the trifluoroacetate (5.50 μ), the malonate (5.61 and 5.64 μ), and the oxalate (5.55 and 5.64 μ). The *gem*-dinitro absorptions occurred between 6.32–6.35 and 7.52–7.56 μ except for the malonate (6.30 and 7.51 μ), the trifluoroacetate (6.30 and 7.47 μ), and the 2-trifluoromethylacrylate (6.31, 7.45 μ, and 7.54 sh).

EXPERIMENTAL

Trifluoroacetic anhydride (TFAA) esterification method. One-fourth mole of the acid was slowly added to 55 g. (0.26 mole) of trifluoroacetic anhydride with stirring and cooling. To this stirred solution an equivalent amount of the alcohol was added at such a rate as to maintain gentle refluxing. After the addition was complete the solution was maintained at 60° for 4–5 hr., after which volatiles were stripped from the reaction mixture at 60°/40–50 mm. The residue was dissolved in ether, washed with ice water, washed free of acid with 5% sodium bicarbonate solution, and finally with water. After drying the solution with anhydrous magnesium sulfate, the ether was removed, and the product distilled through a 12-cm. vacuum-jacketed Vigreux column or a Hickman molecular still. Several of the crystalline esters were further purified by recrystallization from suitable solvents.

Polyphosphoric acid (PPA) esterification method. To a solution or suspension of 0.25 mole of the acid or anhydride in 150 g. of polyphosphoric acid at 50° an equivalent amount of the alcohol was added in portions with stirring. When the mildly exothermic reaction diminished, the reaction mixture was warmed to 75° for 3–4 hr., poured over ice while still warm, and the product extracted with ethyl acetate or ether. After washing free of acid with 5% sodium bicarbonate solution, the product was isolated and purified as described in the above method.

2,2-Dinitropropyl N-ethylcarbamate. A solution of 8.2 g. (0.114 mole) of ethyl isocyanate and 17 g. (0.113 mole) of 2,2-dinitropropanol in 200 ml. of chloroform was heated under reflux for 18 hr. Removal of the chloroform under reduced pressure and distillation of the residue from a Hickman still at 78–80°/0.02 mm. gave the theoretical yield of product with the properties given in Table I.

2,2-Dinitropropyl N-ethyl-N-nitrocarbamate. To a solution of 13.3 g. (0.06 mole) of 2,2-dinitropropyl *N*-ethylcarbamate in 125 ml. of acetic anhydride was added 100% nitric acid (125 ml.) while the temperature was kept below 10°. After 0.5 hr. the nitration mixture was poured over ice and the crude nitro compound was filtered, washed with water, and dried under vacuum giving 6 g. (37%) of product. After one crystallization from 95% ethanol, the 2,2-dinitropropyl *N*-ethyl-*N*-nitrocarbamate had the properties listed in Table I. The carbonyl absorption occurred at 5.59 μ and the nitro at 6.30, 7.50, and 7.72 μ in the infrared.[6]

Tris(2,2-dinitropropyl) phosphate. Phosphorus oxychloride (15 g.; 0.1 mole) was added to a solution containing 45 g. (0.3 mole) of 2,2-dinitropropanol and 0.2 g. of phosphorus trichloride in 100 ml. of toluene. After refluxing the mixture for 16 hr., the volatiles were removed under reduced pressure, 50 ml. of toluene was added, and the solution decolorized by percolating through a small activated charcoal column. Chilling the concentrated solution gave 13 g. (25%) of the ester having the properties listed in Table I.

2,2-Dinitropropyl 2-trifluoromethylacrylate. A solution of 15 g. (0.1 mole) of 2,2-dinitropropanol and 75 ml. of benzene was refluxed in a flask equipped with a water separator until no more water collected in the separator. 2-Trifluoromethylacrylic acid[7] (14 g., 0.1 mole) and 1 ml. of concd. sulfuric acid were added and the mixture refluxed for 16 hr. while 1.5 ml. of water (theory = 1.8 ml.) was collected in the separator. After washing the reaction mixture with 5% sodium bicarbonate solution, then with ice water, and drying over calcium sulfate the solvent was removed under reduced pressure giving 8.6 g. (32%) of crude white solid. Recrystallization from isopropyl ether gave an analytical sample with the properties given in Table I.

2,2-Dinitropropyl 4-nitro-4-azahexanoate. Addition of ethylnitramine to 2,2-dinitropropyl acrylate[8] by the method previously described[9] gave this ester with the properties listed in Table I in 63% yield. The carbonyl absorption occurred at 5.65 μ and the nitro at 6.32, 6.56, 7.55, and 7.74 μ in the infrared.[6]

LOS ALAMOS SCIENTIFIC LABORATORY
UNIVERSITY OF CALIFORNIA
LOS ALAMOS, N. M.

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Tris(*n*-butyl)phosphine Sulfide

RALPH A. ZINGARO AND RAYMOND E. MCGLOTHLIN

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Davies and Jones[1] reported that tris(*n*-butyl)phosphine reacts vigorously with sulfur, and more recently Chernick, Pedley, and Skinner[2] have measured the heat of reaction of tris(*n*-butyl)phosphine with sulfur. However, neither of these groups of investigators isolated or identified tris(*n*-butyl)phosphine sulfide. This compound is not reported by Kosolapoff,[3] and a careful search of the literature indicates that it has not been isolated or characterized. We have had need for this material, and its preparation and properties are herein reported.

Tris(*n*-butyl)phosphine reacts with bromine in hexane to form a heavy white precipitate of tris(*n*-butyl)phosphine dibromide. Addition of hydrogen sulfide to the latter results in the formation of tris(*n*-butyl)phosphine sulfide hydrobromide which separates out as a heavy oil and leaves any tris(*n*-butyl)phosphine oxide in solution, thus simplifying an otherwise difficult separation.

EXPERIMENTAL

The reaction must be carried out in a dry, nitrogen atmosphere. Into a 2-l., three-neck, oven-dried flask containing 101 g. (0.5 mole) of tris(*n*-butylphosphine in 1 l. of dry hexane, equipped with a stirrer, and gas inlet and outlet tubes was added dropwise, 80 g. (0.5 mole) of bromine. A voluminous white precipitate of tris(*n*-butyl)phosphine dibromide was formed. Hydrogen sulfide gas was then bubbled through

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the suspension until all of the solid bromine addition compound was converted to the heavy orange oil, tris(*n*-butyl) phosphine sulfide hydrobromide. The oil, following separation from the hexane layer, was taken up in ether, and washed cautiously with aqueous sodium carbonate until carbon dioxide evolution ceased. The ether layer was dried over anhydrous sodium carbonate, and following evaporation of the ether, the residue was carefully vacuum distilled. A number of distillations were necessary to obtain a pure product in yields of 25–40%. Tris(*n*-butyl)phosphine sulfide is a pale yellow oil possessing the following properties: b.p. 137–138° at 1.1 mm.; n_D^{25} 1.4945; d_{24}, 1.0339 g./ml.

Anal. Calcd. for $C_{12}H_{27}PS$: C, 61.49; H, 11.61; P, 13.22; S, 13.68. Found: C, 61.69; H, 11.76; P, 13.28; S, 13.83.

Tris(*n*-butyl)phosphine, tris(*n*-butyl)phosphine oxide, and tris(*n*-butyl)phosphine sulfide are characterized by infrared absorption bands at 718 and 742 cm.$^{-1}$ which is the region of the P—C and the P—S stretch. However, tris(*n*-butyl)-phosphine sulfide shows a much stronger intensity in the 742 cm.$^{-1}$ band than do the other compounds. This suggests that the P—S and P—C vibrations in the tris(*n*-butyl)-phosphine sulfide molecule overlap at this frequency.

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DEPARTMENT OF CHEMISTRY
AGRICULTURAL AND MECHANICAL COLLEGE OF TEXAS
COLLEGE STATION, TEX.

Synthesis of D,L-Caldariomycin[1]

JONATHAN R. BECKWITH[2] AND LOWELL P. HAGER[3]

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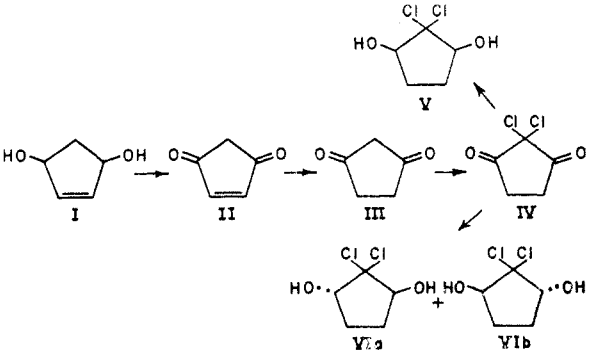
Studies have been initiated in this laboratory into the biosynthesis of caldariomycin,[4a-e] a chlorine-containing metabolite of the mold, *Caldariomyces fumago*. Clutterbuck *et al.*[5] isolated this compound in 1940 and proposed 2,2-dichloro-1,3-cyclopentanediol as the most likely structure for caldariomycin. Caldariomycin is optically active, therefore the natural product was designated as one of the *trans*-hydroxyl isomers (VIa or VIb). Since the structure assignment was based largely on degradative studies and represented a choice between possible alternatives, we proceeded to establish the structure of caldariomycin by synthesis.

We now wish to report the synthesis of a racemic mixture of the *trans*-hydroxyl isomers of caldariomycin by the following steps:



3,5-Cyclopentenediol (I) was separated from a mixture of 3,4- and 3,5-cyclopentenediols[6] by fractional distillation and was oxidized with chromic acid in acetone according to the procedure of DePuy and Zaweski.[7] The product, 3,5-cyclopentenedione (II), obtained in 45% yield, was then reduced with hydrogen over 10% palladium-on-charcoal in chloroform to yield 1,3-cyclopentanedione (III). After recrystallization of III from ethyl acetate, III was chlorinated with a slight excess of sulfuryl chloride. After recrystallization from ether and sublimation, a compound was obtained in 80% yield giving the correct analysis of 2,2-dichloro-1,3-cyclopentanedione (IV). In addition, the strong ultraviolet absorption associated with III had been almost completely eliminated, and a sole carbonyl band was observed in the infrared spectrum at 5.62 μ. Both these spectral features are indicative of the hindrance of any resonance in the formerly highly enolized β-diketone grouping. On the basis of this evidence and the analytical data, the compound was designated as 2,2-dichloro-1,3-cyclopentanedione.

Hantzsch[8] has proposed structure IV for a compound, m.p. 118°, obtained from a base-catalyzed chlorination of phenol. In contrast to IV obtained by the chlorination of III, the Hantzsch product exhibited color with ferric chloride reagent. This latter result would not be expected of IV, since enol formation is strongly inhibited in this compound. In addition, prior to carrying out the present synthesis, we attempted to prepare IV by Hantzsch's procedure without success. It seems most probable, therefore, that Hantzsch incorrectly assigned structure IV to his compound.

When the dichloro diketone (IV) was reduced

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(2) Predoctoral Fellow of the National Institute of Allergy and Infectious Diseases. Present address: Biology Department, Princeton University, Princeton, N. J.

(3) Present address: Chemistry Department, University of Illinois, Urbana, Ill.

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