## CHEMISTRY OF ACETALS

COMMUNICATION 3. REACTION OF THE BIS[DIETHYLACETALS] OF MALONALDEHYDE AND METHYLMALONALDEHYDE WITH ETHYL VINYL AND ETHYL PROPENYL ETHERS

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We previously [1] reported a simple general method for the synthesis of acetals of  $\beta$ -dicarboxyl compounds by the reaction of orthoformic ester with vinyl ethers, and by this method we prepared bis[diethyl acetals] of the malonaldehyde and acetoacetaldehyde series. It was considered to be of interest to study the possibility of further increase in length of the carbon chain, starting with these readily accessible compounds. In the first place we studie the reactions of the bis[diethyl acetals] of malonaldehyde and methylmalonaldehyde with ethyl vinyl and ethyl propenyl ethers. The reaction of malonaldehyde bis[diethyl acetal] with ethyl vinyl ether has been carried out previously by Protopopova and Skoldinov [2], who showed that in presence of boron trifluoride etherate reaction of the vinyl ether with a considerable excess of the acetal gave 1,1,3,5,5-pentaethoxypentane in 34% yield, calculated on the amount of vinyl ether taken.

We studied the reaction between malonaldehyde bis[diethyl acetal] and ethyl vinyl ether in presence of zinc chloride. It was found that in this case reaction was sluggish and to bring it about it was necessary to heat the reaction mixture of  $40-50^{\circ}$ . Irrespective of the molar proportions of the reactants (we tried vinyl ether : acetal ratios of from 1 : 1 to 1 : 4), a mixture of the products of the addition of one, two, and three molecules of vinyl ether was always formed:

 $\begin{array}{rcl} (C_2H_5O)_2 \operatorname{CHCH}_2CH (\operatorname{OC}_2H_5)_2 + n \cdot \operatorname{CH}_2 = \operatorname{CHOC}_2H_5 \rightarrow \\ & \rightarrow & (C_2H_5O)_2 \operatorname{CHCH}_2 [\operatorname{CHCH}_2]_n \operatorname{CH} (\operatorname{OC}_2H_5)_2 \\ & & & | \\ & & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\$ 

The proportions of primary, secondary, and tertiary products varied relatively little with change in the molar proportions of the reactants. Thus, the yield of the primary addition product 3-ethoxyglutaraldehyde bis[diethyl acetal] was 30% (on the acetal that reacted) when the ratio of reactants was 1:1, and 46% when the ratio was 1:4. The yield of the secondary addition product 1,1,3,5,7,7-hexaethoxyheptane increased from 12% to 20% on change in the ratio of reactants from 1:4 to 1:1, and the yield of the tertiary addition product 1,1,3,5,7,9,9-heptaethoxy-nonane increased from 10% to 15% for the same change in the ratio of reactants. The total yield of reaction products was therefore about 65-70%. As the optimum ratio of vinyl ether : acetal for the synthesis of the primary product we chose 1:2, at which the yield of primary product was usually 40-45%.

Apart from this reaction, which was carried out under conditions described in detail in the Experimental Part. we carried out the condensation of malonaldehyde bis[diethyl acetal] with ethyl propenyl ether and of methylmalonaldehyde bis[diethyl acetal] with ethyl vinyl and ethyl propenyl ethers; in the first two cases only the primary reaction products have been studied for the time being;

 $(C_2H_5O)_2CHCH_2CH(OC_2H_5)_2+CH_3CH=CHOC_2H_5$  $- \longrightarrow (C_2H_5O)_2CHCH_2 \begin{bmatrix} CH_3 \\ I \\ CHCH \\ CHCH \\ OC_2H_5 \end{bmatrix}_a CH(OC_2H_5)_2$ 

n = 1, 2, 3.

$$(C_{2}H_{5}O)_{2}CHCHCH(OC_{2}H_{5})_{2}+CH_{2} = CHOC_{2}H_{5} \longrightarrow I$$

$$(C_{2}H_{5}O)_{2}CHCH \qquad (CHCH_{3})_{2} CH(OC_{2}H_{5})_{2}$$

$$(C_{2}H_{5}O)_{2}CHCHCH \qquad (CH_{3})_{2}CH(CH_{3})_{2} + CH_{3}CH = CHOC_{2}H_{5} \longrightarrow I$$

$$(C_{2}H_{5}O)_{2}CHCHCH(OC_{2}H_{5})_{2} + CH_{3}CH = CHOC_{2}H_{5} \longrightarrow I$$

With the object of studying the properties of the bis[diethyl acetals] obtained, and also to confirm their structures, we investigated in the first place the hydrolysis of the bis[diethyl acetals] into the corresponding dialdehydes. It was found that all the bis[diethyl acetals] were extremely readily hydrolyzed, even by simple heating with distilled water in a water bath, with formation of the dialdehydes.

Under these conditions the hydrolysis of 3-ethoxyglutaraldehyde bis[diethyl acetal] (I) went in a complicated way and gave a mixture containing, according to the infrared spectrum,\* glutaconaldehyde (II) (1687 cm<sup>-1</sup>) and 3-ethoxyglutaraldehyde (III) (1718 cm<sup>-1</sup>). On treatment of the mixture with sodium hydroxide it was possible to isolate the sodium salt of the enol form of glutaconaldehyde (IV a), which was characterized as the known acetate (IV b) and benzoate (IV c) [3]. After the separation of the sodium salt, from the neutral part we obtained a little 2,4,6-triethoxytetrahydropyran (V), the structure of which was confirmed by elementary analysis and the infrared spectrum (absence of absorption in the carbonyl region):



Analogous mild hydrolysis of the bis[diethyl acetals] of 3-ethoxy-2-methyl- (VI) and 3-ethoxy-2,4-dimethylglutaraldehydes gave high yields of the aldehydes themselves (VIII) and (IX). Together with these main products a small amount was obtained of the sodium salts of the enol forms of 2-methyl- and 2,4-dimethylglutaconaldehydes:



<sup>\*</sup>The infrared spectra were determined by A. F. Vasil'ev.



The structures of the ethoxy dialdehydes (VIII) and (IX) were confirmed by their conversion respectively into 3-picoline and 3.5-lutidine by reaction with ammonium carbonate. Moreover, the infrared spectra of these dialdehydes contained characteristic absorption bands corresponding to an unconjugated aldehyde group (1718 cm<sup>-1</sup>). The band at 1687 cm<sup>-1</sup>, characteristic for a conjugated aldehyde group, was absent in both cases.

The structures of the enol forms of methyl- and dimethyl-glutaconaldehydes were confirmed by the ultraviolet spectra of their aqueous solutions examined in comparison with the ultraviolet spectrum of the known sodium salt of the enol form of glutaconaldehyde. In all cases there was an absorption maximum characteristic for a system of conjugated double bonds. It is interesting that in the ultraviolet spectra of the sodium salts of the enol forms of methyl- and dimethyl-glutaconaldehydes there are no bands characteristic for a conjugated aldehyde group, whereas in the ultraviolet spectrum of the sodium salt of the enol form of glutaconaldehyde such a maximum is present (at 226 m $\mu$ ). On treatment in alkaline aqueous solution with benzoyl chloride, the sodium salts of the enol forms of methyl- and dimethyl-glutaconaldehydes are converted into the corresponding crystalline benzoates, which correspond in analysis to the benzoates of the enol forms of these substituted glutaconaldehydes.

The hydrolysis of 1,1,3,5,7,7-hexaethoxyheptane (X; n = 2), 1,1,3,5,7,9,9-heptaethoxynonane (X; n = 3), and 1,1,3,5,7,7-hexaethoxy-2,4,6-trimethylheptane (XI) with water or very dilute (0.5%) phosphoric acid led to the corresponding ethoxy dialdehydes in yields of about 60%.



The structures of the ethoxy dialdehydes obtained were confirmed by analysis for ethoxyl content. However, these products were not completely pure, since the infrared spectra showed the presence of small amounts of products of the elimination of ethoxy groups (apart from the band at 1718 cm<sup>-1</sup> there was a very weak band at 1687 cm<sup>-1</sup>).

In continuation of the previous work we studied the reaction of orthoformic ester with some 1-substituted vinyl ethers (ethyl 1-ethylvinyl, ethyl 1-butylvinyl, and ethyl 1-phenylvinyl ethers) and 2-substituted vinyl ethers (1-butyl ethyl and ethyl 1-octenyl ethers). The results then obtained confirmed the general laws of the reaction as established by us earlier [1]. As a result of the reaction we obtained the previously undescribed bis[diethyl acetals]

of 3-oxovaleraldehyde, 3-oxoheptanal, \* and benzoylacetaldehyde, and also the bis[diethyl acetals] of ethyl- and pentyl-malonaldehydes. The structures of all the products were confirmed by their conversion into the corresponding 3(5)- or 4-substituted pyrazoles.

## EXPERIMENTAL

Reaction of malonaldehyde bis[diethyl acetal] with ethyl vinyl ether. A solution of 43.2 g of ethyl vinyl ether in 50 g of malonaldehyde bis[diethyl acetal] was added over a period of four hours to a mixture of 181 g of the bis-[diethyl acetal] and 30 g of saturated ethereal zinc chloride at 55-60°. The mixture was stirred for one hour at the same temperature and then treated with 20% sodium hydroxide solution; the organic layer was separated and dried (magnesium sulfate). Volatile substances were distilled off at the water pump, and the residue was fractionated through a 50-cm column with a full-condensation still ahead. We isolated the following:

1) 149.5 g of the original acetal; b.p. 77-80° (3 mm); n<sup>19</sup>D 1.4115;

2) 49.2 g (45.5% on the acetal that reacted) of 3-ethoxyglutaraldehyde bis[diethyl acetal]; b.p. 120-122° (3 mm); n<sup>19</sup>D 1.4220 Found: C 61.04; 61.23; H 10.80; 10.70%. C<sub>15</sub>H<sub>32</sub>O<sub>5</sub>. Calculated: C 61.61; H 11.03%.

3) 13.5 g of 1.1,3,5,7,7-hexaethoxyheptane; b.p. 145-148° (3 mm); n<sup>22</sup>D 1.4295. Found: C 62.80; 63.00;
 H 10.90; 10.92%. C<sub>19</sub>H<sub>40</sub>O<sub>6</sub>. Calculated: C 62.60; H 11.06.

4) 12.5 g of 1,1,3,5,7,9,9-heptaethoxynonane; b.p. 174-175° (2 mm); n<sup>22</sup>D 1.4350. Found: C 63.62; 63.47; H 10.84; 10.80%. C<sub>23</sub>H<sub>48</sub>O<sub>7</sub>. Calculated: C 63.27; H 11.08%.

Reaction of malonaldehyde bis[diethyl acetal] with ethyl propenyl ether A solution of 17.2 g (0.2 mole) of ethyl propenyl ether in 44 g (0.2 mole) of malonaldehyde bis[diethyl acetal] was added over a period of three hours to a mixture of 44 g (0.2 mole) of the bis[diethyl acetal] and 7.5 ml of a saturated ethereal solution of zinc chloride at 20-22°. The mixture was stirred at 50-60° for four hours. After the usual treatment and vacuum fractionation we isolated:

1) 65.3 g of the original acetal; b.p. 78-80° 2 mm); n<sup>19</sup>D 1.4145;

 2) 15.7 g (43% on the acetal that reacted) of 3-ethoxy-2-methylglutaraldehyde bis[diethyl acetal]; b.p. 112-115° (2 mm); n<sup>19</sup>D 1.4251. Found: C 62, 53; 62.61; H 11.14; 11.08%. C<sub>16</sub>H<sub>34</sub>O<sub>5</sub>. Calculated: C 62.71; H 11.32%.

3) 8.4 g of a fraction of b.p. 137-142° (1 mm); n<sup>19</sup>D 1.4335.

4) 3.9 g of a fraction of b.p. up to 187° (1 mm); n<sup>19</sup>D 1.4365. The substances (3) and (4) were higher addition products whose structures we have not yet studied.

Reaction of methylmalonaldehyde bis[diethyl acetal] with ethyl vinyl ether. A solution of 7.2 g (0.1 mole) of ethyl vinyl ether in 43.4 g (0.1 mole) of methylmalonaldehyde bis[diethyl acetal] was added over a period of 2.5 hr to a mixture of 43.4 g (0.1 mole of the bis[diethyl acetal] and 5 ml of a saturated ethereal solution of zinc chloride. The reaction went with a moderate exothermic effect, and toward the end of the addition of the vinyl ether the rise of temperature reached a maximum of 28°; the mixture was then stirred for one hour at 50°. After the usual treatment and distillation of the reaction product through a 30-cm column with a full-condensation still head we obtained:

1) 27.6 g of the original acetal; b.p. 83-85° (3 mm); n<sup>20.5</sup>D 1.4145.

2) 11.6 g (46.2% on the acetal that reacted) of 3-ethoxy-2-methylglutaraldehyde; b.p. 124-127° (3 mm); n<sup>20</sup>D 1.4260. Found: C 62.60; 62.66; H 11.10; 11.10%. C<sub>16</sub>H<sub>34</sub>O<sub>5</sub>. Calculated: C 62.71; H 11.32%.

In addition we obtained 6.3 g of a product of b.p. up to  $180^{\circ}$  (3 mm) and  $n^{20.5}D$  1.4310.

<u>Reaction of methylmalonaldehyde bis[diethyl acetal] with ethyl propenyl ether</u>. A solution of 17.2 g of ethyl propenyl ether in 46 g of methylmalonaldehyde bis[diethyl acetal] was added over a period of two hours to a mixture

<sup>\*</sup>In the nomenclature of the original Russian this is named throughout as "butyrylacetaldehyde," which in the translator's nomenclature is "3-oxohexanal." However, the reactants stated will give "valerylacetaldehyde," i.e., 3-oxoheptanal, and this structure is in accord with the stated composition of the substance. The name "3-oxoheptanal" is given to this substance throughout.—Publisher.

of 47.6 g of the bis[diethyl acetal] and 7.5 ml of a saturated ethereal solution of zinc chloride at room temperature. The mixture was then stirred for two hours at 40-60°. On the next day, after the usual treatment and fractionation through a 30-cm column with a full-condensation still head, we obtained:

1) 64 9 g of the original acetal; b.p. 82-84° (3-4 mm); n<sup>20</sup>D 1.4145.

2) 16.4 g (42% on the acetal that reacted) of 3-ethoxy-2,4-dimethylglutaraldehyde; b p. 133-136° (4 mm);
117-120° (2 mm); n<sup>20</sup>D 1.4298. Found: C 64.01; 64.17; H 11.01; 11.20%. C<sub>17</sub>H<sub>35</sub>O<sub>6</sub>. Calculated: C 63.71;
H 11.32%.

3) 9.8 g of 1,1,3,5,7,7-hexaethoxy-2,4,6-trimethylheptane; b.p. 162-165° (4 mm); 146-150° (2 mm); n<sup>19</sup>D 1.4405 Found: C 64.85; 64.72; H 11.11; 11.01% C<sub>22</sub>H<sub>46</sub>O<sub>6</sub>. Calculated: C 64.98; H 11.40%.

4) 1.8 g of a fraction of b.p. up to  $195^{\circ}$  and  $n^{20}D$  1.4425.

Hydrolysis of 3-ethoxyglutaraldehyde bis[diethyl acetal] (I) and reactions of the hydrolysis products. 1. A mixture of 26 g (0.089 mole) of 3-ethoxyglutaraldehyde bis[diethyl acetal], 10 ml of 1% phosphoric acid, and 30 ml of water was carefully stirred with heating in a water bath until a homogeneous solution was obtained. When cool, the light-brown solution was extracted twice with ether. The aqueous layer was made alkaline with 4 g of solid so-dium hydroxide, and when the resulting brownish-red solution was cooled with ice there was a precipitate of the known sodium salt of the enol form of glutaconaldehyde in the form of beautiful golden-brown needles (1.6 g);  $\lambda_{max}$  (in water) 226 mµ (log  $\varepsilon$  3.426); 363 mµ (log  $\varepsilon$  4.545).

On shaking an alkaline aqueous solution of 2 g of the sodium salt of the enol form of glutaconaldehyde with 2 g of benzoyl chloride, we obtained 2.5 g of the benzoic ester of this enol compound, m.p. 119-121° (from aqueous alcohol) (the literature [3] gives m.p. 116-118°). Found: C 71.03; 71.17; H 4.90; 4.95%. C<sub>12</sub>H<sub>10</sub>O<sub>3</sub>. Calculated: C 71.28; H 4.99%.

On treatment of the above-described salt with an equimolecular amount of acetic anhydride we obtained the acetic ester of the enol form of glutaconaldehyde, m.p.  $73.5-75^{\circ}$  (from petroleum ether) (the literature [3] gives m.p.  $75^{\circ}$ ).

The ether extract obtained after the hydrolysis of the acetal (see above) was dried with magnesium sulfate; ether was distilled off, and the liquid residue was vacuum-distilled. Almost the whole of the product distilled in the range  $80-82^{\circ}$  (2 mm);  $n^{21}D$  1.4385. We obtained 7.8 g of liquid product, which analysis showed to be a mixture. To establish its composition we carried out the following reactions: a) on addition of a solution of 2 g of sodium hydroxide in 5 ml of water to 2.8 g of the liquid product there was a vigorous reaction and, on cooling, there was a precipitate of 0.9 g of the dihydrate of the sodium salt of the enol form of glutaconaldehyde, which gave a benzoate of m.p. 119-120°, identical with that described above. b) The liquid product (5 g) was mixed with ammonium carbonate (3 g), when heating and frothing of the mixture was observed. The liquid reaction products were distilled distilled off and dissolved in ether; the ethereal solution was dried (potassium hydroxide and magnesium sulfate). By careful fractionation we isolated 1.1 g of pyridine (b.p. 112-114° and  $n^{19}D$  1.5052), the picrate of which (m.p. 161-163.55°) was found to be identical with a known sample.

2. A mixture of 14.6 g (0.05 mole) of 3-ethoxyglutaraldehyde bis[diethyl acetal] and 20 ml of distilled water was stirred while being heated in a water bath until a homogeneous solution was formed. The resulting clear reddishbrown solution was mixed with a solution of 5 g (0.15 mole) of sodium hydroxide in 25 ml of water and cooled with ice. We isolated 5.3 g (68%) of the dihydrate of the sodium salt of the enol form of glutaconaldehyde, which gave its benzoic ester, identical with the sample described above.

The alkaline solution remaining after the isolation of the sodium salt was carefully extracted with ether, the extract was dried (magnesium sulfate), and after fractionation we obtained 1.5 g of 2.4,6-triethoxytetrahydropyran; b.p. 77-77.5° (1 mm);  $n^{20.5}D$  1.4352. Found: C 60.40; 60.70; H 9.95; 10.09%. C<sub>11</sub>H<sub>22</sub>O<sub>4</sub>. Calculated: C 60.52; H 10.16%.

On treatment of 2,4,6-triethoxytetrahydropyran with 20% sodium hydroxide solution we obtained a yield of about 80% of the dihydrate of the sodium salt of the enol form of glutaconaldehyde, which on reaction in an alkaline medium with benzoyl chloride gave the benzoate of this enol compound, identical with the above, described sample. 3. A mixture of 14.6 g (0.05 mole) of 3-ethoxyglutaraldehyde bis[diethyl acetal] (I) and 20 ml of 5% phosphoric acid was stirred while being heated in a water bath until a homogeneous solution was formed. The mixture was cooled and made alkaline with a solution of 2.8 g of sodium hydroxide in 20 ml of water. To the cooled alkaline solution we added 8.5 g (0.05 mole) of benzoyl chloride with vigorous shaking. We obtained 7.4 g (70%) of the benzoic ester of the enol form of glutaconaldehyde, which after crystallization from benzene had m.p. 119.5-121°, undepressed by the sample described above.

<u>Hydrolysis of 3-ethoxy-2-methylglutaraldehyde bis[diethyl acetal]</u> 1) A mixture of 17.7 g of 3-ethosy-2methylglutaraldehyde bis[diethyl acetal] and 20 ml of 1% phosphoric acid was stirred vigorously and heated in a water bath until a homogeneous solution was formed. The mixture was cooled and extracted with ether. The aqueous layer was made alkaline with 2 g of sodium hydroxide. Cooling gave a precipitate of the sodium salt of the enol form of methylglutaconaldehyde (0.6 g), which formed white silky needles,  $\lambda_{max}$  (in water) 363 m $\mu$  (log  $\varepsilon$  2.769).

In a manner similar to that described above we prepared the benzoic ester of the enol form of methylglutaconaldehyde from the sodium salt; slightly brownish needles, m.p. 110-112° (from alcohol). Found: C 72.32; 72.17; H 5.16; 5.21%.  $C_{13}H_{12}O_3$ . Calculated: C 72.21; H 5.59%.

The main ether extract (see above) was dried with magnesium sulfate and vacuum-fractionated. We obtained 7 g (62%) of 3-ethoxy-2-methylglutaraldehyde; b.p. 88-90° (2 mm); n<sup>9</sup>D 1.4395. Found: C 61.10; 60.98; H 9.29; 9.32%. C<sub>8</sub>H<sub>14</sub>O<sub>3</sub>. Calculated: C 60.74; H 8.92%.

For proof of structure, 5 g of 3-ethoxy-2-methylglutaraldehyde was treated with 3 g of ammonium carbonate, as described above for the liquid product isolated after the hydrolysis of 3-ethoxyglutaraldehyde bis[diethyl acetal]. We obtained 1.3 g of 3-picoline, b.p.  $142-145^{\circ}$  and  $n^{15}D$  1.5085, the picrate of which had m.p.  $148-149^{\circ}$ , undepressed by admixture of a known sample.

2) A mixture of 5.4 g of 3-ethoxy-2-methylglutaraldehyde and 10 ml of 1% phosphoric acid was stirred and heated in a water bath until a dark-colored resin began to be precipitated. The solution was decanted from the resinous mass formed; it was cooled with ice, and 2 g of sodium hydroxide was added. The dark-colored mixture formed was diluted with acetone, and on the next day the precipitated sodium salt was separated. It was washed with acetone and ether and dried; this gave 4 g of sodium salt, from which by the usual method we obtained 1.5 g of the benzoic ester, identical with the above-described sample.

<u>Hydrolysis of 3-ethoxy-2,4-dimethylglutaraldehyde bis[diethyl acetal]</u> A mixture of 3-ethoxy-2,4-dimethylglutaraldehyde bis[diethyl acetal] (16.5 g) and 1% phosphoric acid (20 ml) was stirred and heated in a water bath for one hour. After being cooled, the mixture was treated in the usual way. From the aqueous layer we isolated a white crystalline precipitate of the sodium salt of the enol form of 2,4-dimethylglutaconaldehyde (0.8 g);  $\lambda_{max}$  (in water) 275 m $\mu$  (log  $\varepsilon$  2.051). From 0.6 g of the salt in the usual way we obtained 0.5 g of a crystalline benzoic ester m.p. 113-115.5° (from water). Found: C 73.50; 73.50; H 6.07; 5.86%. C<sub>14</sub>H<sub>14</sub>O<sub>3</sub>. Calculated: C 73.02; H 6.13%.

From the ether extract after distillation we isolated 7 g (about 80%) of 3-ethoxy-2,4-dimethylglutaraldehyde; b.p. 101-104° (3 mm);  $n^{20}$ D 1.4390. Found: C 62.85; 62.38; H 9.67; 9.77% C<sub>9</sub>H<sub>16</sub>O<sub>3</sub>. Calculated %: C 62.76; H 9.36%.

From 2.6 g of the dialdehyde obtained and 3 g of ammonium carbonate in a similar way to that described above for the case of 3-ethoxy-2-methylglutaraldehyde we obtained 0.5 g of a liquid having  $n^{20}D$  1.5062, from which we prepared a picrate of m.p. 240-242° (from water), which corresponds to the melting point of 3,5-lutidine picrate [4]. Found: C 46.21; 46.50; H 3.60; 3.67%. C<sub>13</sub>H<sub>12</sub>N<sub>4</sub>O<sub>7</sub>. Calculated: C 46.03; H 3.60%.

<u>Hydrolysis of 1,1,3,5,7,7-Hexaethoxyheptane</u> 1,1,3,5,7,7-Hexaethoxyheptane (18.2 g; 0.05 mole) was hydrolyzed with water (20 ml) in the usual way. The resulting homogeneous solution was extracted with ether. The extract was dried with magnesium sulfate, and fractionation gave 6.5 g (60%) of 3,5-diethoxyheptanedial; b.p. 100.5-102° (0.3-0.5 mm);  $n^{20}$ D 1.4462. Found: C 60.72; 60.65; H 9.31; 9.39; OC<sub>2</sub>H<sub>5</sub> 40.34, 40.72%. C<sub>10</sub>H<sub>20</sub>O<sub>4</sub>. Calculated: C 61.09; H 9.32; OC<sub>2</sub>H<sub>5</sub> 44.12%.

Hydrolysis of 1,1,3,5,7,9,9-heptaethoxynonane. The hydrolysis procedure was similar. From 10.9 g of 1,1,3,5,7,9,9-heptaethoxynonane we obtained about 3 g of 3,5,7-triethoxynonanedial; b.p. 140-145° (in the bath) at 0.5 mm;  $n^{20.5}D$  1.4510. Found:  $OC_2H_5$  44.57; 45.02%.  $C_{15}H_{28}O_5$ . Calculated:  $OC_2H_5$  46.87%.

The results of the carbon and hydrogen determinations were low (by 0.7-0.8% for C and 0.5-0.6% for H). The product was therefore not sufficiently pure. The low results are most readily explained by the high oxidizability of the dialdehyde, which rapidly acquires a yellow color when kept.

Hydrolysis of 1 1,3,5,7,7-hexaethoxy-2,4,6-trimethylheptane. The hydrolysis of 13.3 g of 1,1,3,5,7,7-hexaethoxy-2,4,6-trimethylheptane was carried out by heating it in a water bath with 15 ml of 1% phosphoric acid for 2.5 hr. After the usual treatment and two distillations we obtained 2.5 g of 3.5-diethoxy-2,4,6-trimethylheptanedial; b.p. 112-115° (2 mm);  $n^{18}D$  1,4580. We did not succeed in isolating the dialdehyde in an analytically pure state; as in the preceding case, the results of carbon and hydrogen determinations were low, probably because of the high oxidizability of the dialdehyde. Found:  $OC_2H_5$  36.06; 36.81%.  $C_{12}H_{24}O_4$ . Calculated:  $OC_2H_5$  38.78%.

Preparation of benzoylacetaldehyde bis[diethyl acetal]. Slowly, at not above 30-35°, 14.8 g (0.1 mole) of ethyl 1-phenylvinyl ether was added to 29.6 g (0.2 mole of orthoformic ester and 10 ml of a saturated ethereal solution of zinc chloride; the mixture was stirred for one hour at 40-45° and then treated with 20% sodium hydroxide solution. The organic layer was separated, dried (magnesium sulfate), and vacuum-fractionated. We obtained 19.5 g (65%) of benzoylacetaldehyde bis[diethyl acetal], b.p. 148-150° (8 mm) and  $n^{22}D$  1.4692; on standing it crystallized. Found: C 68.89; 68.70; H 9.38; 9.38%. C<sub>17</sub>H<sub>28</sub>O<sub>4</sub>. Calculated: C 69.89; H 9.52%.

For confirmation of the structure, 16.3 g of the bis[diethyl acetal] was added to a solution of 3.7 g of hydrazine hydrochloride and 2.5 ml of 2 N HCl in 10 ml of water at 45-50°. The mixture was heated for one hour at this temperature and then for 10-15 min in a boiling water bath. The clear solution was cooled and treated with 50 ml of 40% sodium hydroxide solution; the mixture was extracted with ether, and the extract was dried with magnesium sulfate. Distillation gave 5.2 g (69%) of 3(5)-phenylpyrazole, b.p. 155-157° (3 mm), which solidified. After crystal-lization from water the crystals had m.p. 76.5-79°, which is in accord with data in the literature [5]. Found: N 19.19; 19.24%.  $C_9H_8N_2$ . Calculated: N 19.43%.

The picrate prepared from the phenylpyrazole had m p. 172-172.5°, which is in accord with the literature [5].

Preparation of 3-oxoheptanal bis[diethyl acetal]. Proceeding as in the preceding case, from 12.8 g (0.1 mole) of 1-butylvinyl ethyl ether and 29.6 g of orthoformic ester we obtained 15.6 g (56%) of 3-oxoheptanal bis[diethyl acetal]; b.p. 120-122° (9 mm); n<sup>22</sup>D 1 4260. Found: C 65.37; 65.19; H 11.36; 11.26%. C<sub>15</sub>H<sub>32</sub>O<sub>4</sub>. Calculated: C 65.18; H 11.67%.

Proceeding as in the preceding case, from 11.7 g of the bis[diethyl acetal] we obtained 2.7 g (50%) of 3(5)butylpyrazole, b.p. 115-117° (6 mm) and  $n^{19.5}$ D 1.4830, the picrate of which had m.p. 110.5-111.5° (from benzene). Found: N 20.45; 20.25%. C<sub>13</sub>H<sub>15</sub>O<sub>6</sub>N<sub>5</sub>. Calculated: N 20.76%.

<u>Preparation of 3-Oxovaleraldehyde bis[diethyl acetal]</u>. Analogously, from 20 g (0.2 mole) of ethyl 1-ethylvinyl ether and 59.2 g (0.4 mole) of orthoformic ester we obtained 29.1 g (60%) of 3-oxovaleraldehyde bis[diethyl acetal]; b.p. 71-73° (1 mm);  $n^{17.5}$ D 1.4222. Found: C 62.65; 62.74; H 11.12; 11.10%. C<sub>13</sub>H<sub>28</sub>O<sub>4</sub>. Calculated: C 62.87; H 11.37%.

By the above-described method, from 12.4 g of the bis[diethyl acetal] we obtained 2 g (40%) of 3(5)-ethylpyrazole, b.p. 95-96° (7 mm) and  $n^{20}D$  1.4918, the picrate which had m.p. 129.5-130.5° (from benzene), which is in accord with the literature [6].

<u>Preparation of ethylmalonaldehyde bis[diethyl acetal]</u>. Analogously, from 13.7 g (0.137 mole) of 1-butenyl ethyl ether and 29.6 g (0.2 mole) of orthoformic ester in presence of 5 ml of a saturated ethereal solution of zinc chloride we obtained 23.2 g (69%) of ethylmalonaldehyde bis[diethyl acetal]; b.p. 116-118° (16 mm);  $n^{20}$ D 1.4190. Found: C 62.88; 63.02; H 11.41; 11.40%. C<sub>13</sub>H<sub>28</sub>O<sub>4</sub>. Calculated: C 62.87; H 11.37%.

In the usual way, from 4.8 g of the bis[diethyl acetal] we obtained 1.5 g of 4-ethylpyrazole, b.p. 87-89° (2 mm) and  $n^{20}D$  1.4868, the picrate of which had m.p. 142-145.5° (from benzene). Found: N 21.21; 21.23%. C<sub>11</sub>H<sub>11</sub>N<sub>5</sub>. Calculated: N 21.53%.

<u>Preparation of pentylmalonaldehyde bis[diethyl acetal]</u>. In the usual way, from 14.2 g (0.1 mole) of ethyl 1-octenyl ether and 22.2 g (0.15 mole) of orthoformic ester we obtained 18.8 g (65%) of pentylmalonaldehyde bis[diethyl acetal]; b.p. 143-146° (15 mm); n<sup>19</sup>D 1.4252. Found: C 66.05; 66.03; H 11.66; 11.67%. C<sub>16</sub>H<sub>34</sub>O<sub>4</sub>. Calculated: C 66.16; H 11.80%.

In the usual way, with the exception that 15 ml of 1 : 1 hydrochloric acid was used, from 14.5 g of the bis-[diethyl acetal] we obtained 1.4 g of 4-pentylpyrazole, b.p. 118-120° (2 mm) and  $n^{16.5}D$  1.4792, the picrate of which had m.p. 75.5-77.5° (from benzene). Found: N 16.63; 16.70%. C<sub>14</sub>H<sub>17</sub>O<sub>7</sub>N<sub>5</sub>. Calculated: N 16.80%.

## SUMMARY

1. A study was made of the possibility of using the bis[diethyl acetals] of malonaldehyde and methylmalonaldehyde in chain-lengthening reactions with ethyl vinyl and ethyl propenyl ethers.

2. A method was developed for the preparation of the bis[diethyl acetals] of 3-ethoxyglutaraldehyde, 3-ethoxy-2-methylglutaraldehyde, and 3-ethoxy-2,4-dimethylglutaraldehyde, and the hydrolysis of these acetals was studied.

3. The bis[diethyl acetals] of 3-oxovaleraldehyde, 3-oxoheptanal, benzoylacetaldehyde, ethylmalonaldehyde, and pentylmalonaldehyde were prepared for the first time.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. Some or all of this periodical literature may well be available in English translation. A complete list of the cover-tocover English translations appears at the back of this issue.