

sis of the compound at the amide linkage to 2,4,5-triamino-6-hydroxypyrimidine occurred.

Also, heating II with oxalic acid<sup>7</sup> failed to bring about the desired ring closure.

When II was boiled with formamide,<sup>8</sup> analysis for carbon and hydrogen of the material isolated showed that it was not the desired product but might be guanine; however, a subsequent analysis for nitrogen proved that it was not the latter compound.

*Anal.* Calcd. for  $C_6H_8N_5O$ : C, 39.73; H, 3.33; N, 46.36. Found: C, 39.26; H, 3.02; N, 40.32, 40.28.

(7) E. Fischer and L. Ach, *ibid.*, **28**, 247 (1895).

(8) R. K. Robins, K. J. Dille, C. H. Willits and B. E. Christensen, *THIS JOURNAL*, **76**, 263 (1953).

DEPARTMENT OF CHEMISTRY  
TEMPLE UNIVERSITY  
PHILADELPHIA 22, PENNA.

## The Synthesis of $\beta,\beta'$ -Dithiolisobutyric Acid

BY JOSEPH CORSE AND EUGENE F. JANSEN

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Several years ago<sup>1</sup> a sulfur-containing polymeric material was obtained from asparagus juice which gave  $\beta,\beta'$ -dithiolisobutyric acid on reduction by sodium in liquid ammonia. Recent interest in dithiol acids following the characterization of  $\alpha$ -lipoic acid<sup>2</sup> (6-thioctic acid) have made it desirable to have a readily available source of this lower analog.

$\beta,\beta'$ -Diiodoisobutyric acid, the starting material for the syntheses attempted, was found to be more accessible from the hydroiodination of  $\alpha$ -iodomethylacrylic acid<sup>3</sup> than by reduction and displacement of  $\alpha$ -hydroxy- $\beta,\beta'$ -dichloroisobutyric acid previously used.<sup>4</sup>

Reaction of  $\beta,\beta'$ -diiodoisobutyric acid with thiourea gave the diisothiuronium salt in excellent yield. However, all efforts to hydrolyze this derivative to the desired  $\beta,\beta'$ -dithiolisobutyric acid failed. The reaction of sodium  $\beta,\beta'$ -diiodoisobutyrate with sodium benzyl mercaptide gave a good yield of  $\alpha$ -benzylmercaptomethylacrylic acid and apparently no  $\beta,\beta'$ -dibenzylmercaptoisobutyric acid. A successful synthesis of the  $\beta,\beta'$ -dibenzylmercapto acid was achieved by a method paralleling that recently published by Reed and Niu<sup>5</sup> for  $\alpha$ -lipoic acid.  $\beta,\beta'$ -Diiodoisobutyric acid was converted to its methyl ester with diazomethane. This in turn gave good yields of methyl  $\beta,\beta'$ -dibenzylmercaptoisobutyrate on reaction in ethyl acetate solution with sodium benzylmercaptide. The saponification of the methyl ester could be effected by shaking with alcoholic potassium hydroxide at room temperature. Attempts to speed the hydrolysis by warming resulted in  $\beta$ -elimination and the formation of  $\alpha$ -benzylmercaptomethylacrylic acid. The free  $\beta,\beta'$ -dibenzylmercaptoisobutyric acid did not crystallize and was characterized as its disulfone. Reduction of the dibenzylmercapto acid by sodium in liquid ammonia was always attended by the formation of a polymeric

gum in addition to the expected  $\beta,\beta'$ -dithiolisobutyric acid.

### Experimental

**$\beta,\beta'$ -Diiodoisobutyric Acid.**—Ethyl bis-(hydroxymethyl)-malonate<sup>3,6</sup> was refluxed with hydriodic acid to give  $\alpha$ -iodomethylacrylic acid.<sup>3</sup> An intimately ground mixture of 87.5 g. (0.46 mole) of  $\alpha$ -iodomethylacrylic acid and 109 g. of potassium iodide was made into a paste with 196 g. of 95% phosphoric acid and heated for six hours on a steam-bath.<sup>7</sup> The reaction mixture was poured into ice-water, triturated to break up lumps and the product was collected on a filter. After drying over phosphorus pentoxide it was recrystallized from ethyl acetate-petroleum ether; m.p. 128–129°, yield 81 g. (52%). A mixture melting point with an authentic specimen prepared from dichloroacetone<sup>4</sup> showed no lowering.

**Methyl  $\beta,\beta'$ -Diiodoisobutyrate.**—An excess of ethereal diazomethane was added to 81 g. of the solid acid described above. The solution was dried over anhydrous magnesium sulfate, filtered and the ether removed *in vacuo*. This material was used for analysis; yield 77 g. (92%), m.p. 20.5–21°.

*Anal.* Calcd. for  $C_5H_8I_2O_2$ : C, 16.97; H, 2.28. Found: C, 17.4; H, 2.41.

**Methyl  $\beta,\beta'$ -Dibenzylmercaptoisobutyrate.**—A solution of 9.67 g. of sodium in 100 ml. of methanol was treated with 52.1 g. (0.42 mole) of benzyl mercaptan and evaporated to dryness *in vacuo*. A solution of 77 g. (0.21 mole) of methyl  $\beta,\beta'$ -diiodoisobutyrate in 100 ml. of ethyl acetate was then added and the mixture was refluxed for 1 hour and then poured into ice-water. The organic layer was separated, washed with cold 0.1 N sodium hydroxide solution, with water and then dried over magnesium sulfate. The solvent was removed *in vacuo* and the residue was recrystallized from methanol; yield 55.1 g. (73%), m.p. 44°.

*Anal.* Calcd. for  $C_{15}H_{22}O_2S_2$ : C, 65.86; H, 6.40. Found: C, 65.6; H, 6.49.

**Hydrolysis of Methyl  $\beta,\beta'$ -Dibenzylmercaptoisobutyrate.**—A mixture of 34.6 g. (0.1 mole) of methyl  $\beta,\beta'$ -dibenzylmercaptoisobutyrate in 120 ml. of 0.83 N potassium hydroxide in 90% methanol was shaken for 5 hours at room temperature. At that time another 20 ml. of the 0.83 N base was added and shaking continued for another hour. After being stored in the refrigerator overnight, the reaction mixture was acidified with concd. hydrochloric acid, filtered and concentrated *in vacuo*. The residue was dissolved in ethyl acetate, washed with water and again the solvent was removed *in vacuo*. The free  $\beta,\beta'$ -dibenzylmercaptoisobutyric acid remained as a non-crystalline gum. It was characterized by oxidation of its acetic acid solution with 30% hydrogen peroxide to  $\beta,\beta'$ -dibenzylsulfonoisobutyric acid which was recrystallized from dilute acetic acid; m.p. 181–182°.

*Anal.* Calcd. for  $C_{18}H_{20}O_6S_2$ : C, 54.5; H, 5.09. Found: C, 54.8; H, 5.33.

If the hydrolysis were carried out by warming, considerable quantities of the elimination product,  $\alpha$ -benzylmercaptomethylacrylic acid, would separate in crystalline form. After recrystallization from nitromethane it melted at 93° dec.

*Anal.* Calcd. for  $C_{11}H_{12}O_2S$ : C, 63.43; H, 5.81. Found: C, 63.0; H, 5.90.

**$\beta,\beta'$ -Dithiolisobutyric Acid.**—A solution of 11.5 g. (0.034 mole) of non-crystalline gummy  $\beta,\beta'$ -dibenzylmercaptoisobutyric acid in 20 ml. of toluene was added to 200 ml. of liquid ammonia. Small pieces of sodium were then added until a permanent blue color resulted. The excess sodium was destroyed with a little ammonium chloride, and the ammonia was allowed to evaporate in a nitrogen stream. The residue was acidified with concd. hydrochloric acid and extracted with ethyl acetate. The ethyl acetate solution was washed with water, dried and concentrated. The resulting gum was extracted with two 1-l. portions of warm petroleum ether (b.p. 90–100°) and these extracts were chilled to –30° for several days. The petroleum ether was decanted from the impure crystals and used to reextract the reduction product. There remained, insoluble in petroleum

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(2) See O. A. Bessey, H. J. Lowe and L. L. Salomon, *Ann. Rev. Biochem.*, **22**, 545 (1953).

(3) K. N. Welch, *J. Chem. Soc.*, 257 (1930).

(4) J. W. E. Glattfeld and J. M. Schneider, *THIS JOURNAL*, **60**, 415 (1938).

(5) L. J. Reed and C. Niu, *ibid.*, **77**, 416 (1955).

(6) H. Gault and A. Roesch, *Bull. soc. chim.*, [5] **4**, 1411 (1937).

(7) H. Stone and H. Schleeter, *Org. Syntheses*, **30**, 33 (1950).

ether, 2.8 g. of an almost colorless gum whose structure was not investigated. The partly crystalline dithiol acid was purified by vacuum sublimation followed by recrystallization from petroleum ether; yield 2.13 g. (41% from the gum), m.p. 59–61°. A mixture melting point with a sample isolated from asparagus juice showed no depression.

$\beta,\beta'$ -Disothiuroniumisobutyric Acid Dihydroiodide.—A solution of 1.70 g. (0.005 mole) of  $\beta,\beta'$ -diiodoisobutyric acid was added to a solution of 0.76 g. (0.01 mole) of thiourea in 30 ml. of acetone and refluxed for 30 minutes. About half of the acetone was distilled off and benzene was added to precipitate an oil which readily crystallized; yield, quantitative. For analysis, it was recrystallized from water, m.p. 160–163° dec.

*Anal.* Calcd. for  $C_6H_{14}I_2N_2O_2S_2$ : C, 14.6; H, 2.87; N, 11.4. Found: C, 15.0; H, 3.02; N, 11.3.

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WESTERN UTILIZATION RESEARCH BRANCH  
AGRICULTURAL RESEARCH SERVICE  
FRUIT PROCESSING SECTION  
ALBANY 10, CALIFORNIA

### The Structures of the Diterpenoid Alkaloids Laurifoline and Cuauchichicine. Nomenclature Alteration

BY CARL DJERASSI, C. R. SMITH, A. E. LIPPMAN, S. K. FIGDOR AND J. HERRAN

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We have recently reported<sup>1</sup> the isolation and structure elucidation of a new diterpenoid alkaloid, named laurifoline, from the Mexican tree *Garrya laurifolia* Hartw. It has now been called to our attention by Prof. M. Tomita of the University of Kyoto that the name "laurifoline" has been used already by him for an aporphine-like alkaloid isolated<sup>2</sup> from *Cocculus laurifolius* DC. In view of the priority of the Japanese workers and in order to avoid any confusion in the alkaloid literature, we propose that the name of our alkaloid<sup>1</sup> be changed to "garryfoline."

(1) C. Djerassi, C. R. Smith, A. E. Lippman, S. K. Figdor and J. Herran, *THIS JOURNAL*, **77**, 4801 (1955).

(2) M. Tomita and F. Kusuda, *Pharm. Bull. (Japan)*, **1**, 1 (1953).

DEPARTMENT OF CHEMISTRY  
WAYNE UNIVERSITY  
DETROIT, MICHIGAN, AND  
INSTITUTO DE QUIMICA  
UNIVERSIDAD NACIONAL AUTONOMA DE MEXICO  
MEXICO, D. F.

### The Pyrolysis of Trifluoromethyl Sulfur Pentafluoride and its Reaction with Perfluoropropylene

BY RICHARD DRESDNER

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The pyrolysis of  $CF_3SF_5$ , trifluoromethyl sulfur pentafluoride, and its reaction with  $C_3F_6$ , perfluoropropylene, have been investigated. The experiments were carried out at temperatures between 425 and 518°. The only products found when  $CF_3SF_5$  was heated, under the conditions outlined, were  $C_2F_6$ , perfluoroethane, and  $SF_4$ , sulfur tetrafluoride. When  $CF_3SF_5$  and  $C_3F_6$  were heated together at elevated temperatures, a series of fluorocarbons was isolated and identified.

### Experimental

**Apparatus.**—The experiments were carried out in a closed system at approximately atmospheric pressure. The gases to be pyrolyzed or reacted were condensed air-free into a valved 1600-cc. stainless steel container. They were allowed to come to equilibrium at room temperature. The flow rate of the gases through the system was observed by their passage through a small bubbler containing a few cc. of dibutyl phthalate. The gas flow was controlled by the settings on the container valve and the stopcock on a liquid air cooled condenser-collector at the end of the system. The reactor was made from a 0.5" i.d. nickel tube 18" long and filled with extruded nickel packing. The reaction zone was wrapped with 0.25" copper wire and heated in a Hoskins furnace. The reaction temperatures were noted with a 22-gauge chromel-alumel thermocouple placed at the center of the reaction zone. The temperatures at the surface of the reactor at equilibrium were 2 to 5° higher than those observed inside the unpacked tube.

**Conditions.**—All experiments were carried out at approximately atmospheric pressure. The average mass flow rates were held between 0.20 and 0.40 g./min. Temperatures were maintained within  $\pm 3^\circ$  of the reported values.

**Materials.**—Trifluoromethyl sulfur pentafluoride: this material was prepared by the electrochemical process.<sup>1</sup> The starting materials were a solution of  $(CH_3)_2S$ , dimethyl sulfide, in anhydrous  $HF$ .<sup>2</sup> The  $CF_3SF_5$  was purified by fractionation and had a b.p. of  $-20.5^\circ$  and a molecular weight of not less than 193 and not more than 196.

**Perfluoropropylene.**—This material was obtained from the Peninsular Chemical Research Co., Gainesville, Fla. It had a molecular weight of 150, b.p.  $-30^\circ$ .

### Results

Two trials were made to pyrolyze  $CF_3SF_5$ . The first was made at 450°, a flow rate of 0.40 g./min., and an average pressure of 760 mm. No products were recovered that were characterized as different from the starting material. The second trial was made at 500°, a flow rate of 0.20 g./min. and the same pressure as in trial 1. Two grams of  $C_2F_6$  and 2 g. of  $SF_4$  were isolated and identified and some 16 g. of starting material was recovered out of 21 g. of  $CF_3SF_5$  passed through the system. The nickel packing was very slightly attacked during the second trial.

Five trials were made with  $CF_3SF_5$  and  $C_3F_6$ . Generally, the unreacted starting materials were recovered from each trial and reused in the succeeding trial. The conditions and results of these trials are presented in Table I.

TABLE I

SUMMARY OF REACTIONS OF  $CF_3SF_5$  AND  $C_3F_6$  IN A NICKEL-PACKED REACTOR

$C_3F_6$ , g.	$CF_3SF_5$ , g.	Flow, g./m.	Temp., °C.	Mm.	Products in g.			
					$C_2F_6$	$SF_4$	SM <sup>a</sup>	b. above -19°
17	21	0.29	425	735	Tr.	Tr.	37	1
16	20	.32	485	740	1	1	28	4
26	33	.28	512	760	1	13	15	17
60	75	.40	515	760	2	27	70	38
45	55	.28	518	740	1	27	25	47
					5	68		107

<sup>a</sup> Starting materials.

The products boiling above  $-19^\circ$  were collected and fractionated in appropriate columns. The main fractions isolated and identified were 17 g.  $C_4F_{10}$ , 7 g.  $C_6F_{12}$ , 15 g.  $C_6F_{14}$  and 9 g.  $C_7F_{16}$ .

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(2) A. F. Clifford, H. K. El-Shamy, H. J. Emelús and R. N. Haszeldine, *J. Chem. Soc.*, 2372 (1953).