

*Anal.* Calcd for  $C_{11}H_{12}ClN_3O$ : C, 55.58; H, 5.09; Cl, 14.92; N, 17.68. Found: C, 55.57; H, 5.08; Cl, 14.69; N, 17.37.

**7-Chloro-2-tetralone (2).**—The procedure described above for the synthesis of **1** was repeated with *m*-chlorophenylacetyl chloride. Vacuum distillation was used to purify the oily ketone recovered after base treatment of the crystalline bisulfite adduct: yield 47%; bp 145° (0.6 mm); mp 43–46° (solid formed in the receiver);  $\nu_{max}^{KCl}$  1720  $cm^{-1}$ . Analysis of this material by glpc (150°)<sup>11</sup> showed two peaks with retention times of 3.6 and 6.4 min, respectively. The ratio of peak areas was approximately 3:1. The nmr spectrum indicated the presence of two compounds in unequal proportions. The principal isomer, assumed to be **2**, showed a singlet at  $\tau$  6.56 (ArCH<sub>2</sub>CO). A smaller singlet at  $\tau$  6.53 was also observed, suggesting the probable presence of some 5-chloro-2-tetralone.

*Anal.* Calcd for  $C_{10}H_9ClO$ : C, 66.49; H, 5.02; Cl, 19.63. Found: C, 66.66; H, 5.28; Cl, 19.93.

**5,7-Dichloro-2-tetralone (3).**—3,5-Dichlorobenzoic acid was reduced in 78% yield with lithium aluminum hydride in refluxing ether,<sup>16</sup> with formation of 3,5-dichlorobenzyl alcohol, mp 78° (lit.<sup>16</sup> mp 78–79°). A mixture of this alcohol (125 g, 0.71 mol) and thionyl chloride (113 g, 0.95 mol) was refluxed 3 hr to give 94 g (68%) of 3,5-dichlorobenzyl chloride,<sup>17</sup> bp 83° (1.8 mm) [lit. bp 60° (0.35 mm),<sup>16</sup> 115–123° (10 mm)<sup>18</sup>]. To a stirred suspension of sodium cyanide (13 g, 0.27 mol) in dry dimethyl sulfoxide (50 ml) was added dropwise under nitrogen at 50° a solution of the above benzyl chloride (45 g, 0.23 mol) in dry dimethyl sulfoxide (150 ml). After being stirred overnight at room temperature, the mixture was diluted with water (400 ml), and extracted with chloroform (three 300-ml portions). The combined extracts were washed with water (100 ml), dried, and evaporated to dryness. Distillation of the residue gave 28 g (66%) of 3,5-dichlorophenylacetonitrile, bp 101–103° (0.1 mm) [lit.<sup>8</sup> bp 165–168° (17 mm)]. The dinitrile was heated for 6 hr under reflux with a mixture of concentrated sulfuric acid (28 ml), glacial acetic acid (28 ml), and water (28 ml). The hydrolysis mixture was cooled, and the precipitate was filtered and washed thoroughly with ice-cold water to give 24 g (78%) of 3,5-dichlorophenylacetic acid, mp 110–112° (lit.<sup>8</sup> mp 112–115°). This acid (139 g, 0.68 mol) was allowed to react overnight with thionyl chloride (100 g, 0.84 mol) in refluxing benzene (200 ml). Removal of the solvent and unreacted thionyl chloride under reduced pressure and distillation of the residue gave 99 g (66%) of 3,5-dichlorophenylacetyl chloride, bp 114–118° (2 mm).<sup>19</sup> The general procedure used in the preparation of **1** was repeated with this acid chloride to give a 58% yield (best run) of **3**: mp 76–78°;  $\nu_{max}^{KCl}$  1730  $cm^{-1}$  (C=O); positive "tetralone blue" test.

*Anal.* Calcd for  $C_{10}H_8Cl_2O$ : C, 55.84; H, 3.75; Cl, 32.97. Found: C, 56.04; H, 3.97; Cl, 33.10.

The 2,4-dinitrophenylhydrazone of **3** had mp 172.5–174° (EtOH).

*Anal.* Calcd for  $C_{18}H_{12}Cl_2N_4O_4$ : C, 48.12; H, 3.06; Cl, 17.94; N, 14.17. Found: C, 48.44; H, 3.29; Cl, 18.03; N, 14.01.

**6,7-Dichloro-2-tetralone (4).**—The general procedure used for the synthesis of **1** was repeated with 3,4-dichlorophenylacetyl chloride to give a 58% yield (best run) of **4**. Glpc analysis (200°)<sup>11</sup> showed a single peak with a retention time of 4.75 min. For microanalysis, a portion of the crude crystalline product was recrystallized from 1:2 carbon tetrachloride–petroleum ether (bp 60–80°): mp 97–98°;  $\nu_{max}^{KCl}$  1720  $cm^{-1}$ .

*Anal.* Calcd for  $C_{10}H_8Cl_2O$ : C, 55.84; H, 3.75; Cl, 32.97. Found: C, 55.57; H, 3.80; Cl, 32.87.

The semicarbazone of **4** had mp 224–225° (EtOH).

*Anal.* Calcd for  $C_{11}H_{11}Cl_2N_3O$ : C, 48.55; H, 4.08; Cl, 26.06; N, 15.44. Found: C, 48.72; H, 4.16; Cl, 26.34; N, 15.16.

**Registry No.**—**1**, 17556-18-2; **1** semicarbazone, 17605-22-0; **2**, 17556-19-3; **3**, 17556-20-6; **3** 2,4-dinitrophenylhydrazone, 17556-21-7; **4**, 17556-22-8; **4** semicarbazone, 17556-23-9; 2-tetralone, 530-93-8.

(16) R. Fuchs and D. M. Carlton, *J. Amer. Chem. Soc.*, **85**, 104 (1963).

(17) 3,5-Dichlorobenzyl chloride has also been prepared from the alcohol by reaction with phosphorus pentachloride [F. Asinger and G. Loek, *Monatsh. Chem.*, **62**, 344 (1933)], and also from 3,5-dichlorotoluene by direct photocatalytic chlorination at 180° (see ref 18).

(18) British Patent 923,128 (April 10, 1963); *Chem. Abstr.*, **60**, 1048 (1964).

(19) A 79% yield of acid chloride was obtained in a subsequent experiment, in which the acid was added in small portions to an equal weight of thionyl chloride on the steam bath, and the mixture was refluxed for 3 hr.

## Base-Catalyzed Conversion of Thiocarbonate Esters into Sulfides. Reactions of Xanthate Esters

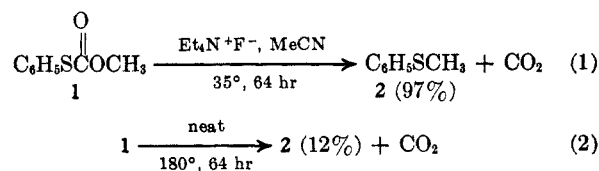
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Thiocarbonate and xanthate esters are well known to be readily solvolized by protonic solvents under basic conditions,<sup>1</sup> but little is known of their base-catalyzed reactions under aprotic conditions. This Note describes our study of such reactions of representative thiocarbonates and xanthates.

**Thiocarbonate esters.**—We have found that certain aprotic Lewis bases strongly catalyze conversion of thiocarbonates into sulfides with loss of CO<sub>2</sub>. In favorable cases, the reaction goes under mild conditions in quantitative yields. For example, liquid *O*-methyl-*S*-phenyl thiocarbonate (**1**) is converted into methyl phenyl sulfide (**2**) and CO<sub>2</sub> in high yield at 35° by solutions containing fluoride ion (eq 1). Without a catalyst **1** is thermally stable to about 180°, where slow (0.25%/hr) conversion into **2** occurs (eq 2). An analogous reaction of cyclic ethylene thiocarbonate was reported to give ethylene sulfide.<sup>2</sup>



A number of bases were tested as catalysts for conversion of **1** into **2** in nitrobenzene (Table I). Mixtures of solvent, **1**, and catalyst in a 40:10:1 ratio by weight was heated at 85 ± 1° for 1.0 hr. Yields were estimated by nmr analysis.

TABLE I  
CATALYSTS FOR CONVERSION OF **1** INTO **2**

| Catalyst   | Conversion, % | Catalyst  | Conversion, % |
|--|---------------|---|---------------|
| Et <sub>4</sub> N <sup>+</sup> F <sup>-</sup>                    | 100           | (Me <sub>2</sub> NCH <sub>2</sub> ) <sub>2</sub>                    | 100           |
| Bu <sub>4</sub> N <sup>+</sup> Br <sup>-</sup>                   | 9             | Pyridine  | 52            |
| Et <sub>3</sub> P  | 99            | Quinoline   | 2             |
| (C <sub>6</sub> H <sub>17</sub> ) <sub>3</sub> P                 | 94            | Imidazole   | 2             |
| (C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> P                  | 18            | (C <sub>6</sub> H <sub>5</sub> )N=N(C <sub>6</sub> H <sub>5</sub> ) | Trace         |
| Et <sub>3</sub> N  | 100           | (C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> PS                    | Trace         |
| (C <sub>6</sub> H <sub>5</sub> )CH <sub>2</sub> NMe <sub>2</sub> | 86            | None  | Trace         |

These data show that tertiary phosphines, tertiary amines, and soluble fluorides are good catalysts. Similar tests at 35° revealed that fluoride ion is far more active than pyridine; fluoride appears to be the best catalyst for difficult cases. Trioctylphosphine is also a useful catalyst, being nonvolatile, easily handled, and

(1) E. E. Reid, "Organic Chemistry of Bivalent Sulfur," Vol. IV, Chemical Publishing Co., Inc., New York, N. Y., 1962, pp 137, 165–167.

(2) (a) D. D. Reynolds, *J. Amer. Chem. Soc.*, **79**, 4951 (1957). (b) D. D. Reynolds, U. S. Patent 2,828,318 (1958); *Chem. Abstr.*, **52**, 14651f (1958).

fairly active. Tertiary amines are active but cause darkening during the reaction.

Similar experiments demonstrated a strong solvent effect on the reaction. Mixtures of solvent, 1, and triphenylphosphine in a 40:5:1 ratio were heated at 85° for 1 hr. In solvents of relatively low polarity (chloroform, benzene, *o*-dichlorobenzene) the conversion into 2 was 1.6 to 2%. Increasing polarity gave higher conversions into 2: acetonitrile (5%), nitrobenzene (9%), dimethyl sulfoxide (~45%), and *N,N*-dimethylformamide (55%).

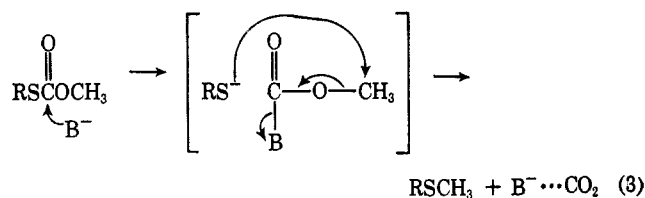
The scope of the reaction as a synthetic method was examined in representative cases (Table II).

TABLE II  
SYNTHESIS OF SULFIDES FROM THIOLCARBONATES

|                                |                                   | $\text{RSCOR}' \xrightarrow{\text{base}} \text{RSR}' + \text{CO}_2$ |                    |          |          |          |
|--------------------------------|-----------------------------------|---|--------------------|----------|----------|----------|
| R                              | R'                                | Base  | Solvent            | Temp, °C | Time, hr | Yield, % |
| C <sub>6</sub> H <sub>5</sub>  | CH <sub>3</sub>                   | (C <sub>6</sub> H <sub>17</sub> ) <sub>3</sub> P                    | None               | 100      | 20       | 100      |
| C <sub>6</sub> H <sub>13</sub> | CH <sub>3</sub>                   | (C <sub>6</sub> H <sub>17</sub> ) <sub>3</sub> P                    | None               | 100      | 18       | 97       |
| C <sub>6</sub> H <sub>5</sub>  | C <sub>2</sub> H <sub>5</sub>     | (C <sub>6</sub> H <sub>17</sub> ) <sub>3</sub> P                    | None               | 100      | 17       | 26       |
| C <sub>6</sub> H <sub>5</sub>  | C <sub>2</sub> H <sub>5</sub>     | Et <sub>4</sub> N <sup>+</sup> F <sup>-</sup>                       | CH <sub>3</sub> CN | 70       | 20       | 98       |
| C <sub>6</sub> H <sub>5</sub>  | CH(CH <sub>3</sub> ) <sub>2</sub> | Et <sub>4</sub> N <sup>+</sup> F <sup>-</sup>                       | DMF                | 153      | 10       | 24       |
| C <sub>6</sub> H <sub>5</sub>  | C <sub>6</sub> H <sub>5</sub>     | Et <sub>4</sub> N <sup>+</sup> F <sup>-</sup>                       | DMF                | 145      | 15       | 0        |

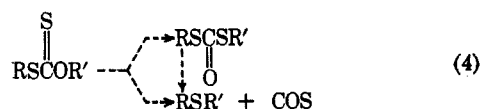
These results show that branching at R' strongly impedes the reaction. No reaction occurs when R' is phenyl.

A reasonable mechanism for sulfide formation involves initial attack of the catalyst on the carbonyl carbon (eq 3). This mechanism is consistent with the



strong solvent effect and with the fact that the rates apparently parallel the ease of nucleophilic substitution at R'. This mechanism suggests that the nature of group R is relatively unimportant, in agreement with the limited experimental data. We have not determined whether the reaction is intra- or intermolecular.

**Xanthate Esters.**—Xanthate esters could potentially react analogously to give sulfides and COS. A competing reaction, isomerization to dithiolcarbonates, is also possible (eq 4). Bond energy data indicate that isomerization is exothermic by about 24 kcal/mol.<sup>3</sup>



Scattered reports of thermal reactions of xanthate esters which cannot undergo Chugayev elimination suggest that isomerization predominates.<sup>4,5</sup> Internally catalyzed isomerization of tertiary amino<sup>5</sup> and al-

lylic<sup>6</sup> xanthate esters to dithiolcarbonate esters occurs in high yields.

We briefly examined thermal and base-catalyzed reactions of *S*-benzyl *O*-methyl xanthate (3) (Table III). We found that isomerization and elimination occur readily and at competitive rates (eq 5).

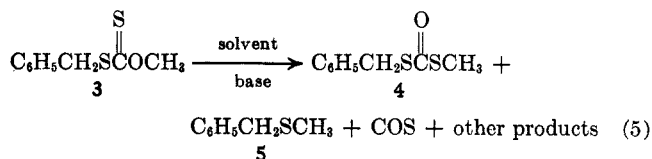


TABLE III  
PRODUCT COMPOSITION FROM REACTION OF 3

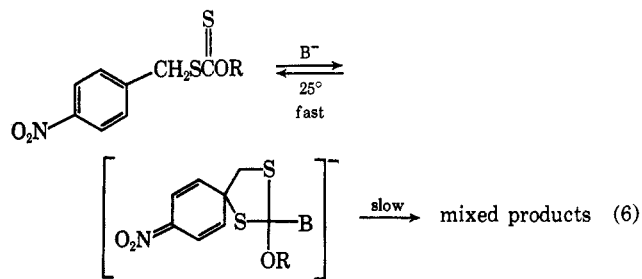
| Catalyst   | Solvent                                     | Temp, °C | Time, hr | Product composition, %— |    |        |
|--|---|----------|----------|-------------------------|----|--------|
|  |   |          |          | 4                       | 5  | Others |
| None   | None  | 176      | 18       | 66                      | 10 | 24     |
| (C <sub>6</sub> H <sub>17</sub> ) <sub>3</sub> P | CDCl <sub>3</sub>                           | 60       | 19       | 40                      | 40 | 10     |
| (C <sub>6</sub> H <sub>17</sub> ) <sub>3</sub> P | C <sub>6</sub> H <sub>12</sub> <sup>a</sup> | 60       | 19       | 44                      | 32 | 20     |
| Et <sub>4</sub> N <sup>+</sup> F <sup>-</sup>    | MeCN  | 25       | 24       | 50                      | 15 |        |
| Et <sub>4</sub> N <sup>+</sup> F <sup>-</sup>    | MeCN  | 60       | 24       | 73                      | 19 | 8      |

<sup>a</sup> C<sub>6</sub>H<sub>12</sub> = cyclohexane.

These results suggest that usable syntheses of sulfides and dithiolcarbonates from xanthate esters could be developed, but further reactions of the products during work-up make this route unattractive. For example, when xanthate 3 was treated with Et<sub>4</sub>N<sup>+</sup>F<sup>-</sup> and the product was distilled at low pressure, further equilibration of thiomethyl and thiobenzyl groups occurred to give a gross mixture of products, including trithiolcarbonates.

These base-catalyzed reactions could occur during synthesis of xanthate esters, particularly with reactive alcohols. Xanthate esters should be synthesized under the mildest possible conditions (e.g., in acetone at 0° or in CH<sub>2</sub>Cl<sub>2</sub>-H<sub>2</sub>O at 25°). Some "xanthate esters" reported in the older (preinfrared) literature are probably dithiolcarbonates.

*S*-(4-Nitrobenzyl) *O*-methyl and *O*-ethyl xanthates gave intensely violet solutions when treated with fluoride, cyanide, or azide salts. The color may be caused by fast, reversible cyclization as indicated in eq 6. Neutral nucleophiles give little or no color. The



(4) D. H. Rawers and D. S. Tarbell, *J. Amer. Chem. Soc.*, **78**, 70 (1956); H. R. Al-Kazimi, D. S. Tarbell, and D. Plant, *ibid.*, **77**, 2479 (1955); P. V. Laasko, *Suomen Kemistilehti B*, **16**, 19 (1943); *Chem. Abstr.*, **40**, 4687; D. L. Vincent and C. B. Purves, *Can. J. Chem.*, **34**, 1302 (1956); G. E. Risinger, *Nature*, **198**, 382 (1963); V. S. Etlis, *Zh. Obshch. Khim.*, **34**, 2996 (1964); *J. Gen. Chem. USSR*, **34**, 3032 (1964).

(5) T. Taguchi and S. Kasuga, *Chem. Pharm. Bull. (Tokyo)*, **13**, 241 (1965); T. Taguchi, Y. Kawazoe, K. Yoshihira, H. Kanayama, M. Mori, K. Tobata, and K. Harano, *Tetrahedron Lett.*, 2117 (1965); T. Taguchi and M. Nakao, *Tetrahedron*, 245 (1962); T. Taguchi, Y. Kawazoe, and M. Nakao, *Tetrahedron Lett.*, 131 (1963).

(6) D. L. Garmaise, A. Uchiyama, and A. F. McKay, *J. Org. Chem.*, **27**, 4509 (1962).

(3) E. S. Kooyman in "Organosulfur Chemistry," M. J. Janssen, Ed., Interscience Publishers, New York, N. Y., 1967, Chapter 1.

colored intermediates react slowly at 25° to give a mixture of 20 or more products.

#### Experimental Section<sup>7</sup>

**Synthesis of Thiocarbonates.**—S-Phenyl O-isopropyl thiocarbonate was prepared by stirring a mixture of 32 g (0.27 mol) of O-phenylthiocarbonyl chloride (K and K Laboratories), 30 g of potassium carbonate, and 210 g of 2-propanol overnight at 25° and for 5 hr at 85°. Gas evolution was noted at 85°. Filtration and fractionation through a spinning-band column gave 9 g (17%) of product: bp 77–80° (0.3 mm); nmr  $\delta$  7.44 (m, 5), 5.11 (septet, 1), 1.28 (d, 6).

*Anal.* Calcd for C<sub>10</sub>H<sub>12</sub>O<sub>2</sub>S: C, 60.94; H, 6.54; S, 16.26. Found: C, 61.00; H, 6.23; S, 16.06.

The other thiocarbonates were prepared by treating tetrahydrofuran solutions of phenyl or hexyl mercaptans first with an equimolar amount of butyllithium in hexane and then with chloromethyl, chloroethyl, or chlorophenyl carbonates. Data are in Table IV.

TABLE IV  
THIOLCARBONATES

| RSCOOR'  | Yield, % | Bp (mm) or mp, °C | Lit. bp (mm) or mp, °C |
|--|----------|-------------------|------------------------|
| C <sub>6</sub> H <sub>5</sub> SCOOCH <sub>3</sub> <sup>a</sup> (1) | 69       | 88–89.5 (2.4)     |                        |
| H <sub>13</sub> C <sub>6</sub> SCOOCH <sub>3</sub> <sup>b</sup>    | 67       | 70–71 (2.0)       |                        |
| C <sub>6</sub> H <sub>5</sub> SCOOCH <sub>2</sub> H <sub>5</sub>   | 80       | 69.5–70 (0.3)     | 130 (16) <sup>c</sup>  |
| C <sub>6</sub> H <sub>5</sub> SCOOCH <sub>2</sub> H <sub>5</sub>   | 47       | 50–60             | 56 <sup>c</sup>        |

<sup>a</sup> *Anal.* Calcd for C<sub>8</sub>H<sub>8</sub>O<sub>2</sub>S: C, 57.13; H, 4.79. Found: C, 57.63; H, 4.96. <sup>b</sup> *Anal.* Calcd for C<sub>8</sub>H<sub>10</sub>O<sub>2</sub>S: C, 54.51; H, 9.15. Found: C, 54.70; H, 9.25. <sup>c</sup> H. Rivier, *Bull. Soc. Chim. Fr.*, (4) 1, 733 (1907).

**Nmr Tube Experiments.**—Mixtures of solvent, 1, and catalyst in the ratio 40:10:1 by weight (Table I) and 40:5:1 (solvent-effect experiments) were prepared. Samples were placed in nmr tubes and heated in an oil bath thermostatically controlled at 85 ± 1° for 1.0 hr. The compositions of the resulting mixtures were estimated from the integrals of the methyl peaks of 1 at  $\delta$  3.78 and 2 at  $\delta$  2.37. Other products were seldom detected, never in amounts exceeding 2%.

Similarly, a solution of 0.20 g of 1 and 0.02 g of tetraethylammonium fluoride in 0.78 g of acetonitrile-*d*<sub>3</sub> were heated at 35° for 64 hr; nmr analysis showed 97% conversion into 2. A solution of 0.20 g of 1 in 0.80 g of pyridine gave 72% conversion into 2 and 28% unreacted 1 under these conditions.

**Thermal Stability of O-Methyl S-Phenyl Thiocarbonate (1).**—An nmr tube containing 1 was heated in an oil bath at 154° for 4 hr. The nmr spectrum was unchanged. When a sample was heated for 3 days at 180°, nmr analysis showed 12% conversion into C<sub>6</sub>H<sub>5</sub>SCH<sub>3</sub>, 88% unchanged starting material.

**Methyl Phenyl Sulfide (2).**—A mixture of 1.00 g of triethylphosphine in 5.00 g (0.030 mol) of 1 was heated at 100 ± 1° for 19 hr in a Schlenk tube. Slow evolution of gas was noted. Flash distillation at 1  $\mu$  gave 3.72 g (100%) of colorless 2. Glpc at 125° on a 2-m column of 20% Triton X-305<sup>®</sup> on Gas Chrom R<sup>®</sup> showed 99.6% purity.

**Hexyl Methyl Sulfide.**—This reaction was run similarly using 8.82 g (0.05 mol) of S-hexyl O-methyl thiocarbonate. Flash distillation gave 6.50 g (98% of *n*-hexyl methyl sulfide, 97% pure by glpc on a 1-m column of 20% Triton X-305<sup>®</sup> on Gas Chrom R<sup>®</sup> with linear programming from 100 to 250°.

**Ethyl Phenyl Sulfide.**—A mixture of 11.1 g (0.061 mol) of O-ethyl S-phenyl thiocarbonate and 0.3 g of tetraethylammonium fluoride was heated and stirred at 70°. No gas evolved. Acetonitrile (11.6 g) was added to give a homogeneous solution. Heating at 70° was continued for 20 hr as gas slowly evolved. Glpc on a 0.6-m column of 10% Apiezon L<sup>®</sup> on Gas Chrom R<sup>®</sup> with linear programming from 100 to 250° showed 98% conversion into product and 2% conversion into an unidentified by-product. Distillation gave 7.48 g (89%) of ethyl phenyl sulfide, bp 81–83° (8.6 mm) [lit.<sup>8</sup> bp 86–87° (14 mm)].

(7) Melting and boiling points are uncorrected. Infrared spectra were determined using a Perkin-Elmer Model 21 spectrophotometer. Nmr spectra were produced on a Varian Model A-60 device using 49:1 CDCl<sub>3</sub>-Me<sub>2</sub>Si as solvent, except as noted.

(8) H. Brintzinger and M. Langheck, *Ber.*, **87**, 325 (1954).

**Isopropyl Phenyl Sulfide.**—A solution of 8.0 g of O-isopropyl S-phenyl thiocarbonate and 0.23 g of tetraethylammonium fluoride in 20 g of N,N-dimethylformamide was stirred at 130° for 16 hr. Little or no gas evolved. The solution was heated at reflux for 10 hr. Gas evolved slowly. The solution was poured into water. The oil was extracted with methylene chloride, dried, and concentrated. Analysis by glpc and nmr showed approximately 24% conversion into product (nmr  $\delta$  3.33) and 50% unchanged starting material.

**S-Benzyl O-Methyl Xanthate (3).**—To a solution of 43.4 g (0.33 mol) of sodium methyl xanthate in 300 ml of acetonitrile was slowly added 57.1 g (0.33 mol) of benzyl bromide at 10–20°. The solution was concentrated under high vacuum and filtered, always keeping the product at 25° or lower. The residue was 67 g (100%) of product, 99% pure by nmr [ $\delta$  7.29 (5), 4.35 (2), 4.12 (3)]. Distillation gave 28 g of 3, bp 107–109° (0.4 mm), containing several per cent isomer 4 and sulfide 5.

Rapid addition of benzyl bromide to an equimolar amount of sodium methyl xanthate in warm methanol gave a fast, exothermic reaction. A 42% yield of benzyl methyl sulfide, bp 72° (2.4 mm), was obtained by fractionation of the product.

**Reactions of 3.**—These reactions were performed in nmr tubes or the equivalent as described above. The methyl and methylene peaks of isomer 4 were at  $\delta$  2.36 and 4.35, respectively. The corresponding peaks of sulfide 5 were at  $\delta$  1.93 and 3.62.

**O-Methyl S-(*p*-Nitrobenzyl) Xanthate.**—A solution of 16.6 g (0.013 mol) of sodium methyl xanthate and 27.4 g (0.013 mol) of *p*-nitrobenzyl bromide in 300 ml of acetonitrile was kept at 25° for 3 hr. Solvent removal and recrystallized from toluene-methanol gave 21.7 g (70%) of product: mp 76.5–77.5°; nmr  $\delta$  7.88 (q, 4), 4.48 (2), 4.20 (3); ir no C=O peak.

*Anal.* Calcd for C<sub>9</sub>H<sub>9</sub>NO<sub>3</sub>S<sub>2</sub>: C, 44.43; H, 3.73; N, 5.76; S, 26.36. Found: C, 44.54; H, 3.90; N, 5.70; S, 26.38.

**O-Ethyl S-(*p*-Nitrobenzyl) Xanthate.**—This ester, mp 62–63° (lit.<sup>9</sup> mp 65–66°), was prepared as described above for the methyl ester in 83% yield. The product was recrystallized from toluene-pentane: nmr  $\delta$  7.84 (4), 4.65 (q, 2), 4.43 (2), 1.40 (t, 3); ir no C=O peak.

*Anal.* Calcd for C<sub>10</sub>H<sub>11</sub>NO<sub>3</sub>S<sub>2</sub>: C, 46.67; H, 4.27; N, 5.44; S, 24.92. Found: C, 46.85; H, 4.26; N, 5.44; S, 24.91.

**Reactions of S-(*p*-Nitrobenzyl) Xanthates.**—Treatment of these xanthates with soluble F<sup>-</sup>, CN<sup>-</sup>, or N<sub>3</sub><sup>-</sup> salts gave intensely violet colors which slowly faded during several days. Acetonitrile solutions containing equimolar quantities of the O-methyl xanthate and Et<sub>4</sub>NF had  $\lambda_{max}$  520 m $\mu$  ( $\epsilon$  2500), 303 (11,000), 277 (12,800); aging caused these peaks to shift in wavelength and intensity. Nmr study of such solutions showed that mixtures were present at all times. Chromatography of a week-old solution gave more than 20 colored fractions.

**Registry No.**—1, 3186-52-5; 3, 17659-13-1; 5-phenyl O-isopropyl thiocarbonate, 17659-14-2; H<sub>13</sub>C<sub>6</sub>SCOOCH<sub>3</sub>, 17659-15-3; O-methyl S-(*p*-nitrobenzyl) xanthate, 15183-56-9; O-ethyl S-(*p*-nitrobenzyl) xanthate, 17659-17-5.

**Acknowledgment.**—We are indebted to Mr. Jake Graff and Mr. Paul Sanders for technical assistance and to Dr. R. A. Clement for helpful discussions.

(9) A. L. Morrison and F. R. Atherton, British Patent 675,779 (1952).

### The Specific Debenzylation of Alkylated Carbohydrates via Bromination-Hydrolysis

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We wish to report a new method for the debenzyla-tion of carbohydrates. This method has been used successfully with hexopyranosides, an acyclic hexose,