index must be at least partially due to peroxide formation.

As a result of the above observations, all propionaldehyde samples[2] were distilled and collected in a nitrogen atmosphere, and the Pyrex receivers were boiled out with water for twenty to thirty minutes and thoroughly dried in an oven. The boiling procedure may remove an adsorbed oxygen layer from the glass surface.

Carefully cleaned copper, zinc, aluminum, tin, and stainless steel surfaces showed reaction when immersed in the aldehyde. The evidence of reaction, surface corrosion, coloration of solution, and crystalline solids in the solution was less pronounced in the oxygen-free aldehyde samples than in those which gave positive peroxide tests. It has been assumed that these reactions were due to the formation of an acid.

During preliminary determinations of the density of propionaldehyde at $-64.2°$, it was observed that while the pycnometer was warming to room temperature, a relatively large volume of gas was evolved. A moderate quantity of a white solid, which melted near $-20°$, appeared to be the source of the gas bubbles. The pycnometer was closed with ground glass caps after filling, so continued absorption of oxygen from the atmosphere could not have occurred. When the pycnometer had been thoroughly flushed with dry nitrogen before it was filled with aldehyde, the solid and gas bubbles were not observed. The peroxide would be more stable at the lower temperatures and when warmed would decompose with liberation of oxygen.

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A Condensation Reaction of Thiols with Phenol Alcohols

BY I. W. RUDERMAN AND E. M. FETTES

We wish to report that thiols condense directly with phenol alcohols when treated with hydrogen chloride or boron trifluoride in the absence of water. This previously unrecorded reaction, which may be represented by the formula

$$o\text{- or } p\text{-(OH)RCH}_2\text{OH} + \text{R'SH} \longrightarrow (\text{OH})\text{RCH}_2\text{SR'} + \text{H}_2\text{O}$$

where R is an aryl and R′ is an aryl or alkyl group, offers a convenient new synthesis of pure methylene thioethers of phenols in high yield. The preparation of such thioethers was recently reported[1] to be possible either through the reaction of a phenol, formaldehyde and a thiol (from which reaction it should be difficult to isolate a pure product because of isomer and polymer formation), or through the condensation of an *o*- or *p*-(dialkylaminomethyl)-phenol[2] with a thiol.

(1) R. F. McCleary and S. M. Roberts, U. S. Patent 2,322,376, June 22, 1943. No preparation of a *pure* thioether is given.

(2) H. A. Bruson and C. W. MacMullen, THIS JOURNAL, **63**, 270 (1941).

The synthesis of 2-hydroxy-α^1,α^3-bis-(butylmercapto)-mesitylene was accomplished as follows. One-half mole of 1-butanethiol and 0.05 mole of 2-hydroxy-α^1,α^3-mesityleniediol were dissolved in 125 ml. of glacial acetic acid, and dry hydrogen chloride gas was passed into the solution for two hours. The temperature rose seventeen degrees during the first fifteen minutes of the reaction, and then dropped gradually to room temperature. The reaction vessel was stoppered and set aside for two days. Water was added, and the oil which separated out was washed with water and then steam-distilled to remove unreacted thiol. A yellow oil remained, and it was distilled in a molecular still at a pressure of less than 1 micron. Ten and four-tenths grams (60% yield) of a clear, pale yellow liquid, n^{20}D 1.5490, was collected when the pot temperature was 100–105°.

Anal. Calcd. for $C_{17}H_{28}OS_2$: C, 65.33; H, 9.03; S, 20.52. Found: C, 65.40; H, 9.00; S, 20.46.

The phenyl urethan derivative was prepared according to the method of Shriner and Fuson[3]; colorless crystals, m. p. 92.8–93.2°, were obtained after one recrystallization from petroleum ether–chloroform.

Anal. Calcd. for $C_{24}H_{33}NO_2S_2$: C, 66.78; H, 7.71; N, 3.25; S, 14.86. Found: C, 67.04; H, 7.67; N, 3.34; S, 15.43.

By analogy with the condensation of phenols with phenol alcohols under similar conditions,[4] the condensation of phenol di- or trialcohols with polythiols should yield polymers.

(3) R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," 2nd edition, John Wiley and Sons, Inc., New York, N. Y., 1940, p. 136.

(4) J. B. Niederl and I. W. Ruderman, THIS JOURNAL, **67**, 1176 (1945).

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A Counter-Current Distribution System for the Separation and Determination of Streptomycin Types

BY G. W. E. PLAUT[1] AND R. B. MCCORMACK

As a means of extraction and purification of streptomycin, it was found that a 5% stearic acid solution in Pentasol[2] would extract streptomycin from an aqueous concentrate at *p*H 9. However, when a double extraction was made with this system, the distribution coefficient of this second extraction was appreciably lower than the first (Table I). The streptomycin content was determined by conversion to maltol.[3]

These observations indicated mixtures of streptomycin types in our original solution. A method of separation of these types into pure preparations or for analysis using counter-current procedures was suggested by these data.

For analytical purposes, applying the Craig counter-current technique,[4] the distribution co-

(1) Present address: Dept. of Biochemistry, Univ. of Wisconsin, Madison, Wisconsin.

(2) A mixture of synthetic amyl alcohols made by Sharples Chemicals, Inc.

(3) J. R. Schenck and M. A. Spielman, THIS JOURNAL, **67**, 2276 (1945).

(4) L. C. Craig, *J. Biol. Chem.*, **155**, 519 (1944).