

higher boiling material and 30.0 g. of undistillable residue. The high boiling material despite repeated fractional distillations did not yield fractions with constant refractive indices. Thus there was obtained in all 111.6 g. of isopropylidenediglycerol and 71.8 g. of diisopropylidenediglycerol.

The higher boiling material was hydrolyzed as indicated in the next experiment to yield a polyhydric material whose hydroxyl content (32.1%) indicated that it was a mixture of triglycerol (hydroxyl content = 35.4%) with higher polyglycerols. These experiments show that 100 g. of polyglycerol (hydroxyl content = 40.0%) yields 88.5 g. of distillable isopropylidene derivatives and 10 g. of undistillable residue. Of the distillate 42% is isopropylidenediglycerol, 27% is diisopropylidenediglycerol, and 31% consists of the isopropylidene derivatives of tri- and higher polyglycerols.

Diglycerol.—A solution of diisopropylidenediglycerol (71.0 g.), water (75 cc.), and concentrated hydrochloric acid (5 cc.) was heated on a steam-bath for a few minutes after which the volatile material was removed under reduced pressure. There resulted the theoretical quantity (48.0 g.) of previously characterized diglycerol³ which distilled at 184° (0.28 mm.) and at 207° (1.2 mm.) and possessed a n_D^{20} of 1.4885.

Periodate Oxidation of Diglycerol.—The periodate oxidation of the diglycerol was carried out at 24° using aqueous 0.05 M periodate (buffered, pH 4.2) prepared from trisodium paraperiodate and acetic acid.¹¹ In two

(11) (a) D. H. Craugaard, J. H. Michell and C. B. Purves, *THIS JOURNAL*, **61**, 1290 (1939); (b) O. A. Moe, S. E. Miller and M. H. Iwen, *ibid.*, **69**, 2621 (1947). The authors are indebted to Miss Marjorie Iwen for the performance of the oxidations.

experiments the diglycerol consumed 2.00 and 2.01 moles of oxidant per mole.

Summary

Allylation and subsequent distillation has provided a means for identifying, separating and estimating the amounts of the constituents of polyglycerol mixtures. These mixed polyglycerols were prepared by improved procedures.

Acetonation and subsequent distillation has provided an alternate means for the same process. This has an advantage in that isopropylidene derivatives are readily hydrolyzed to the parent compounds, and pure diglycerol can be obtained from a polyglycerol mixture by this procedure. A higher boiling fraction which could not be purified by fractional distillation consisted primarily of the isopropylidene derivatives of triglycerol together with a small amount of the isopropylidene derivatives of higher polyglycerols.

O-Tetraallyldiglycerol, O-pentaallyltriglycerol and diisopropylidenediglycerol are described.

The diglycerol obtained has been shown to be linear by periodate oxidation.

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[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

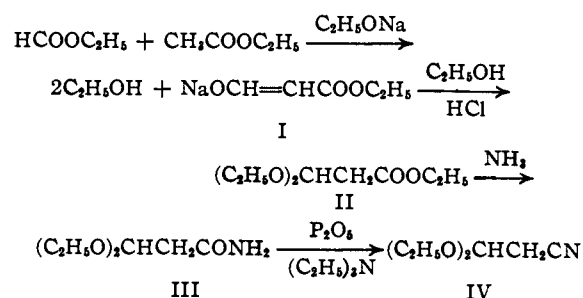
The Preparation, Alcoholysis and Reduction of Cyanoacetaldehyde Diethylacetal. Malonaldehyde Tetraethylacetal

By S. M. McELVAIN AND ROBERT L. CLARKE¹

In the development of certain work in this Laboratory the orthoesters corresponding to cyanoacetaldehyde diethylacetal (IV) and malonaldehyde tetraethylacetal were desired. It therefore became necessary to prepare this cyanoacetal in sufficient quantity that further reactions utilizing it could be studied. The preparation of this cyanoacetal from the corresponding bromoacetal has been reported.² The procedure and results obtained by Uhle and Jacobs^{2b} were duplicated in the present work, but this method did not seem suitable for our purposes, since the yield is low (14%) and the product requires long and careful fractionation for purification.³ Consequently an

alternative method of preparation of cyanoacetal was developed.

This method employed the following sequence of reactions



The lowest yields encountered were in the preparation of II and it is believed that these yields are a consequence of the quality of the sodium enolate (I). This enolate was prepared by the method of Cogan,⁴ who reported that the salt obtained from the indicated ester condensation was composed of 63% of the enolate (I), 23% of the sodium enolate of acetoacetic ester, and 12% sodium formate. However, the salt obtained by Cogan's procedure in the present work appeared

(4) Cogan, *Bull. soc. chim.*, **8**, 128 (1941).

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(2) (a) Hartung and Adkins, *THIS JOURNAL*, **49**, 2517 (1927); (b) Uhle and Jacobs, *J. Org. Chem.*, **10**, 81 (1945); cf. Hartung and Adkins, *THIS JOURNAL*, **69**, 1535 (1947).

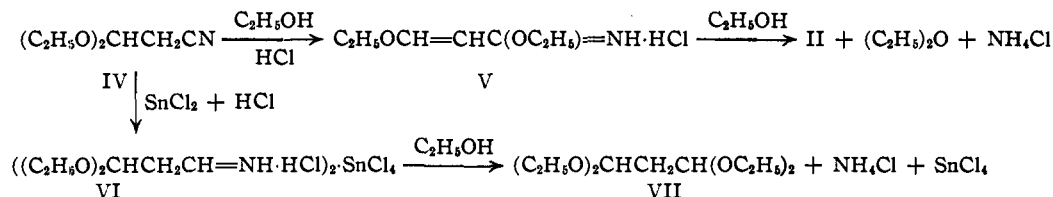
(3) Since 67% of unchanged bromoacetal was recovered from this reaction after forty hours of heating the reactants in refluxing aqueous alcohol, the reaction time was doubled. The same yield of cyanoacetal and same recovery of starting material was obtained. Sodium iodide is used in this reaction, presumably to form the more reactive iodoacetal. That the iodoacetal is an intermediate in the reaction is shown by the fact that the same results were obtained when iodoacetal was used instead of the bromoacetal. Evolution of ammonia was noted throughout the course of the reaction, indicating that hydrolytic destruction of the cyanide ion proceeds at a greater rate than does the replacement of the halogen of the acetal.

to contain only 39–40% of the enolate (I), no sodium enolate of acetoacetic ester, and quite probably no sodium formate.⁵ The conversion of the salt containing I to the acetal-ester (II) gave consistent yields of 34% of II (assuming the salt to be 100% I) in a series of twenty-three experiments.⁶ That these low yields of II were not due to an unfavorable equilibrium between ethyl formyl acetate and II, was shown by the fact that the equilibrium, when approached from the acetal side, was found to be 93% complete in favor of the acetal. This extent of reaction applied to the 34% yield of II, together with the 3% yield of ethyl trimesate (from the trimerization of ethyl formylacetate) which always accompanied II, leads to the conclusion that no more than 39–40% of I could have been present in the salt obtained from the condensation of ethyl formate with ethyl acetate. This calculated maximum

the salt was converted to the amide (III)). However, the expected orthoester was not obtained, but instead ethyl β,β -diethoxypropionate (II) and diethyl ether were isolated from the reaction mixture. The formation of the ester instead of the orthoester during the alcoholysis of the iminoester salt (V) has been noted in other cases in this Laboratory and will be discussed in a subsequent paper.

The conversion of the cyanoacetal (IV) to malonaldehyde tetraethylacetal by a modification of the Stephen procedure was readily accomplished.⁸ The intermediate iminoaldehyde hydrochloride–stannic chloride complex (VI) was obtained without difficulty and alcoholized directly to malonaldehyde tetraethylacetal (VII), which was isolated in 35% over-all yield from cyanoacetal.

These transformations of cyanoacetal are illustrated by the reactions



yield of I corresponds to the amount of alcohol produced in the condensation.⁵

β,β -Diethoxypropionamide (III) was obtained in 80% yield from the ester (II), and the dehydration of this amide to the cyanoacetal (IV) with phosphorus pentoxide in the presence of triethylamine proceeded in 80% yield.⁷ Generally a 5–10% yield of β -ethoxyacrylonitrile, resulting from the loss of alcohol from the cyanoacetal, also was obtained. This alcohol can readily be replaced to form IV by treatment of the unsaturated nitrile with alcohol in the presence of sodium ethoxide.

Treatment of the nitrile (IV) with alcohol and hydrogen chloride converted it to ethyl β -ethoxyiminoacrylate hydrochloride (V). The alcoholysis of this salt required a temperature of 40–45° and then proceeded only to the extent of 38% (the yield of ammonium chloride; the remainder of

(5) This conclusion is based on the following observations: (a) only 39% of the expected alcohol was found in the volatile portion of the reaction mixture; (b) the yields of II (34%) and ethyl trimesate (3%) that were consistently obtained from the salt; and (c) the failure to isolate any acetoacetic ester from the reaction mixture that contained II.

(6) These yields were not appreciably affected by: variation of the reaction time from one to twenty-four hours; variation of the reaction temperature from 5 to 25°; variation of the sodium enolate-hydrogen chloride ratios from 1:1.5 to 1:5.5 (*cf.* Dyer and Johnson, *THIS JOURNAL*, **56**, 222 (1934); Sugasawa, *Chem. Zentr.*, **98**, II, 1814 (1927)). The yield, however, was decreased by increased age of the salt. The calculated quantity of alcohol for the reaction gave a 25% yield of II, whereas a 15-fold excess of alcohol raised this yield to 34%.

(7) Substitution of N-ethylmorpholine for triethylamine gave only a 47% yield of the cyanoacetal; for the dehydration of another acid-sensitive amide, diethoxyacetamide, see McElvain and Clarke, *THIS JOURNAL*, **69**, 2661 (1947).

The preparation of malonaldehyde tetraethylacetal was reported in 1903, but seven years later the claim was withdrawn.⁹ Malonaldehyde has been reported by Huttel¹⁰ as an unstable solid, m. p. 72–74°. The acetal as prepared in the present work should furnish a stable source of this aldehyde.

Experimental

Ethyl Sodium Formylacetate (I).—Cogan's procedure⁴ was followed for the preparation of this salt, except that the stirring period for the reaction was lengthened to forty hours, after which time an easily filterable suspension of salts was obtained. The filtered salt was freed of all volatile material under reduced pressure and without the use of heat.

All condensable volatile material from the reaction was collected by efficient cold traps. The amount of unreacted esters (15 mole per cent.) was determined by saponification of an aliquot of the volatile portion. Following saponification of the esters in the remaining portion of the volatile portion, the total alcohol content was determined by fractional distillation. After subtraction of the amount of alcohol produced by ester saponification, there remained an amount of alcohol equivalent to a 39% yield based on the expected condensation reaction to produce I.

The dry salt residue from the reaction was investigated in the following manner. To a stirred solution of 55 g. (1.6 moles) of dry hydrogen chloride in 800 ml. of dry diethyl ether was slowly added 138 g. (1.0 mole) of the condensation product calculated as ethyl sodium formylacetate. The precipitated sodium chloride, separated and washed with ether, weighed 57.6 g. or 98.5% of the theoretical amount. The filtrate and washings were

(8) Stephen (*J. Chem. Soc.*, **125**, 1874 (1925)) reports nearly quantitative yields of both aromatic and aliphatic aldehydes by this procedure, but Williams (*THIS JOURNAL*, **61**, 2248 (1939)) reported rather poor yields of the aliphatic aldehydes that he prepared by this method.

(9) Harries, *Ber.*, **26**, 3659 (1903); *Ann.*, **374**, 319 (1910).

(10) Huttel, *Ber.*, **74**, 1825 (1941).

combined and distilled at atmospheric pressure in a system connected with a carbon dioxide absorption train. When almost all the ether had distilled, an evolution of carbon dioxide began. A total of 4.2 g. of carbon dioxide was collected; this amounted to a 10 mole per cent. yield. The bath temperature was 125° at the end of the decarboxylation reaction. The combined distillate and undistilled portion were neutralized with sodium bicarbonate, filtered and fractionated. After the ether was removed, 37 g. (0.80 mole) of ethyl alcohol was collected. This does not equal the amount of alcohol actually produced since some reacts with ethyl formylacetate to form ethyl β,β -diethoxypropionate. After the alcohol was removed, the pressure was reduced to 28 mm. Nothing distilled at a bath temperature of 125°. The boiling point of ethyl acetoacetate is 88° (28 mm.). The pressure was then lowered to 9 mm. and 6 g. of ethyl β,β -diethoxypropionate distilled at 85–90°, this being the first material to distil after the alcohol. From this experiment it may be concluded that no detectable amount of ethyl acetoacetate was produced in the reaction.

Any sodium formate present in the original condensation product should have been converted to formic acid by the acidification with hydrogen chloride and then separated from the reaction products upon neutralization of the solution and filtration following the decarboxylation reaction. The precipitate removed following the neutralization with sodium bicarbonate failed to produce any decoloration in a 2% permanganate solution. Since sodium formate decolorizes this reagent, it may be concluded that none of this salt was present in the condensation product studied.

Determination of the Conversion of Ethyl Formylacetate to II at Equilibrium.—To a solution of 7.6 g. (0.22 mole) of dry hydrogen chloride and 3.80 g. (0.211 mole) of water in 250 ml. (4.35 moles) of absolute alcohol at room temperature was added 40 g. (0.211 mole) of pure ethyl β,β -diethoxypropionate. The mixture was shaken thoroughly and then allowed to stand for sixteen hours. The acid was neutralized by the addition of 50 g. of solid sodium bicarbonate and the alcohol was removed by distillation at atmospheric pressure. Sufficient water was added to the residue to make a thin slurry of the salts; this slurry was extracted twice with 75-ml. portions of ether and the combined extracts were dried over potassium carbonate. The ether was removed by distillation at atmospheric pressure and the residue was fractionated under reduced pressure. The amounts of the products isolated were: 37.3 g. (93%) of ethyl β,β -diethoxypropionate, 0.29 g. (1.5%) of ethyl trimesate and 1.0 g. of liquid held by the column.

Ethyl β,β -Diethoxypropionate (II).—This ester was obtained in 34% yield from the solid salt (assuming this salt to be I) by the method of Dyer and Johnson (see ref. 6). In an attempt to determine quantitatively the products formed in the preparation of II, the following experiment was carried out.

To a stirred solution of 60.7 g. (1.32 mole) of absolute alcohol and 45 g. (1.25 mole) of dry hydrogen chloride in 460 ml. of dry ether chilled in an ice-bath was added 91 g. (0.66 mole) of ethyl sodium formylacetate. After the mixture was stirred in the cold for two hours, it was allowed to warm to room temperature and the stirring was continued for fourteen hours. The hydrogen chloride in the mixture was neutralized by addition of 84 g. (1 mole) of solid sodium bicarbonate and the solid material was separated by decantation, addition of 200 ml. of ether to the residue, decantation, addition of 200 ml. of ether, and filtration. The combined ether solutions were carefully fractionated into: 81.7 g. of alcohol, d_{25}^{25} 0.811, which is equivalent to 74.3 g. (1.62 mole) of ethyl alcohol and 7.4 g. of water, a 2.2-g. intermediate fraction which was largely water, 31.4 g. (0.165 mole or 25%) of ethyl β,β -diethoxypropionate, 1.9 g. (1.1%) of ethyl trimesate and 5.3 g. of a high boiling residue. Since the expected recovery of alcohol was 1.32 mole (originally introduced) minus 0.33 mole (required for acetal formation) or 0.99 mole, the amount (1.62 mole) actually isolated was 0.63 mole more than expected. This could come only from the

decomposition of the sodium salts used in the reaction. No esters were present in this alcohol; nor was any acetoacetic ester found.

β,β -Diethoxypropionamide (III).—A mixture of 285 g. (1.5 mole) of ethyl β,β -diethoxypropionate and 1500 ml. (22.5 moles) of concentrated ammonium hydroxide (sp. gr. 0.90) was stirred at room temperature until it became homogeneous. This required approximately forty hours, depending upon the efficiency of the stirring. The water and excess ammonia were removed from the reaction mixture at 50° by means of reduced pressure. Since β,β -diethoxypropionamide decomposes when heated to approximately 90° for a short time to form a high-melting yellow solid, it is important that the preparation be conducted well below this temperature. After the water was removed, the mixture was heated for thirty minutes at 60° under a pressure of 10 mm. The residue was dissolved in 200 ml. of benzene and 600 ml. of petroleum ether (40–60°) was added. When this mixture was cooled to 0° with vigorous shaking, the product separated as a voluminous precipitate of fine needles. After separation by filtration, the product was spread on porous plates to dry.

A further quantity of the amide was obtained from the mother liquor. The benzene and petroleum ether were removed under reduced pressure and the residue was shaken with 60 ml. of 20% aqueous potassium carbonate. The resulting solution was extracted with four 75-ml. portions of ether and the combined ether extracts were dried over potassium carbonate. The ether was removed under reduced pressure, the residue dissolved in 10 ml. of benzene and 70 ml. of petroleum ether added to this solution. Cooling and shaking this mixture resulted in the precipitation of an additional quantity of amide which was separated as before. The total yield of β,β -diethoxypropionamide obtained amounted to 193 g. or 80% of the theoretical amount. The product thus obtained softened at 49° and melted at 51–53°, an indication that it was slightly impure. A sample of this amide recrystallized from a mixture of equal parts of benzene and petroleum ether softened at 53.5° and melted at 54.5–54.8°.

Anal. Calcd. for $C_7H_{15}NO_3$: N, 8.70. Found: N, 8.63.

Cyanoacetaldehyde Diethylacetal (IV).—In a 1-liter, round-bottom, three-neck flask fitted with a rubber sealed stirrer, an efficient, large bore reflux condenser closed with a drying tube, and a large bore rubber tube for addition of solid material, were placed 115 g. (0.71 mole) of β,β -diethoxypropionamide, 250 ml. of benzene, and 145 g. (1.42 mole) of triethylamine. Both the benzene and the triethylamine were previously dried over phosphorus pentoxide. The stirrer was started and 135 g. (0.95 mole) of phosphorus pentoxide was slowly shaken into the reaction mixture from a 500-ml. erlenmeyer flask attached to a side arm of the reaction flask by the large-bore rubber tubing. This addition required about five minutes. The tube and erlenmeyer flask then were replaced by a stopper.

Reaction was initiated in this mixture by heating the flask to 80–90° with an oil-bath. When the exothermic reaction had started, as evidenced by vigorous refluxing, the oil-bath was lowered. As the reaction subsided the oil-bath was again raised and the mixture was kept refluxing moderately for one hour. With the stirrer still in operation, the condenser was replaced by a still head and most of the benzene and excess triethylamine were distilled at a maximum bath temperature of 120°. Finally, with a Dry Ice-acetone trap in the system, all liquid possible was distilled under gradually decreasing pressure. A final pressure of 10 mm. at a bath temperature of 140° was employed.

All the distillates were combined and fractionated. After the benzene and triethylamine were removed at atmospheric pressure, the pressure was reduced. The portion boiling at 90–95° (12 mm.), n_D^{20} 1.4177, was collected. This n_D indicated the product to be a mixture of 93% cyanoacetaldehyde diethylacetal and 7% β -ethoxyacrylonitrile.

In order that the reaction product might be obtained as

pure cyanoacetal, it was added to 268 g. of absolute ethyl alcohol in which 0.05 g. of sodium metal had previously been dissolved. After the solution stood for an hour it was neutralized with glacial acetic acid using phenolphthalein as an indicator. The ethyl alcohol was removed at room temperature under reduced pressure and the residue was fractionated. Pure cyanoacetal was collected at 91–93.5° (11 mm.); n_D^{25} 1.4153; d_4^{25} 0.947. The yield amounted to 83 g. (81%). This product contained 62.2% ethoxyl and 9.64% nitrogen (calcd. 62.9 and 9.78%, respectively). Uhle and Jacobs^{2b} report the following constants for this cyanoacetal: b. p. 99° (14 mm.); n_D^{20} 1.4155; d_4^{20} 0.9496.

β -Ethoxyacrylonitrile.—This nitrile was formed along with cyanoacetal when β,β -diethoxypropionamide was dehydrated by phosphorus pentoxide in the presence of triethylamine. It was separated from cyanoacetal by careful fractionation and found to boil at 71–72° (8 mm.); n_D^{25} 1.4520; d_4^{25} 0.945.

Anal. Calcd. for C_4H_7NO : C_4H_7O , 46.4; N, 14.4. Found: C_4H_7O , 45.6; N, 13.4.

Treatment of this nitrile with alcohol in the presence of a small amount of sodium ethoxide resulted in a quantitative addition of alcohol to form cyanoacetal. Heating 60 g. of cyanoacetal with four drops of concentrated sulfuric acid at 135° for twenty-four hours resulted in the isolation of 4.4 g. (23%) of alcohol and 16.3 g. (40%) of β -ethoxyacrylonitrile.

Ethyl β -Ethoxyiminoacrylate Hydrochloride (V).—In a 200-ml. round-bottomed flask fitted with a gas inlet tube bubbler and an outlet tube closed with a calcium chloride tube was placed 30 g. (0.21 mole) of cyanoacetal and 8.2 ml. (0.14 mole) of absolute ethyl alcohol. The mixture was chilled in an ice-bath and 20 g. (0.55 mole) of dry hydrogen chloride was passed in. After standing for three hours in the ice-bath the mixture was allowed to warm to room temperature and stand for an additional fifteen hours. The resulting viscous liquid was extracted with five 30-ml. portions of dry diisopropyl ether and the residue put under vacuum for sixteen hours to remove ether and excess hydrogen chloride. The resulting yellow solid was triturated with cold diisopropyl ether and the ether was removed by filtration. The solid was placed in a vacuum desiccator at 8 mm. for two hours. The yield amounted to 27 g. (72%).

Anal. Calcd. for $C_7H_{14}ClNO_2$: Cl, 19.8. Found: Cl, 19.7.

In this preparation only 60–70% of the theoretical quantity of alcohol is added, the rest being supplied by alcohol elimination from the cyanoacetal. More alcohol than this promotes excessive miscibility with the extracting ether while less appears to diminish the yield.

To a mixture of 9 g. of potassium carbonate, 20 ml. of diethyl ether and 11 ml. of water, cooled to -10° , was added 12.2 g. of finely ground ethyl β -ethoxyiminoacrylate hydrochloride. The mixture was shaken vigorously for one minute and the layers were quickly separated. The aqueous layer was extracted three times with 20-ml. portions of ether and the combined ether extracts were dried over potassium carbonate. After the ether was removed on a steam-bath the residue was fractionated. Ethyl β -ethoxyiminoacrylate was collected at 59–61° (1 mm.); n_D^{25} 1.4620; d_4^{25} 0.985; M_D 39.9 (calcd. 40.3). The yield amounted to 3.2 g. (33%).

Anal. Calcd. for $C_7H_{12}NO_2$: C_7H_8O , 62.9. Found: C_7H_8O , 61.6.

Alcoholysis of Ethyl β -Ethoxyiminoacrylate Hydrochloride.—A mixture of 53 g. (0.3 mole) of ethyl β -ethoxyiminoacrylate hydrochloride and 161 g. (3.5 moles) of absolute ethyl alcohol was heated in an oil-bath at 40–45° for six days. The precipitated ammonium chloride, removed by filtration, amounted to 6.0 g. (38%). The solution was made alkaline to phenolphthalein by addition of sodium ethoxide in absolute ethyl alcohol and the ethyl alcohol removed at room temperature under reduced pressure. The residue boiled at 61–66° (2 mm.). Fractionation of this distillate gave partial separation and revealed it to be a mixture of ethyl β,β -diethoxypropionate (identi-

fied by b. p., n_D and conversion to β,β -diethoxypropionamide) as the principal constituent and a lower boiling unsaturated compound with an ethoxyl value somewhat lower than that of ethyl β,β -diethoxypropionate. The latter is believed to be ethyl β -ethoxyacrylate. The yield of these esters amounted to approximately 32% of the theoretical amount. Since the amide produced by pyrolysis of the iminoester hydrochloride is destroyed at the boiling point of the accompanying esters, it was not isolated.

To determine if diethyl ether and the normal ester were produced by pyrolysis of the orthoester, the alcoholysis was carried out in a stoppered flask, following which the mixture was chilled in an ice-bath and the liquid decanted from the ammonium chloride produced. When this decantate was heated to gentle reflux, a small quantity of ether distilled and was identified by its boiling point and that of its boron trifluoride addition compound. No evidence of ethylene was obtained.

Malonaldehyde Tetraethylacetal (VII).—The anhydrous stannous chloride used for this preparation was prepared by heating the dihydrate in an erlenmeyer flask at 200° for one hour. The anhydrous salt was finely powdered in a mortar.

In a 2 liter, round-bottomed flask fitted with a stirrer, gas inlet tube and a gas outlet tube closed with a calcium chloride tube were placed 1 liter of dry ether and 142 g. (0.75 mole) of anhydrous stannous chloride. The mixture was chilled in an ice-bath and saturated with dry hydrogen chloride (this required four hours). Usually at this point a heavy oily layer separated but in one experiment it was necessary to let the mixture stand at room temperature overnight before the layer separated. Then 50 g. (0.35 mole) of cyanoacetaldehyde diethylacetal was added and the resulting mixture stirred vigorously for two hours, after which time it was allowed to stand at room temperature for five days. The β,β -diethoxyiminopropionaldehyde hydrochloride-stannic chloride complex (VI) that precipitated amounted to 51 g., 47% of the theoretical amount. After the solid was removed by filtration the oily layer was separated from the ether layer and subjected to alcoholysis as described below.

To the solid salt complex was added 100 ml. of absolute ethyl alcohol. This mixture was heated at 45° for three and one-half days before alcoholysis was complete. It was neutralized with solid sodium bicarbonate, the solid material was filtered and washed with alcohol, and the alcohol was removed from the combined filtrate and washings under reduced pressure. The residue was fractionated and 14.7 g. of malonaldehyde tetraethylacetal collected at 77–78° (3 mm.); n_D^{25} 1.4101; d_4^{25} 0.916; M_D 59.5 (calcd. 59.6).

Anal. Calcd. for $C_{11}H_{20}O_4$: C_2H_5O , 81.8. Found: C_2H_5O , 80.5.

The oily layer set aside above was mixed with 500 ml. of absolute alcohol and heated for three days at 45°. It was then worked up in a manner similar to the treatment of the precipitated salt. An additional 12.6 g. of VII was isolated. The total yield for the preparation was 27.3 g. or 35% of the theoretical amount.

Summary

A new method for the preparation of cyanoacetaldehyde diethylacetal is described.

This cyanoacetal is converted by alcohol and hydrogen chloride to ethyl β -ethoxyiminoacrylate hydrochloride, which yields ethyl β,β -diethoxypropionate on alcoholysis.

Malonaldehyde tetraethylacetal is prepared by the direct alcoholysis of the iminoaldehyde-stannic chloride complex obtained from the Stephen reduction of the cyanoacetal. This is a novel method for the preparation of an acetal.

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