

at slightly above room temperature, under an infrared lamp (in experiments in which the two phases were separated at this time and worked up individually, no improvement in yield was observed). The solution was then treated with 400 ml. of concentrated hydrochloric acid and concentrated under an infrared lamp over 24 hours to a volume of about 300 ml. in order to hydrolyze the amides, formed in the reaction, cooled, diluted with water to 1500 ml., and separated from a small amount of insoluble brown gum (this was base-insoluble and presumably consisted of products of tertiary substitution). Magnesium and diethylamine were removed by means of ion exchange. A column was prepared from 700 g. of Dowex 50-X8 resin (100–200 mesh; the weight was that of resin containing 50% moisture), the resin bed being 4.5 cm. in diameter and 53 cm. high. The reaction solution was passed through the resin in three batches of 450, 450 and 600 ml., respectively; each portion, after passage, was combined with 600 ml. of water with which the resin bed was downwashed. The resin bed was regenerated after each such treatment by passage of 1 liter of 1:1 hydrochloric acid, followed by wash water (usually about 1.5 liters) until the effluent was essentially neutral to Alkacid indicator paper.

The reaction mixture and the afterwashes combined with it were free of magnesium and contained only traces of diethylamine. Evaporation was effected by means of an infrared lamp to a volume of 300 ml. The resulting solution was brought to pH 10 by addition, with stirring, of a solution of barium hydroxide, making a total volume of 600 ml. The precipitated barium salts of the polymeric phosphinic acids were separated and washed with 300 ml. of hot water and 500 ml. of cold water. The combined filtrates were again evaporated by means of an infrared lamp to a volume of 400 ml., thereby expelling the residual traces of diethylamine. The barium ions in the solution were carefully precipitated by addition of 1:1 sulfuric acid; the precipitate, washed with 200 ml. of water, was discarded. The combined filtrates were evaporated to constant weight under an infrared lamp, yielding 20 g. of brownish viscous liquid, which was then dried by means of benzene azeotrope for 18 hr., 5 ml. of an aqueous phase being separated during that time. The benzene solution was then treated with 31 g. of phosphorus pentachloride, added gradually, and the mixture was refluxed for 2 hours until the evolution of hydrogen chloride ceased. The dark-brown solution was freed of benzene and phosphorus oxychloride by distillation on a water-bath at 30 mm. vacuum and the viscous residue was added slowly to an ice-cooled solution of 4.6 g. of sodium in 150 ml. of dry butanol. After stirring for three hours the mixture was filtered from sodium chloride and distilled, yielding 9 g. of crude butyl pentamethylenephosphinate, a viscous liquid, b.p. 85° (1.5 mm.).

Anal. Calcd. for $C_9H_{19}O_2P$: P, 16.3. Found: P, 15.0, 14.9.

The ester was hydrolyzed by refluxing overnight with 50 ml. of concentrated hydrochloric acid and the solution was evaporated to dryness. The residue was taken up in 50 ml. of water, decolorized with charcoal, and again evaporated to dryness. The residue was taken up in 20 ml. of benzene and part of the solvent was boiled off in order to remove the traces of moisture. The benzene solution was then cooled, diluted with hexane, and chilled in order to precipitate the bulk of pentamethylenephosphonic acid. The acid was removed by filtration and a second crop was obtained by evaporating the filtrate and adding more hexane to the residue. The product was recrystallized for a 1:6 mixture of benzene-hexane, yielding 5.8 g. of the acid, in the form of short stubby needles, m.p. 128–129°. The acid gave a titration curve with a single inflection at pH 7.5.

Anal. Calcd. for $C_9H_{11}O_2P$: P, 23.15; equiv. wt., 134. Found: P, 23.1, 23.05; equiv. wt., 133.2.

The distillation residue, after the removal of the above-described ester, was a dark, viscous undistillable material, which showed signs of decomposition on strong heating *in vacuo*. Presumably it consisted of the esters of polymeric phosphinic acids; these were apparently carried through the barium salt step by virtue of some solubility of these salts in water.

The isolation procedure described above appears to be the most satisfactory one, yielding 10.2% of the desired product. Direct distillation of the amides gave a very poor yield of

crude material, b.p. 85–105° (1 mm.) from the ether-soluble phase of the reaction mixture. Distillation of the phosphinyl chloride (after treatment with phosphorus pentachloride as described above) gave 6 g. of yellowish product, b.p. 150–152° (30 mm.), which was hydrolyzed to the above-described acid; however, the yield of the chloride was but 6 g. and the distillation was attended by much decomposition.

The insoluble barium salt precipitate was slurried in water, dissolved by addition of hydrochloric acid, and was freed of barium with sulfuric acid. Evaporation of the filtrate yielded the mixed polymeric products in the form of yellowish viscous semi-solid mass, a sample of which was titrated. The titration curve of this specimen indicated the presence of between five and six secondary acidic hydrogens per two primary acidic hydrogens. The curve was not sharply defined and a more accurate estimation was not justified.

A portion of the pure pentamethylenephosphinic acid was converted to the *n*-butyl ester, by conventional conversion to the acid chloride (b.p. 151–152° (30 mm.)) with phosphorus pentachloride, followed by treatment with sodium butoxide in dry butanol. The pure butyl pentamethylenephosphinate was a colorless liquid, b.p. 80° (1 mm.); n_D^{20} 1.4405; d_4^{20} 0.9771 (*MR* calcd. 51.31; *MR* found 51.30).

Anal. Calcd. for $C_9H_{19}O_2P$: P, 16.3. Found: P, 16.1, 16.2.

Reaction of Pentamethylene-bis-magnesium Bromide with Dibutyl Phosphite.—The reaction was run essentially as described above with 98 g. of pentamethylene bromide, 20.8 g. of magnesium and 55 g. of dibutyl phosphite. The reaction mixture gradually set to a nearly solid mass after the mixing of the components. The hydrolyzed mixture, after the removal of ether, was oxidized by the addition of bromine water to convert the P-H groups to P-OH groups, and the mixture was worked up essentially as described above. No detectable monomeric material could be isolated. The reaction products consisted of base-soluble and base-insoluble waxy semi-solids. The former were similar to the polymeric material isolated from the reaction described above. The base-insoluble material appeared to be the product of trisubstitution. These were not examined further.

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Catalysis of the Dehydration of 1,1,1-Trichloro-2-methyl-2-propanol *via* Thionyl Chloride. Intermediate Chlorosulfonic Ester Formation¹

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The reaction between thionyl chloride and hydroxy compounds is catalyzed by tertiary amines and amine hydrochlorides.³ In Gerrard and French's work typical alcohols gave high yields (about 95%) of the corresponding chlorides upon catalysis by tertiary amines.

The dehydration of 1,1,1-trichloro-2-methyl-2-propanol to 3,3,3-trichloro-2-methyl-1-propene is found to be similarly catalyzed by a variety of ten amines, tetramethylammonium chloride and aniline hydrochloride. In each case a small amount (0.007 to 0.06 mole) of the amine or amine salt markedly accelerates the reaction as shown by an immediate evolution of hydrogen chloride.

(1) A preliminary report of part of this work appeared in the Abstracts of Papers, American Chemical Society, Omaha, Nebraska, November, 1954.

(2) This paper is abstracted in part from the Ph.D. Thesis of Huey Pledger, Jr., and the M.S. Thesis of Louis E. Ott, submitted as partial fulfillment for these degrees at Kansas State College.

(3) W. Gerrard and K. H. V. French, *Nature*, **159**, 263 (1947).

With catalyzed reactions average yields of 80% were attained in 6 to 8 hours, while control reactions required 30 hours to reach similar yields.

Ethyl cyclopentanol-1,2-diacetate⁴ and ethyl cyclohexanol-1-acetate⁵ have been dehydrated by thionyl chloride in pyridine. In these cases the hydrogen chloride was stoichiometrically abstracted by the pyridine.

With seven of the twelve additives, small amounts (3–10%) of the isomerized product, 1,1,3-trichloro-2-methyl-1-propene, were also isolated. The five which gave no isomer were aniline, *t*-butylamine, di-*n*-butylamine, *N,N*-dimethylaniline and triethylamine. On the other hand, use of tetramethylammonium iodide (0.013 equiv.) as the additive yielded only the allylic isomer (88%). The iodide ion underwent exchange with the chlorine in thionyl chloride, free molecular iodine being observed. This trace of iodine apparently catalyzed the isomerization.

Gerrard⁶ also reported that equimolecular quantities of pyridine with various typical alcohols and thionyl chloride react, depending upon the conditions, to form sulfites, the chlorosulfinic ester and alkyl chlorides.

The chlorosulfinic ester of 1,1,1-trichloro-2-methyl-2-propanol is produced quantitatively in one hour when purified thionyl chloride in carbon tetrachloride is allowed to react with the anhydrous alcohol in the presence of a small amount of pyridine. The uncatalyzed reaction gave a lower yield of crude product in eight hours.

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Experimental⁷

General Procedure.—One mole of the 1,1,1-trichloro-2-methyl-2-propanol was mixed with 4 moles of thionyl chloride. On warming, hydrogen chloride was evolved. The catalyst (0.0124 mole) was added, and the mixture held at reflux (79°) until evolution of hydrogen chloride substantially ceased.

Each reaction mixture was fractionated through a glass helices packed column with total reflux, variable take-off head. 3,3,3-Trichloro-2-methyl-1-propene (TMP) was collected at b.p. 130–137°, the allylic propenyl chloride at b.p. 152–158°. The intermediate fraction (between the recovered thionyl chloride and the first propene fraction) contained small amounts of TMP (never above 12%). This TMP was isolated by treating the intermediate fraction with crushed ice. The organic layer was separated, washed with water and dried over potassium carbonate. Distillation gave TMP, b.p. 130–137°, n_D^{20} 1.4790–1.4793. TMP that is pure according to infrared analysis⁸ has n_D^{20} 1.4793–1.4795. These values agree well with those of De La Mare and Vernon⁹ who reported n_D^{20} 1.4785.

Summary of Results.—Numbers in % specify the yields of TMP isolated for each of the amines or amine salts: aniline (0.06 equiv.), 79%; *t*-butylamine (0.007), 79%; *t*-octylamine (0.007), 74%; di-*n*-butylamine (0.04), 78%; piperidine (0.01), 79%; diphenylamine (0.035), 76%; *N,N*-dimethylaniline (0.055), 83%; triethylamine (0.05), 83%;

quinoline (0.0085), 93%; pyridine (0.012), 83%; tetramethylammonium chloride (0.02), 82%; aniline hydrochloride (0.025) added as such, 78%.

Ammonia was ineffective as an additive and formed ammonium chloride, which precipitated, unlike the amine hydrochlorides.

Controls (no additive) required 30 hours reaction time to yield 81% TMP which still contained a little (5–15%) of the starting trichloromethylpropanol.⁸

Chlorosulfinic Ester of 1,1,1-Trichloro-2-methyl-2-propanol.—Purified thionyl chloride (145 ml., 2.0 mole) dissolved in 500 ml. of absolute carbon tetrachloride along with 177.5 g. (1 mole) of the anhydrous propanol and 5 ml. (0.06 mole) of pyridine was heated. At 45° hydrogen chloride came off rapidly. The temperature was slowly raised to 78° (45 minutes) when evolution of HCl slowed up markedly. One mole of HCl had come off (titration of the water absorber). The reaction mixture was cooled, and a liquefied pyridine hydrochloride which floated on the surface was removed. The remaining clear liquid was evacuated; the residue solidified as white needles of the chlorosulfinic ester, 260 g. (100%), m.p. 56.5–57.5° (sealed tube).

The chlorosulfinic ester hydrolyzes rapidly in the moisture of air to give off HCl and was found unsuitable for handling in the usual quantitative ultimate analyses. However, with extreme care, it was found possible to make a stoichiometric titration as follows. A 200-mg. sample of the dry white needles of chlorosulfinic ester was treated with 10 ml. of absolute ethyl alcohol under anhydrous conditions. The reacted sample was titrated rapidly with standard sodium hydroxide and gave neut. equiv. 257 (calcd. 260).

To simulate conditions in which the chlorosulfinic ester was formed *in situ* from the trichloromethylpropanol and excess thionyl chloride and decomposed to TMP in the presence of a trace of amine hydrochloride, the isolated chlorosulfinic ester (m.p. 56.5–57.5°) (0.49 mole) was dissolved in 108 ml. (1.5 moles) of thionyl chloride. Then, 0.03 mole equivalent of pyridine was added. The mixture was heated at 79° and required 7 hours to obtain 78% conversion to pure TMP.

Heating of the chlorosulfinic ester (65 g., 0.25 mole) alone at 79° required 23 hours to arrive at the point of very little gas evolution and a 79% yield of pure TMP.

Comparative Times Taken for Formation of the Chlorosulfinic Ester.—The purpose here was to evaluate the time necessary for conversion to the ester when pyridine hydrochloride was present and when it was not. One mole (177.5 g.) of the pure anhydrous trichloromethylpropanol, 146 ml. (2 moles) of thionyl chloride and 500 ml. of absolute carbon tetrachloride were dissolved together and the solution divided equally. To one portion was added 2.5 ml. (0.03 mole equivalent) of pyridine. The other portion was tested without any additive as a control. Both solutions were heated at 79°. When pyridine hydrochloride was present, one hour was required to complete the reaction (*i.e.*, liberation of 0.5 mole of HCl); eight hours was required by the uncatalyzed reaction. The catalyzed reaction gave 122 g. (95%) of the pure chlorosulfinic ester, m.p. 56–57°. The control gave a 73% yield of crude ester, quite impure, as it contained both TMP and unreacted 1,1,1-trichloro-2-methylpropanol which could not be satisfactorily removed from the crystals of the ester.

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Preparation and Oxidation of Certain Aryl Benzhydryl Sulfides

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The comparative ease of cleavage of the benzhydryl and trityl phenyl sulfides has been investigated by Tarbell and Harnish.¹ Knoll² reported

(1) D. S. Tarbell and D. P. Harnish, *THIS JOURNAL*, **74**, 1862 (1952).

(2) R. Knoll, *J. prakt. Chem.*, **113**, 40 (1926).

(4) R. P. Linstead and E. M. Meade, *J. Chem. Soc.*, 942 (1934).

(5) J. W. Cook and C. A. Lawrence, *ibid.*, 1637 (1935).

(6) W. Gerrard, *ibid.*, 99 (1939).

(7) All b.p.'s and m.p.'s are uncorrected.

(8) All infrared analyses by Dr. Alvin W. Baker.

(9) P. B. D. De La Mare and C. A. Vernon, *J. Chem. Soc.*, 3629 (1952).