

supernatant liquid and washings, cooled in an ice-bath, was added solid iodine, in small portions, allowing each portion to react before adding more, until the brown color persisted for at least ten minutes. This required about 122 g. of iodine. The crystalline disulfide precipitate was filtered, washed with small portions of 95% alcohol and then with small portions of water until most of the yellow color was removed. The mother liquor on evaporation gave additional crops of substantially pure material. White glistening platelets formed on crystallization from ethylene chloride; temperatures above 80° were avoided because it was found that decomposition with subsequent discoloration of the product resulted. A yield of 65 g. (59%) of salicylyl disulfide melting at 142° (Pyrex capillary) was obtained.

Although the diacetyl derivative was expected, analyses indicated the free hydroxyl compound. This was confirmed by the following facts: attempted saponification did not alter the compound; the precipitate, originally supposed to be sodium chloride, weighed more than calculated due presumably to sodium acetate; and acetylation gave a new product (see below) analyzing correctly for the diacetate.

Anal. Calcd. for $C_{14}H_{10}O_4S_2$: C, 54.81; H, 3.28; S, 20.93. Found: C, 54.93; H, 3.45; S, 20.19, 20.38.

Acetylsalicylyl Disulfide.—To 0.64 g. of salicylyl disulfide were added 3.5 ml. of acetic anhydride and two drops of concd. sulfuric acid. On stirring, the disulfide dissolved and the stoppered flask was allowed to stand one-half hour. Crystals of the acetylated material started to settle and a pasty mass resulted on cooling. While continuing the cooling, water was added with vigorous stirring. The reaction mixture was allowed to stand one-half hour, filtered and the product crystallized from hot 95% ethanol. A yield of 0.79 g. (97%) melting at 101.2° was obtained.

Anal. Calcd. for $C_{18}H_{14}O_6S_2$: C, 55.37; H, 3.61; S, 16.42. Found: C, 55.61; H, 3.70; S, 16.41, 16.61.

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Crystalline Natural α -Tocopherol Acetate

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In the course of work on the purification of tocopherols from natural sources, natural α -tocopherol acetate has been prepared in crystalline form. The procedure is published because it may be of assistance in the purification of synthetic α -tocopherol acetate, recently adopted as the international standard for the biological assay of vitamin E.¹ The preparation of natural or synthetic α -tocopherol acetate in crystalline form has not been reported in the literature to the writer's knowledge.

In the preparation, an α -tocopherol concentrate from a natural source (52.5 g., 68% α -tocopherol

(1) Hume, *Nature*, **148**, 472 (1941).

by Emmerie-Engel assay) was esterified with acetic anhydride (26 g.) in pyridine (9.5 cc.) for two hours at 75°. The reaction mixture was added to water and ether extracted. The extract was washed with 5% hydrochloric acid and water to remove pyridine. The residue after the removal of solvent was distilled in a cyclic molecular still and the fractions distilling at 130–180° at 3 μ pressure were combined for crystallization (35.9 g., $E_{1\text{cm.}}^{1\%}$ (286 m μ) = 35.6).

The acetate was crystallized from a 1.25% solution (g. per 100 cc.) in methyl alcohol at -30°. After recrystallization from a 2.5% solution in methyl formate at -30°, α -tocopherol acetate was obtained in needle-like crystals m. p. 26.5–27.5°; $E_{1\text{cm.}}^{1\%}$ (286 m μ) = 41.2; yield, 13.3 g.

By saponification in an atmosphere of nitrogen, α -tocopherol was obtained $E_{1\text{cm.}}^{1\%}$ (292 m μ) = 73.8. Analyzed by the Emmerie-Engel procedure, standardized against pure natural α -tocopherol, the preparation assayed 99.4% tocopherol. A sample of natural α -tocopherol prepared by another procedure had $E_{1\text{cm.}}^{1\%}$ (292 m μ) = 73. Thus the crystalline α -tocopherol acetate appeared to be pure.

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Synthesis of 4,4'-Diamidinostilbene Hydrochloride

By PETER P. T. SAH

4,4'-Diamidinostilbene has been prepared by the action of ammonia or ammonium salts on the bis-iminoether hydrohalides of 4,4'-dicyanostilbene.¹

In this communication, an alternative route to the diamidine, a substance of recent pharmacological interest,² is described. *p*-Iodobenzaldehyde, from *p*-iodobenzonitrile³ by Stephen's method, is converted through pyrolysis of the corresponding azine to 4,4'-diiodostilbene. The latter, which may alternately be obtained from 4,4'-diaminostilbene by the Sandmeyer reaction, is transformed through its dimagnesium derivative on reaction with ethyl orthocarbonate into the hexaethyl bis-ortho ester of stilbene-4,4'-dicarboxylic acid. On treatment with ammonia, the bis-ortho ester is transformed into the desired

(1) British Patent 510,097; *Chem. Abstr.*, **34**, 4079 (1940).

(2) Yorke, *Trans. Roy. Soc. Trop. Med. and Hyg.*, **33**, 463 (1940).

(3) Sah and Wang, *Rec. trav. chim.*, **59**, 365 (1940).