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The Preparation of Acyl Alkoxycarbonyl Sulfides and the Related Compounds

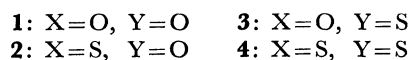
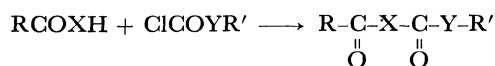
Shinichi MOTOKI and Hikaru SATSUMABAYASHI

Department of Chemistry, Faculty of Science, Science University of Tokyo, Kagurazaka, Shinjuku-ku, Tokyo

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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⁾



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

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'

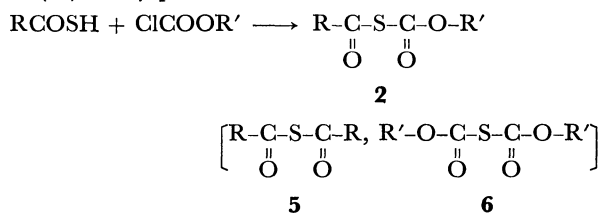
Compound	R	R'	Bp (°C/mmHg)	Yield (%)	Found (%)			Calcd (%)		
					C	H	S	C	H	S
2a	CH ₃	CH ₃	60—61/6	23	35.37	4.50	23.44	35.81	4.51	23.90
2b	CH ₃	C ₂ H ₅	63—65/5	23	41.07	5.55	21.20	40.53	5.44	21.64
2c	CH ₃	<i>n</i> -C ₃ H ₇	52—53/1	26	44.95	6.23	20.11	44.43	6.21	19.77
2d	CH ₃	<i>i</i> -C ₄ H ₉	66.5—67/1.5	24	47.81	6.81	18.03	47.71	6.86	18.19
2e	C ₂ H ₅	<i>n</i> -C ₃ H ₇	63.5—64.5/1.5	30	47.95	6.79	17.92	47.71	6.86	18.19
2f	C ₂ H ₅	<i>i</i> -C ₄ H 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

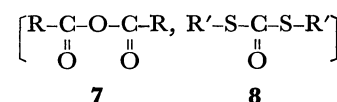
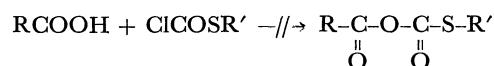
Diacyl sulfides, (RCO) ₂ S				Bis(alkoxycarbonyl)sulfides, (R'OCO) ₂ S						
Compound	R	Bp (°C/mmHg)	Yield ^{a)} (%)	Compound	R'	Bp (°C/mmHg)	Yield ^{a)} (%)	Found (Calcd)		
								C(%)	H(%)	S(%)
5a	CH ₃	38—39.5/5 (lit, 63/20)	45	6a	CH ₃	79.5/7 (mp 34—35)	35	31.72 (32.00)	4.29 (4.03)	21.10 (21.35)
5b			45	6b	C ₂ H ₅	87—88/4.5 (lit, 118/22)	47	40.75 (40.44)	5.71 (5.66)	18.01 (17.99)
5c			27	6c	<i>n</i> -C ₃ H ₇	87—88/1.5	22	46.64 (46.59)	6.60 (6.84)	15.68 (15.55)
5d			39	6d	<i>i</i> -C ₄ H ₉		21			
5e	C ₂ H ₅	54—55/3	36	6e	<i>n</i> -C ₃ H ₇		23			
5f			66	6f	<i>i</i> -C ₄ H 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; $2 \text{ RCOSCOOR}' \longrightarrow (\text{RCO})_2\text{S} + (\text{R}'\text{OCO})_2\text{S}$, [Ann., **730**, 121 (1969)].

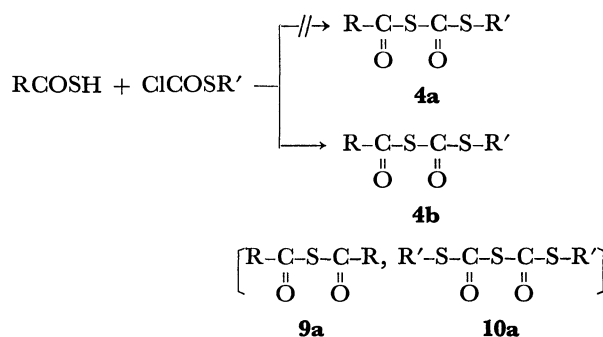
pared from thiocarboxylic acid and alkyl chloroformate in THF at -50°C in the presence of triethylenediamine (Table 1). In the preparation, diacyl sulfides (**5a—f**) and bis(alkoxycarbonyl)sulfides (**6a—f**) were isolated as by-products (Table 2). The NMR spectra and the analytical values were in accord 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 benzoyloxycarbonyl sulfide (**2i**) was obtained as pale yellow crystals by a similar procedure, accompanied by no bis(*p*-nitrobenzoyl)sulfide (**5i**) or bis(benzoyloxycarbonyl)sulfide (**6i**) as by-products.



a: R = CH₃, R' = CH₃ **e:** R = C₂H₅, R' = *n*-C₃H₇
b: R = CH₃, R' = C₂H₅ **f:** R = C₂H₅, R' = *i*-C₄H₉
c: R = CH₃, R' = *n*-C₃H₇ **i:** R = *p*-O₂NC₆H₄,
d: R = CH₃, R' = *i*-C₄H₉ R' = C₆H₅CH₂



a: R = CH₃, R' = C₂H₅



a: R = CH₃, R' = C₂H₅

b: R = *p*-O₂NC₆H₄, R' = C₆H₅CH₂

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 Yanovitskaya⁶ 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 Alkoxy carbonyl Sulfides (2a–f). To a cooled solution of 0.1 mol of triethylenediamine in 500 ml 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

alkoxy carbonyl sulfide (**2a–f**), diacyl sulfide (**5a–f**) and bis(alkoxy carbonyl)sulfide (**6a–f**). The results are shown in Tables 1 and 2.

***p*-Nitrobenzoyl Benzylloxycarbonyl 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 ml of anhydrous ether, 1.12 g (0.01 mol) of triethylenediamine in a mixture of 20 ml of ether and 10 ml 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 C₁₅H₁₁O₅NS: C, 56.78; H, 3.49; N, 4.41; S, 10.10%. IR (CHCl₃) 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 ml 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 ml) 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 C₁₅H₁₁O₄NS₂: C, 54.04; H, 3.33; N, 4.20; S, 19.24%. IR (CHCl₃) 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 C₁₄H₈O₆N₂S: C, 50.60; H, 2.43; N, 8.43; S, 9.65%.

4) Bp 108–109°C/1 mmHg, Found: C, 34.62; H, 4.85; S, 45.30%. Calcd for C₆H₁₀O₂S₃: 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).