THE SYNTHESIS AND REACTIONS OF NEW VINYL ESTERS

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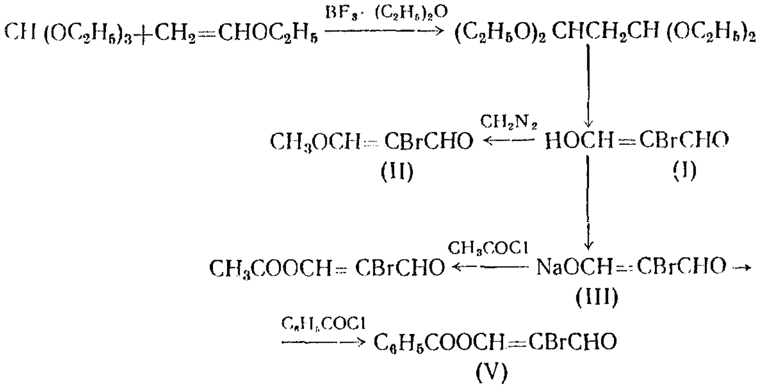
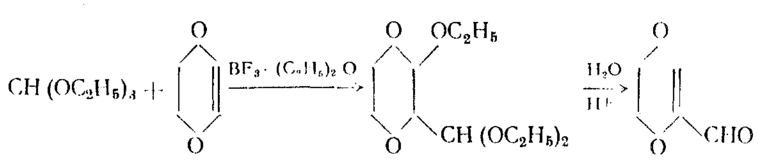
In studying in our laboratory the methods of synthesis of new vinyl esters, we have obtained some ester of 3-hydroxyacrolein. As is known, acrolein easily undergoes the diene condensation with vinylethers [1-4]. It seemed interesting to see whether ethers and esters of 3-hydroxyacrolein would undergo the diene condensation. We obtained the latter by the following scheme:



$$\begin{tikzcd}
\mathrm{CH(OC_2H_5)_3+CH_2{=}CHOC_2H_5} \arrow[r, "\mathrm{BF_3\cdot(C_2H_5)_2O}"] & \mathrm{(C_2H_5O)_2CHCH_2CH(OC_2H_5)_2} \arrow[d] & \\
\underset{\mathrm{(II)}}{\mathrm{CH_3OCH{=}CBrCHO}} & \underset{\mathrm{(I)}}{\mathrm{HOCH{=}CBrCHO}} \arrow[l, "\mathrm{CH_2N_2}"'] \arrow[d] & \\
\mathrm{CH_3COOCH{=}CBrCHO} & \underset{\mathrm{(III)}}{\mathrm{NaOCH{=}CBrCHO}} \arrow[l, "\mathrm{CH_3COCl}"'] \arrow[r, "\mathrm{C_6H_5COCl}"] & \underset{\mathrm{(V)}}{\mathrm{C_6H_5COOCH{=}CBrCHO}}
\end{tikzcd}$$

2-Bromo-3-hydroxyacrolein (bromomalonic aldehyde) (I), prepared according to [5-7] was converted by treatment with diazomethane into the methyl ether (II) and by the action of acetyl chloride on the sodium salt (III) we formed the acetate (IV); the same process gave the benzoate (V). These ethers and esters (II), (IV), and (V) were very easily hydrolyzed by water and moist air, and when kept, easily condensed.

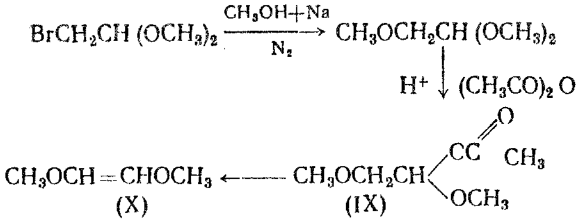
The diene condensation of (II), (IV), and (V) with vinylbutyl ester was not successful, since the reaction product completely resinified, probably because of the hydrogen bromide which was evolved at high temperature. Therefore, we decided to study the condensation of ethyl orthoformate with dioxene [8] in order to convert the resulting reaction product into 2-formyl-p-dioxene (VII) which is also a substituted acrolein. It was shown that the reaction occurs smoothly in the presence of boron trifluoride etherate:



(VII)

Here there is formed 2-ethoxy-3-diethoxymethyl-p-dioxane (VI) which is converted by saponification into 2-formyl-p-dioxene (VII). The resulting unsaturated aldehyde (VII) is very hygroscopic and was usually isolated as the hydrate. The cyclic structure which we ascribed to aldehyde (VII) was confirmed by the absence of a reaction with ferric chloride, by the results of elementary analysis, and also from spectroscopic data (presence of frequencies in the Raman spectrum characteristic for the bond groups $-C=C-C=O$).

We also studied a method for preparing 1,2-dimethoxyethylene (X) which we obtained as follows:



1,1,2-Trimethoxyethane, obtained from the acetal of bromoacetaldehyde [9] by boiling with acetic anhydride in the presence of a trace of p-toluenesulfonic acid, was converted into the acylal (IX) which by slow distillation was transformed into 1,2-dimethoxyethylene (X). However, the yield of (X) did not exceed 20%. The resulting dimethoxyethylene (X) was a mixture of isomers in the ratio 3.5 : 1, the study of which will be continued.

EXPERIMENTAL

2-Bromo-3-methoxyacrolein (II). To an ether solution of diazomethane obtained from 5 g of nitrosomethylurea was added gradually 5 g of bromomalonic aldehyde (I) and after one hour the ether was distilled off and the residue recrystallized from a mixture of ligroin and ether. We thus obtained 4.46 g (81.6%) of 2-bromo-3-methoxyacrolein (II) with m.p. 56-57°. Found: C 29.24; 29.11; H 3.46; 3.36; Br 48.24; 48.30%. $C_4H_5O_2Br$. Calculated: C 29.1; H 3.05; Br 48.46%.

2-Bromo-3-acetoxyacrolein (IV). A water solution of 6.04 g of bromomalonic aldehyde (I) was neutralized with 1 N sodium carbonate solution to a neutral reaction to phenolphthalein (40 ml). The solution was evaporated in a vacuum of 50 mm at a bath temperature of 35-45°, to dryness. The residue was washed with acetone and the sodium salt (III) which separated was filtered off and dried in a desiccator over sulfuric acid. In all we obtained 6.02 g (87%) of the sodium salt of bromomalonic aldehyde (III) [10]. To 1 g of this salt and 25 ml of ether we added with stirring in the course of 5 minutes and dropwise 0.45 g of acetyl chloride; stirring was continued for 15 minutes more, after which the reaction mixture was filtered and the filtrate was evaporated. We thus obtained 0.71 g (67.3%) of 2-bromo-3-acetoxyacrolein (IV) with m.p. 72-74° (after recrystallization from a mixture of ligroin and ether). Found: C 29.62; 29.71; H 2.92; 3.02; Br 43.64; 43.48%. $C_5H_5O_3Br$. Calculated: C 31.1; H 2.61; Br 41.43%.

2-Bromo-3-benzoxyacrolein (V). To 1 g of sodium salt of bromomalonic aldehyde obtained by the method described above and 30 ml of ether we added 0.71 g of benzoyl chloride with stirring in the course of 5 minutes. Stirring was continued for another six hours after which the solid was filtered and the filtrate was evaporated. The residue after recrystallization from a mixture of ligroin and ether had a m.p. 100-102°. We thus obtained 1.05 g (81.6%) of 2-bromo-3-benzoxyacrolein (V). Found: C 47.21; 47.16; H 3.09; 3.06; Br 30.69; 30.7%. $C_{10}H_7O_3Br$. Calculated: C 47.01; H 2.75; Br 31.33%.

2-Ethoxy-3-diethoxymethyl-p-dioxane (VI). To 15 g (0.1 M) of ethyl orthoformate and 0.1 g of boron trifluoride etherate we added dropwise 9 g (0.1 M) of dioxene with stirring at a temperature of 40-45°. Addition lasted 20 minutes, after which the mixture was stirred for 1 hour more at the same temperature. To the reaction mixture we added 2 g of finely ground sodium bicarbonate, and stirring was continued for three hours at 25°, after which the residue was filtered off and the filtrate was distilled in a vacuum. We thus isolated 8.5 g of orthoformic ester with b.p. 46-47° (16 mm) and 8 g (77.8%) of 2-ethoxy-3-diethoxymethyl-p-dioxane (VI) with b.p. 135-137° (20 mm); n_D^{20} 1.4337. Found: C 56.14; 56.0; H 9.37; 9.29%. $C_{11}H_{22}O_5$. Calculated: C 56.38; H 9.46%.

2-Formyl-p-dioxene (VII). A mixture of 4.68 g (0.02 M) of 2-ethoxy-3-diethoxymethyl-p-dioxane (VI) and 15 ml of 2% hydrochloric acid was boiled in a distilling flask; alcohol distilled off and the mixture became homogeneous. The water solution was neutralized with 1 g of sodium bicarbonate and extracted ten times with 15 ml of ether. The ether extract was dried with magnesium sulfate, the ether was removed, and the residue was distilled in a vacuum. We thus obtained 1.13 g (49.6%) of 2-formyl-p-dioxene (VII) with b.p. 216-217° (12 mm). The distilled product crystallized in the receiver and after recrystallization from a mixture of ether and ligroin had m.p. 40-42°. Found: C 52.12; 52.19; H 5.49; 5.3%. $C_5H_6O_3$. Calculated: C 52.63; H 5.3%.

The combination scattering spectrum in dioxane had the following frequencies: 1695, 1635, 1470, 578, 418 cm^{-1}. The lines 1695, 1635 are characteristic for the grouping of atoms $-C=C-C=0$. The substance did not give a color with an alcoholic solution of ferric chloride. The red 2,4-dinitrophenylhydrazone melted at 236-237°.

1,1,2-Trimethoxyethane (VIII) [11]. We dissolved 115 g of metallic sodium in 2.1 liters of methanol and added 710 g of the acetal of bromoacetaldehyde with stirring at 25°. The reaction product was boiled for 24 hours under reflux in a stream of nitrogen, after which the sodium bromide which separated was filtered off (347 g) and the reaction product was distilled in a column with 20 theoretical plates. After removal of the alcohol, we thus separated 236 g (46.8%) of 1,1,2-trimethoxyethane (VIII) with b.p. 125-126° (741 mm), n_D^{25} 1.3930. The literature [12] gives b.p. 126-127.5°, n_D^{25} 1.3901.

1,2-Dimethoxy-1-acetoxyethane (IX). A mixture of 36 g (0.3 M) of 1,1,2-trimethoxyethane (VIII), 31 g (0.3 M) of acetic anhydride, and 0.5 g of para-toluenesulfonic acid was slowly heated so that the methyl acetate which formed distilled as it was formed (during the reaction 19 ml of methyl acetate distilled off) (b.p. 55-58°). After cooling, the reaction product was distilled in a vacuum and we obtained 12.84 g of 1,1,2-trimethoxyethane with b.p. 32-34° (15 mm), and 20.9 g (73.1%) of 1,2-dimethoxy-1-acetoxyethane (IX) with b.p. 64-65° (14 mm), n_D^{25} 1.4055. Found: C 48.58; 48.72; H 8.28; 7.97%. $C_6H_{12}O_4$. Calculated: C 48.64; H 8.16%.

A mixture of 36 g (0.3 M) of 1,1,2-trimethoxyethane (VIII), 80 g (0.78 M) of acetic anhydride, and 1 drop of concentrated sulfuric acid stood for 14 hours at room temperature and then the reaction mixture was poured into 300 ml of ice water and extracted with carbon tetrachloride. The extract was washed twice with a saturated solution of sodium bicarbonate, dried with calcium chloride, and distilled in a vacuum. We thus obtained 19.2 g (43.2%) of 1,2-dimethoxy-1-acetoxyethane (XI) with b.p. 62-64° (12 mm), n_D^{22} 1.4055.

1,2-Dimethoxyethylene (X). We boiled 26 g of 1,2-dimethoxy-1-acetoxyethane (XI) for two hours in a flask with a reflux condenser at 162-165°, after which the resulting mixture of methyl alcohol and dimethoxyethylene was slowly distilled from a Favorskii flask. We thus obtained 20 g of a mixture with b.p. 71-145°. The reaction product was washed with a concentrated soda solution, dried over potash, and distilled from a column with 20 theoretical plates. We thus obtained 2.2 g of 1,2-dimethoxyethylene (X) with b.p. 97-99°, n_D^{22} 1.4184, and 0.61 g of 1,2-dimethoxyethylene (X) with b.p. 103°, $n_D^{20.5}$ 1.4204. The literature [13-14] gives b.p. 97-99°; 102°, n_D^{25} 1.4190.

SUMMARY

1. We have obtained for the first time ethers and esters of 2-bromo-3-hydroxyacrolein.

2. Orthoformic ester condenses with dioxene and the condensation product is easily converted to 2-formyl-p-dioxene.

3. The acylal obtained from 1,1,2-trimethoxyethane gives on pyrolysis 1,2-dimethoxyethylene.

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