=i\text{-}C_4H_9$ $R'=C_6H_5CH_2$



$$RCOOH + ClCOSR' \not\longrightarrow R\text{-}\underset{O}{\underset{\|}{C}}\text{-}O\text{-}\underset{O}{\underset{\|}{C}}\text{-}S\text{-}R' \quad \mathbf{3}$$

$$\left[R\text{-}\underset{O}{\underset{\|}{C}}\text{-}O\text{-}\underset{O}{\underset{\|}{C}}\text{-}R,\ R'\text{-}S\text{-}\underset{O}{\underset{\|}{C}}\text{-}S\text{-}R'\right] \quad \mathbf{7} \quad \mathbf{8}$$

a: $R=CH_3$, $R'=C_2H_5$

$$RCOSH + ClCOSR' \not\longrightarrow R\text{-}\underset{O}{\underset{\|}{C}}\text{-}S\text{-}\underset{O}{\underset{\|}{C}}\text{-}S\text{-}R' \quad \mathbf{4a}$$

$$RCOSH + ClCOSR' \longrightarrow R\text{-}\underset{O}{\underset{\|}{C}}\text{-}S\text{-}\underset{O}{\underset{\|}{C}}\text{-}S\text{-}R' \quad \mathbf{4b}$$

$$\left[R\text{-}\underset{O}{\underset{\|}{C}}\text{-}S\text{-}\underset{O}{\underset{\|}{C}}\text{-}R,\ R'\text{-}S\text{-}\underset{O}{\underset{\|}{C}}\text{-}S\text{-}\underset{O}{\underset{\|}{C}}\text{-}S\text{-}R'\right] \quad \mathbf{9a} \quad \mathbf{10a}$$

a: $R=CH_3$, $R'=C_2H_5$
b: $R=p\text{-}O_2NC_6H_4$, $R'=C_6H_5CH_2$

Although *p*-nitrobenzoic thiolcarbonic anhydrides (**3**) were already prepared by Tarbell,[2)] preparation of acetic ethylthiolcarbonic anhydride (**3a**) was unsuccessful in the present study, and the reaction in the presence of triethylamine afforded acetic anhydride (**7a**) and diethyl dithiolcarbonate (**8a**).

Similarly, *p*-nitrobenzoyl benzylthiocarbonyl sulfide (**4b**) was obtained from *p*-nitrothiobenzoic acid and benzyl thiolchloroformate but acetyl ethylthiocarbonyl sulfide (**4a**) was not obtained from thioacetic acid and ethyl thiolchloroformate. Diacetyl sulfide (**9a**) and bis(ethylthiocarbonyl)sulfide (**10a**)[4] were formed as by-products.

Experimental

Materials. Thioacetic acid was obtained commercially. Thiopropionic acid was prepared by the method of Kitamura.[5] *p*-Nitrothiobenzoic acid prepared by the method of Khaletskii and Yanovitskaya[6] was recrystallized from *n*-hexane, mp 94—95°C (lit,[7] mp 94°C).

Methyl, ethyl, isobutyl, and benzyl chloroformates obtained commercially were purified by distillation. *n*-Propyl chloroformate and benzyl thiolchloroformate were prepared by the method of Tarbell and Longosz.[8]

Commercially available triethylenediamine was used after sublimation.

Acyl Alkoxycarbonyl Sulfides (2a—f). To a cooled solution of 0.1 mol of triethylenediamine in 500 m*l* of anhydrous THF, 0.2 mol of thiocarboxylic acid was added slowly. After cooling the mixture to −50°C, 0.2 mol of alkyl chloroformate was added dropwise over a period of 1 hr with vigorous stirring. The stirring was continued for additional 2 hr and then the temperature of the mixture was allowed to rise to −10°C. The amine hydrochloride was removed by filtration, and the THF was evaporated under reduced pressure. Fractional distillation of the residue gave acyl alkoxycarbonyl sulfide (**2a**—**f**), diacyl sulfide (**5a**—**f**) and bis(alkoxycarbonyl)sulfide (**6a**—**f**). The results are shown in Tables 1 and 2.

p-*Nitrobenzoyl Benzyloxycarbonyl Sulfide (2i).* To a solution of 3.66 g (0.02 mol) of *p*-nitrothiobenzoic acid and 3.41 g (0.02 mol) of benzyl chloroformate in 200 m*l* of anhydrous ether, 1.12 g (0.01 mol) of triethylenediamine in a mixture of 20 m*l* of ether and 10 m*l* of THF was added dropwise over a period of 1 hr with vigorous stirring at −60°C. The stirring was continued for additional 3 hr and then the temperature of the mixture was allowed to rise to 10°C. The amine hydrochloride was filtered, and the solvent was evaporated at room temperature. Recrystallization of the solid residue from chloroform-petroleum ether yielded 2.83 g (45%) of **2i** as pale yellow needles, mp 92—94°C.

Found: C, 56.92; H, 3.57; N, 4.50; S, 10.11%. Calcd for $C_{15}H_{11}O_5NS$: C, 56.78; H, 3.49; N, 4.41; S, 10.10%. IR ($CHCl_3$) cm^{-1}: 1766, 1694 (>C=O).

p-*Nitrobenzoyl Benzylthiocarbonyl Sulfide (4b).* This sulfide was prepared from 3.66 g (0.02 mol) of *p*-nitrothiobenzoic acid, 3.73 g (0.02 mol) of benzyl thiolchloroformate and 1.12 g (0.01 mol) of triethylenediamine in 200 m*l* of THF in a similar way to the preparation of **2i**. After removing the THF, the residue was filtered to yield 2.83 g of solid material which melted at 60—130°C. Petroleum ether (500 m*l*) was added to the solid. The mixture was refluxed for short time, and filtered to remove insoluble material. Cooling the filtrate gave 0.65 g (10%) of **4b** as pale yellow needles, mp 72—73°C with decomposition.

Found: C, 54.04; H, 3.32; N, 4.19; S, 19.27%. Calcd for $C_{15}H_{11}O_4NS_2$: C, 54.04; H, 3.33; N, 4.20; S, 19.24%. IR ($CHCl_3$) cm^{-1}: 1731, 1690, 1646 (>C=O).

Recrystallization of the insoluble material from toluene gave 0.70 g (21%) of bis(*p*-nitrobenzoyl)sulfide (**9b**) as yellow needles, mp 135.5—137°C.

Found: C, 50.63; H, 2.42; N, 8.36; S, 9.52%. Calcd for $C_{14}H_8O_6N_2S$: C, 50.60; H, 2.43; N, 8.43; S, 9.65%.

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[4] Bp 108—109°C/1 mmHg, Found: C, 34.62; H, 4.85; S, 45.30%. Calcd for $C_6H_{10}O_2S_3$: C, 34.25; H, 4.79; S, 45.75%.

[5] R. Kitamura, *Yakugaku Zasshi*, **57**, 31 (1937).

[6] A. M. Khaletskii and A. M. Yanovitskaya, *Zh. Obshch. Khim.*, **19**, 1193 (1949).

[7] F. J. Ritter, Rubber-Stichting, Delft, Commun., No. **324**, (1956) 130 pp.; *Chem. Abstr.*, **50**, 16168 (1956).

[8] D. S. Tarbell and E. J. Longosz, *J. Org. Chem.*, **24**, 774 (1959).