The unusually high strength of the carbon-to-oxygen bond in trichloromethylpropanol is demonstrated by our isolation of 26% of  $Cl_3C-C(CH_3)_2$  $O-P(=O)(OH)_2$ .<sup>3,4</sup> The unusual volatility of 1,1-1-trichloro-2-methyl-2-bromopropane prevented its isolation in more than 5% conversion from I.

### Experimental Part

1,1,1-Trichloro-2-methylpropyl-2-phosphoric Acid (IV).— Preparation of IV is attended by extreme lachrymatory effects. All operations should be carried out in a hood, and with a gas mask and rubber gloves.

Freshly prepared phosphorus pentabromide (295 g., 0.685 mole) and 121.8 g. (0.685 mole) of purified anhydrous 1,1,1-trichloro-2-methyl-2-propanol (I) were mixed in a flask bearing a drying tube, and heated at 100° for 8 hours. The anhydrous reaction mixture and became dark amber in color and was cooled and allowed to stand at 25-30° for two weeks; then it was hydrolyzed slowly at 30-35° (2 to 4 hours) by taking it up with ether and with mechanical stirring, adding dropwise 100 ml. of distilled water. While the hydrolyzed mixture was allowed to stand at room temp., a crystalline mass formed which was collected after six days, and washed repeatedly with 10-ml. portions of carbon tetrachloride until the washes gave no residue on evaporation. The remaining crystals were dried under 20 mm. pressure, wt. 45.8 g. (26%) of IV, m.p. 159-163°, which analyzed for 11.3% phosphorus (calcd. 12.0%). The yield of pure IV, after recrystallization from water, was 30.4 g. (17%), m.p. 181-182.5°.

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Anal. Calcd. for C<sub>4</sub>H<sub>8</sub>Cl<sub>3</sub>O<sub>4</sub>P: Cl, 41.3; P, 12.0; neut. equiv., 257.5. Found: Cl, 41.7, 41.1; P, 12.0, 12.1, 12.2, 12.1, 12.2; neut. equiv., 259.5, 256.1, 261.8.

When this substance is cleaved by 60% aqueous potassium hydroxide at 25–40°, carbon monoxide (molybdenum blue test), phosphate ion (ammonium phosphomolybdate test) and acetone are produced. The last was identified after distillation of the diluted reaction mixture as its 2,4dinitrophenylhydrazone, m.p. 127.5–128°, undepressed by an authentic sample, and by a positive iodoform test (m.p. 118.5–119.5°).

The combined carbon tetrachloride washes were concentrated and the residue was sublimed to give II, m.p. 160-169°, which after recrystallizing from ether was found to be analytically pure, m.p.  $169-170^{\circ}$  (sealed tube).

(3) This finding agrees with the observation reported by W. Gerrard and P. L. Wyvill in *Research* **2**, 536 (1949), that phosphorus trichloride does not interact with I under mild conditions in which tbutyl alcohol readily affords the chloride, and that much more rigorous treatment affords the chlorophosphites ROPCls,  $(RO)_2PCl$ , but still no chloride; also, that an unusually vigorous treatment with phosphorus pentachloride is required to convert I into the corresponding chloride, RCI. Gerrard and Wyvill did convert I into the chloride in apparently about 90% yield only by refluxing I with phosphorus pentachloride for several hours. No product other than the chloride was mentioned.

(4) No method has yet been described, until the present, for converting the hydroxyl of I to a derivative of phosphoric acid.

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# Synthesis of Glycyl and Alanyl Chlorides<sup>1</sup>

### By Sumner Levine

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Fischer<sup>2</sup> has reported a fairly general method for the synthesis of amino acid chlorides. However,

(1) This work was supported by an institutional grant from the Damon Runyon Memorial Fund for Cancer Research.

(2) E. Fischer, Ber., 38, 2914 (1905).

this method suffers from the disadvantage of requiring a preliminary recrystallization of the amino acids and in addition, the reaction is conducted in acetyl chloride as the solvent. Because of these disadvantages and the relatively low yield obtained by Fischer's procedure, a modified method was developed. The synthesis was conducted as a heterogeneous reaction in the more convenient solvent carbon tetrachloride, in which the phosphorus pentachloride is dissolved. Since carbon tetrachloride is hydrophobic and less volatile than acetyl chloride, the product is less sensitive to atmospheric moisture during the filtration operation. In addition, the yield obtained by the present method is consider-ably higher than that of the earlier procedure. The reaction proceeds smoothly according to the equation

$$\begin{array}{c} H & O \\ RCHCOOH + PCl_5 \longrightarrow R - C - C - C + POCl_3 \\ \downarrow \\ NH_2 & NH_2 HCl \end{array}$$

Because of the salt formation at the amino nitrogen further condensation of the product to polypeptides does not occur under these conditions. In addition, since hydrochloric acid generated during the course of the reaction is bound, very little, if any, pressure build-up was noticed.

### Experimental Part

Glycyl Chloride Hydrochloride.—The reaction was conducted in a glass-stoppered vessel. Five grams of glycine was suspended in 200 ml. of purified carbon tetrachloride.<sup>3</sup> Fifteen grams of phosphorus pentachloride was added and the tightly (wired) stoppered vessel shaken vigorously for ten hours at room temperature. The product was filtered on a long necked sintered glass filter. During the filtration, the top of the sintered glass filter. The product was washed three times with carbon tetrachloride and then three times with anhydrous petroleum ether. After a final washing with anhydrous ether, the product was dried on the filter; yield 90 to 95%. The product was recrystallized from redistilled acetyl chloride; yield 75 to 80%.

Anal. Caled. for  $C_2H_5ONCl_2$ : C, 18.48; H, 3.88; N, 10.78; Cl, 54.56. Found: C, 18.50; H, 3.85; N, 10.75; Cl, 54.53.

Alanyl Chloride Hydrochloride.—This compound was prepared by the same method given above; yield 92%.

Anal. Calcd. for C<sub>3</sub>H<sub>7</sub>NOCl<sub>2</sub>: C, 25.02; H, 4.90; N, 9.73; Cl, 49.24. Found: C, 25.05; H, 4.85, N, 9.75; Cl, 49.28.

(3) L. F. Fieser, "Experiments in Organic Chemistry," D. C. Heath and Co., Inc., New York, N. Y., 1941.

DEPARTMENT OF BIOCHEMISTRY FRANCIS DELAFIELD HOSPITAL College of Physicians and Surgeons Columbia University New York, N. Y.

### Oxymercuration of trans-1,2-Diphenyl-1-propene

## By Alan Rodgman and George F Wright Received November 25, 1953

Studies in progress in this Laboratory show that a previous report of a single product from oxymercuration of 1-phenyl-1-propene is erroneous.<sup>1</sup> Since oxymercurations of related compounds such as styrene and 1-phenyl-2-methyl-1-propene give

(1) G. F Wright, THIS JOURNAL, 57, 1993 (1935).

only single products it seemed of interest to examine *trans*-1,2-diphenyl-1-propene. We have found only one product, 1,2-diphenyl-1-chloromercuripropanol-2, by hydroxymercuration in 1,2dimethoxyethane. Methoxymercuration gives only 1,2-diphenyl-1-chloromercuri-2-methoxypropane. These structures have been defined by hydrazine hydrate reduction to 1,2-diphenylpropanol-2 and 1,2-diphenyl-2-methoxypropane.

### Experimental<sup>2</sup>

1,2-Diphenyl-1-chloromercuripropanol-2.—To a suspension of 3.0 g. (0.0155 mole) of trans- $\alpha$ -methylstilbene<sup>3</sup> (m.p. 80.5–81.5°, diffraction [20] 4.88; [16] 6.96, 6.48; [12] 4.52, 3.86; [10] 4.68; [8] 3.79; [6] 3.71; [4] 11.78, 3.25; [2] 5.86; [1] 7.52, 4.35, 4.02) and 9.6 g. (0.031 mole) of mercuric acetate in 125 ml. of 50% aqueous 1,2-dimethoxyethane was added 1.00 g. (0.004 mole) of benzoyl peroxide. After 6 days agitation at 20–25° the system was filtered into 200 ml. of 3% aqueous sodium chloride. The precipitate was filtered off, washed with methanol (50 ml.) and ether (50 ml.), 1.85 g. (28%), m.p. 131–134°. Crystallization from acetone (15 ml./g.) raised the m.p. to 133.5–135.0°.

Anal. Calcd. for C15H15ClHgO: Hg, 45.0. Found: Hg, 44.4.

1,2-Diphenyl-1-chloromercuri-2-methoxypropane.—To a solution of 6.00 g. (0.031 mole) of  $\alpha$ -methylstilbene and 19.1 g. (0.06 mole) of mercuric acetate in 200 ml. of anhydrous methanol was added 1.85 g. (0.0076 mole) of benzoyl peroxide. After 7 days agitation at  $20-25^{\circ}$  the system was filtered into 350 ml. of 4% aqueous sodium chloride. The precipitate was filtered off and washed with 100 ml. of diethyl ether, 7.8 g. (74%), m.p. 81.5–82.5°. Crystallization from absolute ethanol (8 ml./g.) raised the m.p. to 84.3–85.0°. Diffraction is [20] 8.93; [16] 12.27, 3.18; [14] 7.82, 6.96; [10] 4.16; [8] 6.06, 4.79; [4] 4.44, 4.11, 3.82; [2] 4.37, 3.52, 2.94, 2.79, 2.73, 2.66, 2.45, 2.33, 2.23, 2.17; [1] 3.66, 3.42, 2.54, 2.26.

Anal. Calcd. for  $C_{16}H_{17}ClHgO$ : Hg, 43.5. Found: Hg, 43.0,

The etherous extract contained 0.80 g. of unchanged  $\alpha$ -methylstilbene.

1,2-Diphenylpropanol-2.—To a solution of 1.45 g. (0.0033 mole) of 1,2-diphenyl-1-chloromercuripropanol-2 in 10 ml. of methanol was added a solution of 1.27 g. (0.0066 mole) of sodium hydroxide in 2.0 ml. of water, then 2.00 ml. (0.035 mole) of 85% hydrazine hydrate. After 7 hours reflux, the system was filtered to remove 0.62 g. (95%) of mercury. The filtrate was diluted with 60 ml. of water and extracted with a total of 30 ml. of diethyl ether. A colorless oil (0.58 g.) obtained from this extract was distilled, b.p. 145–148° (3 mm.), 0.42 g. (60%), m.p. 49.5–51.0°. Mixture melting point with authentic 1,2-diphenylpropanol-2 was not lowered.

2 was not lowered. A mixture melting point with the alcohol prepared according to the method of Hell<sup>4</sup> was not lowered. We have never been able to reproduce the melting point of 71–72° quoted by Tuot and Guyard.<sup>6</sup> **1,2-Diphenyl-2-methoxypropane.**—To 9.2 g. (0.02 mole) of **1,2-diphenyl-1-chloromercuri-2-methoxypropane** in 40 ml. of methanol was added a solution of 1.60 g. (0.004 mole) of sodium hydroxide in 4 ml of water, then 29 ml (0.05

1,2-Diphenyl-2-methoxypropane.—To 9.2 g. (0.02 mole) of 1,2-diphenyl-1-chloromercuri-2-methoxypropane in 40 ml. of methanol was added a solution of 1.60 g. (0.004 mole) of sodium hydroxide in 4 ml. of water, then 2.9 ml. (0.05 mole) of 85% aqueous hydrazine hydrate. After 450 minutes reflux the system was filtered to remove 3.65 g. (91%) of mercury. The filtrate was diluted to 150 ml. with water and extracted with a total of 140 ml. of ether. Evaporation of this extract left an oil which was distilled, b.p. 110-112° (13 mm.), 1.33 g. (29%).

Anal. Calcd. for  $C_{16}H_{18}O$ : C, 83.9; H, 8.04. Found: C, 83.9; H, 8.50.

When this ether (1.13 g., 0.005 mole) was heated at 70-75° for 150 minutes with 3.3 ml. (0.025 mole) of 47% hydro-

(3) C. F. Koelsch and R. V. White, J. Org. Chem., 6, 602 (1941).

- (4) C. Hell, Ber., 37, 453 (1904).
- (5) M. Tuot and M. Guyard, Bull. soc. chim. France, 1086 (1947).

bromic acid in 6.5 ml. of glacial acetic acid, a yield of 0.90 g. (90%) of 1,2-diphenylpropanol-2, m.p.  $50.5-51.5^{\circ}$ , was obtained. A mixture melting point was not lowered.

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## Action of 9-Diazofluorene on $\omega$ -Nitrostyrenes and its Substituted Derivatives

### By Ahmed Mustafa and Abdel Hamid Elsayed Harhash

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Recently, Parham and Bleasdale<sup>1</sup> have shown that the condensation of nitroölefins (I) which contain no hydrogen atom alpha to the nitro group with diazomethane results in the formation of products (presumably nitropyrazolines (II)) which yield 3,4disubstituted pyrazoles (III) in good yields when treated with mineral acids or heat. In two cases the intermediate nitropyrazolines were obtained as crystalline solids. When diazomethane was allowed to react with  $\omega$ -nitrostyrene (Ia) at room temperature, a quantitative yield of additive product was obtained. However, the product appeared to be polymeric and had no properties commensurate with those of the expected nitropyrazolines (II).



We have now investigated the action of 9-diazofluorene on the  $\omega$ -nitrostyrenes (Ia–Ie) listed in Table I and found that they react to give the cyclopropane derivatives V listed in Table II, believed to be formed by way of the intermediate pyrazoline, *e.g.*, IV.<sup>2</sup>



TABLE I

Ia,  $R = C_6H_{5}$ , R' = H; b,  $R = C_6H_4NO_{2^-\rho}$ , R' = H; c,  $R = C_6H_4NO_{2^-m}$ , R' = H; d,  $R = C_6H_4NO_{2^-\rho}$ , R' = H; e, R = 3-pyrenyl ( $C_{16}H_9$ ), R' = H

(1) W. E. Parham and J. L. Bleasdale, THIS JOURNAL, 72, 3843 (1950); 73, 4664 (1951).

(2) The reaction of 9-diazofluorene with acrylonitrile and methyl vinyl ketone leads directly to the formation of cyclopropane derivatives. Cf. L. Horner and E. Lingnau, Ann., 573, 30 (1951).

<sup>(2)</sup> Melting points have been corrected against reliable standards. X-Ray diffraction patterns are expressed at d spacings in Å, with relative intensities  $[I/I_1]$  using CuK $\alpha$  radiation,