

after crystallization from ligroin melted at 72°; the melting point of glycerol tribenzoate crystallized from ligroin is 72°.<sup>11</sup> No depression was observed on mixed melting point with a sample of authentic glycerol tribenzoate.<sup>8</sup>

Benzoylation of a sample of the radioactive glycerol and

(11) A. Fairbourne and G. E. Foster, *J. Chem. Soc.*, **127**, 2759 (1925).

purification of the resulting glycerol tribenzoate by crystallization from ligroin gave a product whose radioactivity per millimole differed by 3% from that of the glycerol; this error lies well within the limits of precision of the radioactivity determination.

All samples were counted as barium carbonate on paper mountings.

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[RESEARCH LABORATORIES, AMERICAN HOME FOODS, INC.]

## 2-Substituted Tetrahydropyranyl Sulfides

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2-Substituted tetrahydropyranyl sulfides have been prepared by the interaction of dihydropyran with mercaptans in the presence of catalytic quantities of hydrogen chloride.

In 1934, Paul<sup>2</sup> reported that it was possible to prepare tetrahydropyran ethers by the interaction of dihydropyran with alkanols in the presence of catalytic amounts of hydrogen chloride. This work was extended by Woods and Kramer<sup>3</sup> who

### Experimental

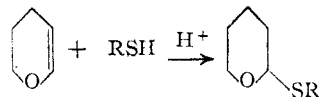
Directions are given for the preparation of ethyl 2-tetrahydropyranyl sulfide. Other sulfides may be prepared by similar methods. The properties of the new materials are listed in Table I.

TABLE I

R	B.P.		Yield, %	Formula	Analyses, <sup>a</sup> %					
	°C.	Mm.			Calculated			Found		
Methyl	47-48	5	57.8	C <sub>6</sub> H <sub>12</sub> OS	54.50	9.14		54.72	9.27	
Ethyl	42	2	40.5	C <sub>7</sub> H <sub>14</sub> OS	57.49	9.65	21.92	57.57	9.99	21.87
<i>n</i> -Propyl	55-58	3	36.7	C <sub>8</sub> H <sub>16</sub> OS	59.95	10.06	20.00	60.09	9.73	20.75
Isopropyl	48	2.5	66.7	C <sub>8</sub> H <sub>16</sub> OS	59.95	10.06	20.00	59.40	10.23	20.30
<i>n</i> -Hexyl	84-86	2.5	25.0	C <sub>11</sub> H <sub>22</sub> OS	65.29	10.96	15.84	65.37	10.48	15.52
Benzyl	86-87	2	42.3	C <sub>12</sub> H <sub>16</sub> OS	69.19	7.74	15.39	69.59	8.06	15.43

<sup>a</sup> Analyses by Oakwold Laboratories, Alexandria, Virginia.

synthesized a series of these ethers by a similar method. It was of interest to us to attempt the preparation of the corresponding sulfides by substituting a mercaptan for the alcohol. These syntheses were realized, and it was found possible to obtain a series of sulfides in comparatively good yields.



The new sulfides are liquids with pleasant, minty aromas, and are quite stable to alkali, but are easily decomposed, even by very dilute acids, to the initial mercaptan and 5-hydroxypental.<sup>4</sup> From a study of the molecular structure of these new compounds, it may be noted that these tetrahydropyranyl sulfides are, in reality, semimercaptals, which are notoriously unstable to acids. An additional analogy may be pointed out here: the sulfides may be considered to be thioglycosides of desoxysugars, and thus are the primitive members of the pyranose form of the carbohydrate series.

(1) Oxford Products, Inc., Cleveland, Ohio.

(2) R. Paul, *Bull. soc. chim.*, [5] **1**, 971 (1934).

(3) G. F. Woods and D. N. Kramer, *This Journal*, **69**, 2246 (1947).

(4) G. F. Woods and H. Sanders, *ibid.*, **68**, 2183 (1946).

**Ethyl 2-Tetrahydropyranyl Sulfide.**—To a 300-ml. pressure bottle chilled in an ice-bath was added 15.5 g. (0.25 mole) of ethyl mercaptan, 21 g. (0.25 mole) of dihydropyran<sup>5</sup> and 5 mg. of hydrogen chloride in 1 ml. of anhydrous ether. The bottle was stoppered immediately, shaken thoroughly and the contents allowed to warm to room temperature, after which the temperature was maintained at 90° for 3 hours. At the end of this time, the bottle was chilled and opened, the contents washed into a separatory funnel with 50 ml. of ether and then shaken with 5 ml. of saturated potassium carbonate solution and separated. The organic layer was dried over calcium sulfate, filtered and the volatiles stripped under slightly reduced pressure. The residue was fractionated through a 20-cm. Vigreux column to give a 40.5% yield of a colorless oil boiling at 42° (2 mm.).

Treatment with ammoniacal sodium nitroprusside gave no coloration, indicating absence of unreacted mercaptan, as well as stability of the sulfide to base. Treatment of the sulfides with sodium nitrite-hydrochloric acid caused the development of a red color<sup>6</sup> indicative of easy hydrolysis to the initial mercaptan, while an immediate pink color was given with fuchsin-sulfur dioxide reagent, confirming hydrolysis to the aldehyde.

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(5) Supplied through the courtesy of E. I. du Pont de Nemours and Company, Wilmington, Delaware. The commercial product was dried with anhydrous potassium carbonate and distilled through a 30-cm. Widmer column.

(6) H. Rheinboldt, *Ber.*, **60**, 184 (1927).