CHEMISTRY OF ACETALS

COMMUNICATION 1. GENERAL METHOD FOR THE SYNTHESIS OF BIS [DIETHYL ACETALS] OF β-DICARBONYL COMPOUNDS*

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From 1949 onward many American [1-7], Japanese [8-13], and Canadian [14-16] patents appeared on the application of the condensation of orthoformic esters with various vinyl ethers as a method for the synthesis of the corresponding acetals of malonaldehyde. Only recently has this reaction been described in greater detail [17, 18], and the method received the most systematic and complete treatment in the paper of Protopopova and Skoldinov [18].

With the object of synthesizing bis [diethyl acetals] of various β-dicarbonyl compounds required by us for use in the lengthening of isoprenoid chains, we studied the addition of triethyl orthoformate to vinyl ethers of the following types: 1) β-substituted vinyl ethers, i.e., ethyl propenyl ether, 2-bromovinyl ethyl ether, ethyl 3-methyl-1-butenyl ether, and ethyl 2-methylpropenyl ether; 2) α-substituted vinyl ethers, i.e., ethyl isopropenyl ether and ethyl 1-methylpropenyl ether ; 3) one cyclic vinyl ether, i.e., 1-ethoxycyclohexene. It was found that ethyl propenyl and 2-bromovinyl ethyl ethers react readily and smoothly with orthoformic ester in equimolecular proportions in presence of catalytic amounts of boron trifluoride etherate, zinc chloride, or other catalyst of the Friedel-Crafts type (e.g., aluminum chloride, tin tetrachloride, titanium tetrachloride) with formation of methyl-1-and bromo-malonaldehyde bis [diethyl acetals], respectively, in high yield (70-80%):

$$\mathrm{RCH{=}CHOC_2H_5 + CH(OC_2H_5)_3 \longrightarrow (C_2H_5O)_2CHCHRCH(OC_2H_5)_2}$$
$$\mathrm{R{=}CH_3,\ Br}$$

In both cases the formation occurred also of small amounts of higher-boiling products, probably secondary products of the addition of the vinyl ether to the dialdehyde bis [diethyl acetal]. The structure of the methylmalonaldehyde bis [diethyl acetal] was confirmed by its conversion by reaction with hydrazine into known 4-methylpyrazole [19], which was identified as its picrate. The structure of the bromomalonaldehyde bis[diethyl acetal] was confirmed by comparison with data in the literature for bromomalonaldehyde bis [diethyl acetal] prepared in a different way and also by acid hydrolysis into the well-known crystalline bromomalonaldehyde, identified by a mixture melting point test with a known sample [21].

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The addition of orthoformic ester to 3-methyl-1-butenyl and 2-methylpropenyl ethyl ethers occurs less vigorously and gives the corresponding isopropyl- and dimethyl-malonaldehyde bis [diethyl acetals] in yields of 20-30%. In this case the greater part of the vinyl ether is recovered unchanged from the reaction. The structures of the bis [diethyl acetals] were confirmed by acid hydrolysis to the corresponding dialdehydes, which, without being isolated, were oxidized with potassium permanganate to the known isopropyl- [22] and dimethyl- [23] malonic acids.

α-Substituted vinyl ethers differ appreciably from β-substituted ethers in the conditions required for reaction with orthoformic ester. It was found that in the case of α-substituted vinyl ethers only zinc chloride has a satisfactory catalytic effect. The use of boron trifluoride etherate leads to the resinification of the α-substituted vinyl ether, and titanium tetrachloride, tin tetrachloride, aluminum chloride etherate, and other catalysts bring about cleavage side reactions, which result in the formation of a complex mixture of low-boiling products, which we did not investigate more closely. Also, in reactions with α-substituted vinyl ethers it is essential to use not less than a two-fold excess of orthoformic ester. Thus, in the reaction of ethyl isopropenyl ether and of ethyl 1-methylpropenyl ether with orthoformic ester at a ratio of 1 : 2 in presence of zinc chloride at 35-45°, we obtained the bis [diethyl acetals] of acetoacetaldehyde and 2-methylacetoacetaldehyde in yields of about 45%:

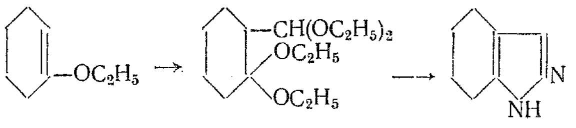
$$\mathrm{RCH{=}C(R')OC_2H_5 + CH(OC_2H_5)_3 \longrightarrow (C_2H_5O)_2CHCHRC(OC_2H_5)_2R}$$

$$\mathrm{R'{=}CH_3;\quad R{=}H \ \text{or}\ CH_3}$$

It must be mentioned that in both cases we obtained up to 10% of secondary reaction products, whose structures will be the subject of future communications.

The structure of the acetoacetaldehyde bis [diethyl acetal], which has been mentioned previously only in a patent [24], was confirmed by its conversion into the known 3 (or 5)-methylpyrazole [25], which was identified as its picrate and as its complex salt with silver nitrate. To confirm the structure of the 2-methylacetoacetaldehyde bis [diethyl acetal] it was converted into 4,5 (or 3)-dimethylpyrazole [26], which was identified as its picrate.

Apart from the examples examined above, we made a detailed study of the reaction between 1-ethoxycylohexene and orthoformic ester. This reaction is again catalyzed only by zinc chloride, and to obtain the maximum yield (about 30%) of 2-oxocyclohexanecarboxaldehyde bis [diethyl acetal] it is necessary to use a considerable excess of orthoformic ester (3-4 moles per mole of 1-ethoxycyclohexene) and an equimolecular amount of zinc chloride.



In this reaction there was formed also a considerable amount of secondary condensation products, the study of which is continuing. On increase in the amount of zinc chloride to above the equimolecular amount, the yield of 2-oxocyclohexanecarboxaldehyde bis [diethyl acetal] diminishes and a considerable amount of resinous products is formed. The structure of the 2-oxocyclohexanecarboxaldehyde bis [diethyl acetal] was confirmed by its conversion into 4,5,6,7-tetrahydro-1H-indazole [27] by reaction with hydrazine in acid medium.

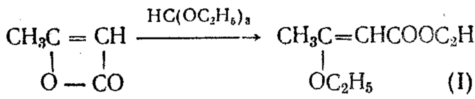
We showed that, apart from the catalysts mentioned in the literature, zinc chloride is a good catalyst for the reaction of ethyl vinyl ether. It is interesting that in the reaction of orthoformic ester with ethyl vinyl ether at a ratio of 1 : 1 at 40-50° in presence of titanium tetrachloride a considerable amount (up to 31%) of 1,1,3,5,5-pentaethoxypentane is formed.

We showed that orthoacetic ester is also able to react with ethyl vinyl ether. The best results were obtained by the use of a mixed catalyst (boron trifluoride etherate and zinc chloride) by heating the mixture at 50-60° for six hours. Under these conditions the above-described acetoacetaldehyde bis [diethyl acetal] was formed in 30% yield:

$$CH_2{=}CHOC_2H_5 + CH_3C(OC_2H_5)_3 \longrightarrow CH_3C(OC_2H_5)_2CH_2CH(OC_2H_5)_2$$

We also tried to bring some vinyl esters into reaction with orthoformic ester. It was found that vinyl acetate with orthoformic ester at 30-40° only in presence of a mixture of boron trifluoride etherate and yellow mercuric oxide, and as a result of double decomposition malonaldehyde bis [diethyl acetal] is formed in 25% yield; by the addition of small amounts of trichloroacetic acid to the reaction mixture the yield can be raised to 40-50%. All attempts to cause 1-cyclohexen-1-ol acetate to react were unsuccessful.

As diketene can be regarded as a peculiar internal vinyl ester, we decided to examine the action of orthoformic ester on this substance. Although diketene reacted readily with orthoformic ester in presence of boron trifluoride etherate, the reaction occurred not with addition at the double bond, but with cleavage of the ester linkage of diketene and formation of a crystalline enol ether (I). The enol ether (I) formed beautiful white crystals having a strong smell of aniseed, m.p. 29-30°; it was found to be identical with ethyl 3-ethoxycrotonate, as prepared previously by Claisen [28], and by reaction with 2,4-dinitrophenyl-hydrazine it gave the 2,4-dinitrophenylhydrazone of acetoacetic ester.



$$CH_3C{=}CH(-O-CO-) \xrightarrow{HC(OC_2H_5)_3} CH_3C(OC_2H_5){=}CHCOOC_2H_5$$

(I)

As we were interested in the possibility of the addition of orthoformic ester to activated double bonds, we investigated its addition to styrene, which could lead to β-ethoxyhydrocinnamaldehyde diethyl acetal:

$$C_6H_5CH{=}CH_2 + CH(OC_2H_5)_3 \longrightarrow C_6H_5CH(OC_2H_5)CH_2CH(OC_2H_5)_2$$

It is known [29] that acetaldehyde diethyl acetal readily adds to styrene with formation of 3-ethoxy-3-phenyl-1-propanol. On the other hand a patent was taken out by Copenhaver [30] for the addition of ortho esters to butene, indene, and cyclopentadiene, and in another patent by the same author [31] it is stated that orthothioformic ester adds to styrene in presence of boron trifluoride etherate when the mixture is heated at 50° for six hours. When treated with 2,4-dinitrophenylhydrazine the product gave the 2,4-dinitrophenylhydrazone of cinnamaldehyde, but the yield is not stated. We carried out a detailed investigation of the reaction of orthoformic ester with styrene. In spite of wide variation of reaction conditions (temperature, time, relative amounts of reactants, introduction of solvents, use of various iodic and free-radical catalysts), the yield of β-ethoxyhydrocinnamaldehyde diethyl acetal did not exceed 5% on the original amount of styrene, and most of the styrene was recovered unchanged.

EXPERIMENTAL

Starting Materials. Ethyl vinyl ether: a commercial preparation was purified by treatment with and distillation over sodium; b.p. 35-36°: n_D^{20} 1.3775. 2-Bromovinyl ethyl ether was prepared by the elimination of hydrogen bromide from 1,2-dibromoethyl ethyl ether with the aid of N,N-diethylaniline [32]; b.p. 44-46° (20 mm); n_D^{20} 1.4728. The remaining vinyl ethers were prepared by the elimination of alcohol from the corresponding acetals, prepared by the reaction of aldehydes and ketones with tetraethyl orthosilicate in presence of phosphoric acid [33] and by Claisen's method [28], using p-toluenesulfonic acid instead of phosphorus pentoxide.

Ethyl Propenyl Ether. A mixture of 164 g of propionaldehyde diethyl acetal (b.p. 120-123°; $n_D^{18.5}$ 1.3900), 0.2 g of p-toluenesulfonic acid, and 8 ml of quinoline was boiled in a flask fitted with a 50-cm column; the distillate was collected in a receiver containing aqueous sodium carbonate solution. The organic layer was washed with sodium carbonate solution, dried with magnesium sulfate, treated with sodium, and after one day distilled over sodium. We obtained 68 g (66%) of ethyl propenyl ether; b.p. 69-72°; n_D^{18} 1.3990. In a similar way we prepared ethyl isopropenyl ether [from acetone diethyl acetal (b.p. 114-116°; n_D^{19} 1.3900);yield 60%; b.p. 62-64°; n_D^{24} 1.3890; ethyl 2-methylpropenyl ether [from isobutyraldehyde diethyl acetal (b.p. 134-135°; n_D^{20} 1.3940); yield 40%; b.p. 80-91°; n_D^{17} 1.4098]; ethyl 3-methyl-1-butenyl ether [from isovaleraldehyde diethyl acetal (b.p. 64-66° at 23-25 mm); n_D^{18} 1.4020], yield 60%; b.p. 110-114°; n_D^{20} 1.4085. Found: C 74.00; 73.90; H 12.50; 12.42%. $C_7H_{14}O$. Calculated: C 73.76; H 12.36%.

Ethyl 1-Methylpropenyl Ether. This was prepared from butanone diethyl acetal (b.p. 118-122°; $n_D^{19.5}$ 1.4000); yield 70%; b.p. 89-92°; n_D^{19} 1.4060. Found: C 71.89; 71.88; H 12.21; 12.30%. $C_6H_{12}O$. Calculated: C 71.95; H 12.08%.

1-Ethoxycyclohexene. This was prepared from cyclohexanone diethyl acetal [b.p. 74-76° (14 mm): n_D^{18} 1.4320] by heating it under reduced pressure (180-190 mm) at 140-160° in presence of p-toluenesulfonic acid and quinoline; yield 77%; b.p. 57-59° (16-18 mm); $n_D^{16.5}$ 1.4592.

Catalysts. Boron trifluoride etherate was purified by distillation; b.p. 126-128°. The zinc chloride catalyst consisted of a solution of 95 g of commercial anhydrous zinc chloride in 165 g of dry ether.

Malonaldehyde Bis [Diethyl Acetal]. To a mixture of 148 g (1 mole) of orthoformic ester and 50 ml of ethereal zinc chloride we added 72 g (1 mole) of ethyl vinyl ether gradually so that the temperature did not exceed 35°. The reaction mixture was heated with stirring for two hours at 40-50°, cooled to room temperature, and washed with excess of 15-20% aqueous sodium hydroxide; the organic layer was separated, and the aqueous layer was extracted with ether. The combined organic and ether layers were dried with magnesium sulfate, and ether was distilled off. Vacuum fractionation of the residue gave 168 g (76%) of malonaldehyde bis [diethyl acetal]; b.p. 90-94° (6-7 mm); n_D^{19} 1.4070. Found: C 59.94; 59.94; H 11.00; 11.00%. $C_{11}H_{24}O_4$. Calculated: C 59.97; H 10.98.

Methylmalonaldehyde Bis [Diethyl Acetal]. A similar procedure was used. From 29.6 g (0.2 mole) of orthoformic ester and 12.9 g (0.15 mole) of ethyl propenyl ether in presence of 5 ml of ethereal zinc chloride, after the usual treatment and distillation, we obtained 25 g (70%) of methylmalonaldehyde bis [diethyl acetal]; b.p. 68-75° (1 mm); n_D^{18} 1.4152. Redistillation gave the pure bis [diethyl acetal]; b.p. 65-67° (1 mm); n_D^{18} 1.4160. Found: C 61.30; 61.20; H 11.20; 12.12%. $C_{12}H_{26}O_4$. Calculated: C 61.50; H 11.18%.

In order to prove its structure we added 23.4 g (0.1 mole) of the bis [diethyl acetal] dropwise to a mixture of 7 g (0.1 mole) of hydrazine hydrochloride, 20 ml of water, and 5 ml of 1 N HCl, and stirring was continued at 45-50° until the organic phase dissolved. When the mixture was cool, it was treated with 30% sodium hydroxide solution; the upper layer was separated, and the alkaline layer was extracted with ether. The combined upper and ether layers were dried with magnesium sulfate and, after the removal of the volatile components on a boiling water bath, the residue was vacuum-fractionated. We obtained 4 g (50%) of 4-methylpyrazole, b.p. 67-68° (2 mm) and $n_D^{16.5}$ 1.4930; the picrate prepared from this in the usual way had m.p. 147-148° (from water or benzene), which corresponds to data in the literature [19]. Found: N 22.53; 22.62%. $C_{10}H_9O_7N_5$. Calculated: N 22.51%.

Bromomalonaldehyde Bis [Diethyl Acetal]. To a mixture of 29.6 g (0.2 mole) of orthoformic ester and 2.5 ml of boron trifluoride etherate we added 30.2 g (0.2 mole) of 2-bromovinyl ethyl ether dropwise so that the temperature did not rise above 40°; the mixture was heated for one hour at 40-50°; and when it was cool 10 ml of pyridine was added. Fractionation gave 46 g (76.6%) of bromomalonaldehyde bis [diethyl acetal], b.p. 125-127° (7 mm) and 108-108.5° (3mm), n_D^{18} 1.4470, which corresponds to data in the literature [20]. Found: C 43.89; 43.96; H 7.67; 7.70%. $C_{11}H_{23}O_4Br$. Calculated: C 44.15; H 7.75%.

In order to confirm the structure, 14 g of bromomalonaldehyde bis [diethyl acetal] was stirred at 50-55° with 20 ml of 1 : 1 hydrochloric acid until it dissolved; when the mixture was cooled there was a crystalline precipitate of bromomalonaldehyde, which was filtered off, washed with ice water, and dried in a vacuum desiccator over calcium chloride. We obtained 1.8 g of bromomalonaldehyde, m.p. 136-138° (from water), undepressed by admixture of a known sample [21].

Isopropylmalonaldehyde Bis [Diethyl Acetal]. The reaction was carried out similarly with 22.2 g (0.15 mole) of orthoformic ester and 11.4 g (0.1 mole) of ethyl 3-methyl-1-butenyl ether in presence of 1.25 ml of boron trifluoride etherate. After two hours at 50-60°, 5 g of sodium carbonate was added and the mixture was stirred for 30 minutes at the same temperature and filtered. Distillation gave 5.8 g (22%) of isopropylmalonaldehyde bis [diethyl acetal]; b.p. 81-82.5° (1 mm); n_D^{18} 1.4300. Found: C 64.53; 64.50; H 11.40; 11.40%. $C_{14}H_{30}O_4$. Calculated: C 64.08; H 11.53%.

In order to confirm the structure, 7 g of the above bis [diethyl acetal] was added dropwise at not above 30° to a solution of 2.18 g of potassium permanganate in 60 ml of 1 N HCl. Manganese dioxide was filtered off, and the filtrate was acidified with concentrated hydrochloric acid and carefully extracted with ether. The ether extract was dried with magnesium sulfate and, after the removal of ether, we obtained about 1 g of isopropylmalonic acid, melting with decomposition at 87° (from benzene), which corresponds to data in the literature [22].

Dimethylmalonaldehyde Bis [Diethyl Acetal]. A mixture of 10 g (0.1 mole) of ethyl 2-methylpropenyl ether, 22.2 g (0.15 mole) of orthoformic ester, and 5 ml of ethereal zinc chloride was heated for three hours at 70° and was then left for several days at room temperature. The product was treated as in the preceding experiment. Fractionation gave 9 g (36%) of dimethylmalonaldehyde bis [diethyl acetal]; b.p. 85° (3 mm); n_D^{17} 1.4210. Found: C 62.22; 62.35; H 11.07; 11.22%. $C_{13}H_{28}O_4$. Calculated: C 62.87; H 11.37%.

The structure was confirmed as in the case of isopropylmalonaldehyde bis [diethyl acetal]. From 7 g of the dimethylmalonaldehyde bis [diethyl acetal] we obtained 1.45 g of dimethylmalonic acid, m.p. 188.5-190.5° (from benzene and petroleum ether), which corresponds to data in the literature [23]. Found: C 45.47; 45.40; H 6.00; 6.03%. $C_5H_8O_4$. Calculated: 45.45; H 6.10%.

Acetoacetaldehyde Bis [Diethyl Acetal]. a) A solution of 8.6 g (0.1 mole) of ethyl isopropenyl ether in 20 g of orthoformic ester was added dropwise at not above 45-48° to a mixture of 19.6 g (0.2 mole) of orthoformic ester and 5 ml of ethereal zinc chloride. The mixture was heated at 50-60° for three hours. After the usual treatment and fractionation we isolated 11 g (48%) of acetoacetaldehyde bis [diethyl acetal]; b.p. 73-76° (2 mm); n_D^{22} 1.4170. Found: C 61.38; 61.14; H 10.71; 10.71%. $C_{12}H_{26}O_4$. Calculated: C 61.50; H 11.18%.

b) A mixture of 16.2 g (0.1 mole) of orthoacetic ester, 1.25 ml of boron trifluoride etherate, and 10 ml of ethereal zinc chloride was stirred at 50-60° for six hours, after which the reaction product was treated with diethanolamine. Fractionation gave 7.2 g (30%) of the above-described acetoacetaldehyde bis [diethyl acetal]; b.p. 96-101° (8 mm); n_D^{20} 1.4138.

In order to confirm the structure, 18.9 g (0.08 mole) of the bis [diethyl acetal] was converted by the method described above into 4 g (60%) of 3 (or 5)-methylpyrazole; b.p. 59° (1 mm); $n_D^{16.5}$ 1.4972. The complex salt with silver nitrate prepared from this had m.p. 120°, which corresponds to data in the literature [25]. The picrate, prepared in the usual way, had m.p. 140-141° (from benzene), which corresponds to data in the literature [25]. Found: N 22.57; 22.77%. $C_{10}H_9O_7N_5$. Calculated: N 22.51%.

2-Methylacetoacetaldehyde Bis [Diethyl Acetal]. A solution of 10 g (0.15 mole) of ethyl 1-methylpropenyl ether in 10 g of orthoformic ester was added dropwise to a mixture of 22.2 g (0.15 mole) of orthoformic ester and 10 ml of ethereal zinc chloride in such a way that the temperature did not exceed 35°; the mixture was then heated at 45-50° for 90 minutes. The usual treatment and fractionation gave 11 g (44%) of 2-methylacetoacetaldehyde bis [diethyl acetal]; b.p. 100-105° (10 mm); n_D^{18} 1.4230. After redistillation the product had b.p. 103-104° (10 mm). Found: C 62.50; H 11.16%. $C_{13}H_{28}O_4$. Calculated: C 62.87; H 11.37%.

In order to confirm the structure, from 6 g (0.024 mole) of the bis [diethyl acetal] we prepared in the usual way 0.3 g of 4,5-dimethylpyrazole; b.p. 110-111° (14 mm). The picrate prepared from this had m.p. 150-152° (from a mixture of benzene and petroleum ether), which corresponds to data in the literature [26]. Found: N 21.80%. $C_{11}H_{11}O_7N_5$. Calculated: N 21.54%.

2-Oxocyclohexanecarboxaldehyde Bis [Diethyl Acetal]. To a mixture of 59.2 g (0.4 mole) of orthoformic ester and a solution of 13.6 g of zinc chloride in 10 ml of dry ether we added 12.4 g (0.1 mole) of 1-ethoxycyclohexene dropwise at not above 30°; the mixture was then heated for one hour at 40°. After the usual treatment and two fractionations we isolated 8.6 g (30%) of 2-oxocyclohexanecarboxaldehyde bis [diethyl acetal]; b.p. 109-113° (7 mm); n_D^{20} 1.4527. The bis [diethyl acetal] was of low stability, so that analysis did not give satisfactory results.

In order to confirm the structure of the bis [diethyl acetal] it was condensed with hydrazine in the usual way; from 4.8 g (0.017 mole) of the bis [diethyl acetal] we obtained 0.8 g (40%) of 4,5,6,7-tetrahydro-1H-indazole, b.p. 152-153° (15 mm) and m.p. 81-82° (from petroleum ether), which corresponds to data in the literature [27]. Found: N 22.46%. $C_7H_{10}N_1$. Calculated: N 22.92%.

The picrate of the tetrahydroindazole had m.p. 154.5-156° (from benzene), which corresponds to data in the literature [27]. Found: N 19.94; 19.89%. $C_{13}H_{13}O_7N_5$. Calculated: N 19.94%.

Reaction of Orthoformic Ester with Diketene. Dropwise addition was made of 50 g (0.58 mole) of diketene to a mixture of 77.8 g (0.52 mole) of orthoformic ester and 1 ml of boron trifluoride etherate at 5-7°. The mixture was left overnight at 0°, and on the next day it was heated for four hours at 40° and left at room temperature until the odor of diketene disappeared. Two fractionations gave 54 g of a product of b.p. 55-58°(3 mm), from which by strong cooling we isolated 36.8 g of crystalline ethyl 3-ethoxycrotonate, m.p. 29-30° (from petroleum ether), which corresponds to data in the literature [28]. Found: C 60.88; 60.94; H 8.98; 8.92%. $C_8H_{14}O_3$. Calculated: C 60.7; H 8.86%.

When treated with a hydrochloric acid solution of 2,4-dinitrophenylhydrazine, the crystalline product gave the 2,4-dinitrophenylhydrazone of acetoacetic ester, which showed no depression of melting point in admixture with a known sample.

SUMMARY

1. A study was made of the addition of triethyl orthoformate to some α- and β-substituted vinyl ethers and 1-ethoxycyclohexene in presence of various catalysts; this permitted the synthesis of bis [diethyl acetals] of various β-dicarbonyl compounds (substituted malonaldehyde and acetoacetaldehyde).

2. The previously undescribed bis [diethyl acetals] of methyl-, isopropyl-, and dimethyl-malonaldehydes, 2-methylacetoacetaldehyde, and 2-oxocyclohexanecarboxaldehyde were prepared and their structures were proved.

3. The condensation of orthoacetic ester with ethyl vinyl ether in presence of a mixed catalyst (boron trifluoride etherate and zinc chloride) was carried out; as a result acetoacetaldehyde bis [diethyl acetal] was obtained.

4. The reactions of orthoformic ester with diketene and with styrene were studied.

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