as by ourselves, that colored solutions are also formed by tungsten hexachloride in various solvents; but we feel that the two cases are not comparable, for the following reasons. (1) Tungsten hexachloride itself has a blood-red color, so that solutions in various solvents showing a red, brown, or yellow color are reasonably to be expected, whereas tungsten hexafluoride itself is colorless. (2) The red solution of the hexafluoride in benzene freezes to a colorless crystalline solid, which on warming regains its color. (3) If the hexafluoride were reduced by solvent to lower valences of tungsten, the solution could not be expected to follow Beer's law, as was found to be the case. Furthermore, the colored solution of the hexafluoride in benzene remained unaltered for weeks, indicating lack of reaction, whereas the hexachloride solutions change gradually, owing to reduction of the tungsten.

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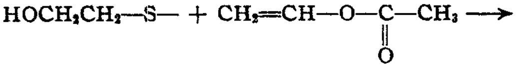
RECEIVED MARCH 11, 1948

Thiodiglycol Monoacetate by the Photochemical Addition of Mercaptoethanol to Vinyl Acetate

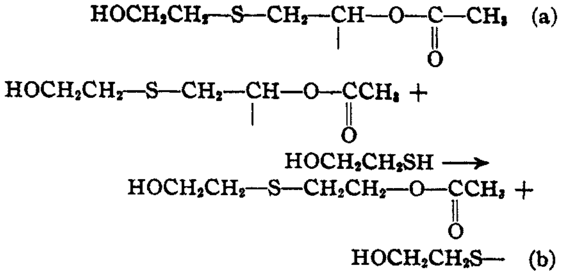
BY WALTER H. C. RUEGGEBERG, JACOB CHERNACK, IRA M. ROSE AND E. EMMET REID

The photochemical addition of mercaptans to olefins has been studied in this Laboratory[1] for several years. Recently, the photoaddition of ethanolmercaptan to vinyl chloride yielding 2-chloroethyl-2-hydroxyethyl sulfide (semi-mustard) was reported by Fuson and Ziegler[2] and from this Laboratory.[3] Inasmuch as the monoacetate of thiodiglycol has not been reported previously in the literature to the best of our knowledge, it appeared worthwhile to synthesize this half-ester through the photochemical addition of ethanolmercaptan to vinyl acetate.

It was soon learned, however, that the reaction rate depended strongly upon the purity of vinyl acetate used. Thus, for example, when freshly distilled vinyl acetate was mixed with mercaptoethanol, the mixture warmed up immediately. Titration of the residual mercaptan with iodine in methanol solution showed that 80% of the mercaptan had reacted after the first hour. On the other hand, if stabilized vinyl acetate (Eastman Kodak Co., practical grade) is employed in the process, no reaction is observed until the mixture is irradiated from an S-4, 100 watt mercury vapor lamp (General Electric Co.) in the presence of 1% of diphenyl disulfide, as catalyst.



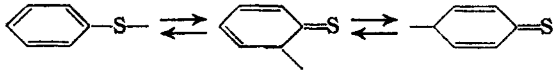
$$\mathrm{HOCH_2CH_2{-}S{-}} + \mathrm{CH_2{=}CH{-}O{-}\underset{\overset{\|}{O}}{C}{-}CH_3} \longrightarrow$$



$$\mathrm{HOCH_2CH_2{-}S{-}CH_2{-}\underset{|}{C}H{-}O{-}\underset{\overset{\|}{O}}{C}{-}CH_3} \quad \text{(a)}$$

$$\mathrm{HOCH_2CH_2{-}S{-}CH_2{-}\underset{|}{C}H{-}O{-}\underset{\overset{\|}{O}}{C}CH_3} + \mathrm{HOCH_2CH_2SH} \longrightarrow \mathrm{HOCH_2CH_2{-}S{-}CH_2CH_2{-}O{-}\underset{\overset{\|}{O}}{C}CH_3} + \mathrm{HOCH_2CH_2S{-}} \quad \text{(b)}$$

Although disulfides such as diamyl disulfide are known to accelerate the photoaddition of mercaptoethanol to vinyl chloride,[3] it has been shown that diphenyl disulfide is a catalyst superior to aliphatic disulfides in this type of reaction.[1] Two reasons for this behavior may be cited. First, diphenyl disulfide absorbs light more strongly than dialkyl disulfides in the visible and near ultraviolet regions of the spectrum,[1] indicating that free radicals are more easily obtained; secondly, the stabilizing influence of resonance on the thiophenyl radicals should prolong their lives thus increasing reaction probability. The three resonance forms of the thiophenyl radicals may be represented by the following equilibria



In the disulfide-free reaction, the primary dissociation is that of the splitting of the S—H bond

$$\mathrm{HOCH_2CH_2SH} + h\nu \longrightarrow \mathrm{HOCH_2CH_2{-}S{-}} + \mathrm{H{-}}$$

This reaction is then followed by a chain mechanism given by equations (a) and (b), above.

Thiodiglycol monoacetate, so prepared, is a water white liquid resembling thiodiglycol itself in odor and having the physical properties listed in Table I. It is soluble in water, benzene, carbon tetrachloride, chloroform, ethyl ether and acetone but insoluble in hexane or cyclohexane.

TABLE I

SOME PHYSICAL PROPERTIES OF THIODIGLYCOL MONOACETATE[a]

Temp., °C.	Density, g./ml.	Refractive index n_{TD}	Molar refractivity[b] found	Viscosity, centipoises
9.5	1.1671	....	...	26.96
10	1.1666	1.4916	40.81	...
20	1.1576	1.4879	40.87	...
25	1.1531	....	...	12.43
30	1.1485	1.4841	40.92	...
35.8	1.1433	....	...	8.22
		Mean	40.87	

[a] Surface tension at 28.9°, 41.2 dynes/cm. (du Noüy method). [b] The calculated value of the molecular refractivity is 40.78.

Experimental

Photosynthesis in the Absence of Catalysts.—Mercaptoethanol, 33.2 g., obtained from the Carbide and Carbon Chemicals Corporation was added slowly to 92.4 g. of freshly distilled, unstabilized vinyl acetate, originally obtained from Eastman Kodak Company. Immediately upon mixing, an exothermic reaction ensued. After

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[1] Rueggeberg, *et al.*, reports on file at the Army Chemical Center; not currently available in the published literature.

[2] Fuson and Ziegler, *J. Org. Chem.*, **11**, 510 (1946).

[3] Rueggeberg, Cook and Reid, *ibid.*, **13**, 110 (1948).

standing one hour, an iodimetric titration of the reaction mixture in methanol indicated that about 80% of the mercaptan had undergone reaction. The mixture was allowed to stand at room temperature for one week prior to being distilled. Distillation of the product resulted in the recovery of unused mercaptoethanol and vinyl acetate and a residue yield of crude thiodiglycol monoacetate weighing 54.4 g. This material on distillation boiled at 137–138° at 8 mm.; yield of distilled product, 51%. *Anal.* Calcd. for $C_6H_{12}O_3S$: S, 19.5. Found: S, 19.2.

Photosynthesis in Presence of Diphenyl Disulfide.—Vinyl acetate, 90 g., (practical grade, stabilized) obtained from the Eastman Kodak Company was mixed with 78 g. of mercaptoethanol obtained from the Carbide and Carbon Chemicals Corporation. No reaction ensued. These reagents together with 0.8 g. of diphenyl disulfide (1% of the mercaptan used) were placed in a 300-ml. Pyrex test-tube and suspended in a water-bath at 20–25°. An S-4, 100-watt mercury vapor lamp was also suspended under water and placed 11 cm. from the center of the test-tube. On turning on the light the temperature of the reaction mixture rose from 22 to 34° receding slowly after about one hour of irradiation. Irradiation was continued for an additional two hours and subsequently, the reaction product was distilled. After two distillations 72 g. of a product was obtained boiling at 147.7 to 148° at 13–14 mm.

Anal. Calcd. for $C_6H_{12}O_3S$: C, 43.9; H, 7.4; S, 19.5. Found: C, 43.7; H, 7.4; S, 19.9.

Acknowledgment.—The authors are indebted to Messrs. N. Beitsch, S. Sass, E. A. Green and B. Zeffert for having performed the analytical and physical work presented in this paper.

CHEMICAL CORPS TECHNICAL COMMAND
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RECEIVED JANUARY 14, 1948

Preparation of Vanillonitrile and Vanillic Acid from Vanillin

BY CONRAD SCHUERCH, JR.

The acid catalyzed condensation of hydrazoic acid with aldehydes is included in the more general Schmidt reaction,[1] and in the case of acetaldehyde, benzaldehyde and *m*-nitrobenzaldehyde, results in the corresponding nitriles and N-substituted formyl derivatives.

$$\text{I.}\quad RCHO + HN_3 \xrightarrow{H^+} RC{\equiv}N + H_2O + N_2$$

$$\text{II.}\quad RCHO + HN_3 \xrightarrow{H^+} RNH{-}CHO + N_2$$

Vanillin has now been found to react readily in the presence of sulfuric acid according to equation I, and crystalline vanillonitrile has been easily isolated in a yield of about 70%. The formanilide, which was presumably formed at the same time according to equation II, did not interfere appreciably in the purification of the nitrile. When the original reaction mixture was diluted with water and boiled, hydrolysis of the nitrile occurred and almost pure vanillic acid crystallized in more than 70% yield from the liquors. This observation is of interest because vanillic acid is not readily available by the direct oxidation of vanillin, and because Pearl's catalytic oxidation with silver oxide[2] was found to be somewhat sensitive to obscure differences in the experimental conditions. Substitution of veratraldehyde for the vanillin used in the condensation with hydrazoic acid resulted in more than an 80% yield of crystalline veratric acid, and a small amount of 4-aminoveratrole (equation II) was also isolated from the hydrolysate.

As would be expected from the known reactions of ketones and the mechanism recently proposed for the Schmidt reaction[3,4,5,6] vanillin reacted with hydrazoic acid in the presence of reagents such as a dioxane solution of hydrogen chloride, that are milder than sulfuric acid. Although it is probable that a proper choice of solvent would give a homogeneous system and a smooth condensation with much smaller quantities of acid than those now used, the decrease might well alter the relative amounts of the products formed.[1]

Acknowledgment.—The author wishes to express his gratitude to Professor C. B. Purves for his kind interest and assistance in this and related work.

Vanillonitrile and Vanillic Acid.—One hundred grams (0.658 mole) of pure vanillin was dissolved completely in 375 ml. of concentrated reagent grade sulfuric acid kept at 0–10° in a 2-liter 3-necked flask, with mercury-sealed stirrer, condenser, thermometer and gas exit tube attached. Powdered sodium azide (45 g., 0.69 mole), contained in a small flask attached to the reaction vessel by means of a rubber connector, was added to the red solution at 0–11° over a period of one and one-half hours. The cooling bath was removed and the mixture was stirred for another half hour. The flask was again chilled and about 900 ml. of distilled water was added cautiously from a separatory funnel without allowing the temperature to rise above 18°. This addition caused the nitrile to separate as a yellow solid which completely filled the aqueous layer. When desired, the nitrile could be extracted with ether, and isolated after washing the extract with small amounts of sodium bisulfite and sodium bicarbonate solutions. The yield from smaller quantities of reactants was about 70% and most of the product melted at 87.5–88.3°; m. p. 89–90° is the recorded value for vanillonitrile.[7]

When vanillic acid was required, the original reaction mixture was diluted with 900 ml. of water as already described. The stirrer and thermometer were then removed and washed with 100 ml. of water which was added to the reaction flask, and the mixture boiled gently under reflux. Crystals of vanillic acid appeared after two and one-half hours, and after three hours of boiling the mixture was allowed to cool overnight. The crystals were filtered with suction under an efficient hood, washed five times with a total volume of 1700 ml. of distilled water and dried: yield of vanillic acid 81.5 g. or 73.8%; m. p., 201–203°; and neutralization equivalent (by electrometric titration to *p*H 7), 171. Calcd. for vanillic acid, neut. equiv., 168. Decolorization and recrystallization from water gave beautiful needles but raised the m. p. only slowly. A melting point of 208–210° was obtained,

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[1] R. Adams, "Organic Reactions," Vol. 3, John Wiley and Sons, New York, N. Y., 1947, article by H. Wolfe, The Schmidt Reaction, p. 307.

[2] Pearl, THIS JOURNAL, **68**, 429 (1946).

[3] Sanford, Blair, Arroya and Sherk, *ibid.*, **67**, 1941 (1945).

[4] Smith, *ibid.*, **70**, 320 (1948).

[5] (a) Newman, Organic Chemistry Symposium, Boston, Mass., 1947; (b) Newman and Gildenhorn, THIS JOURNAL, **70**, 317 (1948).

[6] Schuerch and Huntress, presented at the 112th Meeting of the American Chemical Society in New York, N. Y., September, 1947.

[7] Rupe, *Ber.*, **30**, 2449 (1898).