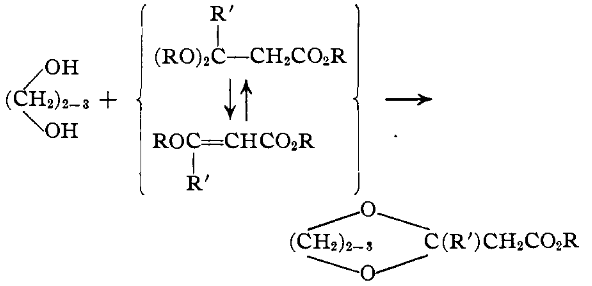
[CONTRIBUTION FROM ROHM & HAAS COMPANY]

Transetherification Reactions. Glycols with Certain β-Alkoxy Esters[1]

BY W. J. CROXALL, J. O. VAN HOOK AND R. LUCKENBAUGH[2]

In a previous paper[1] it was reported that ethyl β-ethoxyacrylate, ethyl β,β-diethoxypropionate and ethyl α,α-diethoxysuccinate underwent a transetherification reaction with alcohols to produce the ethyl esters of β,β-dialkoxypropionates and α,α-dialkoxysuccinates. These results suggested that certain glycols should undergo this reaction with these esters to produce 1,3-dioxolanes and 1,3-dioxanes.

In the present work it is demonstrated that the above esters react with representative 1,2- and 1,3-glycols according to a general equation in which ethylene and trimethylene glycol are used as examples



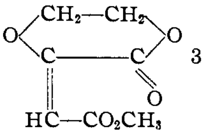
R = CH_3, C_2H_5, C_4H_9
R′ = H, CO_2R

Characterization of specific reaction products to illustrate these results was accomplished with three of the resulting compounds. Saponification of 2-carbethoxymethyl-1,3-dioxolane and 2-carbethoxymethyl-1,3-dioxane yielded ethanol and 2-carboxymethyl-1,3-dioxolane and 2-carboxymethyl-1,3-dioxane respectively. Pyrolysis of these acids gave 2-methyl-1,3-dioxolane and 2-methyl-1,3-dioxane. In a similar manner, 2-carbethoxy-2-carbethoxymethyl-1,3-dioxane produced ethanol and a compound which corresponded to 1,3-dioxo-2,6,10-trioxaspiro[5.4]decane.

The compounds obtained from various glycols and alkyl β-alkoxyacrylates and alkyl β,β-dialkoxypropionates are listed in Table I whereas those obtained from the alkyl α,α-dialkoxysuccinates are reported separately in the Experimental section. The product isolated from glycerol and the acrylate was not characterized to determine whether a hydroxymethyl dioxolane or dioxane was obtained. The yields in general were high when the acrylate or propionate was used. Two exceptions in this series were the products obtained from 1,2-cyclohexanediol and mercapto ethanol. It is interesting to note that pentaerythritol gave 3,9-dicarbethoxymethyl-2,4,8,10-tetroxaspiro[5.5]hendecane in excellent yield. When the succinate was employed the yields on an average were lower; considerable polymeric material was formed in these instances.

The catalysts used for this work were sodium bisulfate, boron trifluoride and aluminum chloride. In the acrylate–propionate reactions the bisulfate catalyst was found to give higher yields. However, in the succinate series aluminum chloride and boron trifluoride appeared to be more satisfactory.

In an experiment with methyl α,α-dimethoxysuccinate and ethylene glycol there was isolated an additional product. Analytical results suggest the following structure.



3-carbomethoxymethylene-2-oxo-1,4-dioxane
I

Acknowledgment.—The analyses were carried out under the direction of Dr. E. L. Stanley and Mr. C. W. Nash. Mr. C. Gianotti and Mrs. R. Albert carried out a number of the experiments herein reported.

Experimental

General Procedure for 2-Carbethoxymethyl-1,3-dioxolanes and 1,3-Dioxanes.—A mixture of one mole of glycol, one mole of ethyl β-ethoxyacrylate or ethyl β,β-diethoxypropionate and 0.1 g. of sodium bisulfate (1 ml. of ether boron trifluoride or 1 g. of aluminum chloride) was fractionated through a short packed column. An equivalent of ethanol corresponding to replacement of the ethoxy group or groups was removed at atmospheric pressure. The dioxolanes or dioxanes were then distilled under reduced pressure. In the case of pentaerythritol, the residue remaining in the distilling flask crystallized on cooling, m. p. 73–75°. Recrystallization from ethanol and then petroleum ether (b. p. 90–100°) gave the pure 3,9-dicarbethoxymethyl-2,4,8,10-tetroxaspiro[5.5]hendecane, m. p. 79°.

2-Carboxymethyl-1,3-dioxolane.—To a stirred solution of 12. g (0.3 mole) of sodium hydroxide dissolved in 110 ml. of water was added 40 g. (0.3 mole) of 2-carbethoxymethyl-1,3-dioxolane. After refluxing five minutes the mixture was distilled to give 70 ml. of distillate, b. p. 75–100°. The distillate was saturated with potassium carbonate, the organic layer separated and dried over anhydrous potassium carbonate. Distillation gave 5 g. (33%) of ethanol, b. p. 78°; $n^{20}D$ 1.3630.

The above saponification residue was acidified, saturated with sodium chloride and extracted four times with an equal volume of ether. Distillation of the combined ether extracts gave, after removal of ether, 12 g. (31%) of crude 1,3-dioxolane, b. p. 110–130° (2 mm.). (There was collected during the distillation 9 g. of liquid in a Dry Ice–acetone cooled trap; $n^{20}D$ 1.3790.) Redistillation of the crude acid gave the pure acid, b. p. 115–120° (2 mm.), which solidified in the receiver, m. p. 42–45°; neutral equivalent, 134 (calcd. 132).

2-Methyl-1,3-dioxolane.—The above acid (11 g.) (0.08 mole) was heated in a distilling flask to 200° to give 1.8 liters (0.08 mole) of carbon dioxide and 5 g. of distillate,

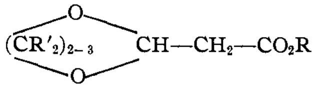
---

(1) For the previous paper in this series see W. J. Croxall, J. O. Van Hook and R. Luckenbaugh, THIS JOURNAL, **71**, 2736 (1949).

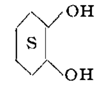
(2) Present address: University of Maryland, College Park, Md.

TABLE I

2-CARBETHOXYMETHYL-1,3-DIOXOLANES AND -1,3-DIOXANES,



$(\mathrm{CR'_2})_{2-3}$ $\mathrm{CH{-}CH_2{-}CO_2R}$

			B. p. (uncor.)					MR.			Analyses, %					
											Calcd.		Found		Sapon. equiv.	
Glycol	R	Catalyst	°C.	Mm.	Yield, %	$n^{20}\mathrm{D}$	d^{20}_{20}	Calcd.	Found	Formula	C	H	C	H	Calcd.	Found
$\mathrm{HOC_2H_4OH}$	$\mathrm{CH_3}$	$\mathrm{NaHSO_4}$	58–62	0.15	95	1.4337	1.180	32.65	32.23	$\mathrm{C_6H_{10}O_4}$	49.31	6.85	49.25	6.93	146	147
$\mathrm{HOC_2H_4OH}$	$\mathrm{C_2H_5}$	$\mathrm{NaHSO_4}$	72–74	3.0	87	1.4331	1.127	37.27	36.70	$\mathrm{C_7H_{12}O_4}$	52.48	7.56	52.00	7.01	160	159
$\mathrm{HOC_2H_4OH}$	$\mathrm{C_2H_5}$	$\mathrm{Et_2OBF_3}$			65											
$\mathrm{HOC_2H_4OH}$	$\mathrm{C_2H_5}$	$\mathrm{AlCl_3}$			72											
$\mathrm{HOC_2H_4OH}$	$\mathrm{C_4H_9}$	$\mathrm{NaHSO_4}$	88–90	0.2	98	1.4360	1.061	46.50	46.33	$\mathrm{C_9H_{16}O_4}$	57.4	8.51	57.75	8.81	188	188
$\mathrm{CH_3CH(OH)CH_2OH}$	$\mathrm{C_2H_5}$	$\mathrm{NaHSO_4}$	70–73	0.3	71	1.4304	1.079	41.88	41.69	$\mathrm{C_8H_{14}O_4}$	55.17	8.05	55.51	8.26	174	172
$\mathrm{CH_2ClCH(OH)CH_2OH}$	$\mathrm{C_2H_5}$	$\mathrm{NaHSO_4}$	85–90	0.2	81	1.4550	1.196	46.75	47.29	$\mathrm{C_8H_{13}O_4Cl}$	46.04	6.23	46.30	6.35		
$\mathrm{CH_2(OH)CH(OH)CH_2OH}$	$\mathrm{C_2H_5}$	$\mathrm{NaHSO_4}$	116–119	0.1	83	1.4550	1.188	43.41	43.59	$\mathrm{C_8H_{14}O_5}$	50.53	7.37	50.10	7.47	190	187
$\mathrm{HSC_2H_4OH}$	$\mathrm{C_2H_5}$	$\mathrm{NaHSO_4}$	78–81	1.0	43	1.4838	1.181	43.58	43.60	$\mathrm{C_7H_{12}O_3S}$	47.70	6.86	48.07	6.83	176	171
 [a]	$\mathrm{C_2H_5}$	$\mathrm{NaHSO_4}$	98	0.2	54	1.4625	1.105	53.54	53.30	$\mathrm{C_{11}H_{18}O_4}$	61.68	8.41	61.71	8.56	214	202
$\mathrm{HO(CH_2)_3OH}$	$\mathrm{C_2H_5}$	$\mathrm{NaHSO_4}$	72–78	0.1	85	1.4400	1.096	41.88	41.85	$\mathrm{C_8H_{14}O_4}$	55.17	8.05	55.05	7.98	174	175
$\mathrm{(CH_3)_2C(OH)CH_2{-}CH(OH)CH_3}$	$\mathrm{C_2H_5}$	$\mathrm{NaHSO_4}$	74–76	0.14	79	1.4370	1.006	55.74	56.26	$\mathrm{C_{11}H_{20}O_4}$	61.11	9.26	61.14	9.46	216	210
$\mathrm{HOCH_2C(C_2H_5)(C_4H_9){-}CH_2OH}$	$\mathrm{C_2H_5}$	$\mathrm{NaHSO_4}$	126–129	0.4	94	1.4500	0.999	69.49	69.96	$\mathrm{C_{14}H_{26}O_4}$	65.12	10.08	65.19	10.13	258	258
$\mathrm{C(CH_2OH)_4}$	$\mathrm{C_2H_5}$	$\mathrm{NaHSO_4}$	M. p. 79°		96					$\mathrm{C_{15}H_{24}O_8}$	54.22	7.23	54.28	7.27	166	165

[a] Mixture of *cis* and *trans* (Dimroth and Resin, *Ber.*, **75B**, 322 (1942)).

b. p. 47–62°. Redistillation of the distillate gave 4 g. of pure dioxolane, b. p. 80.3°; $n^{20}\mathrm{D}$ 1.3976.[3]

2-Carboxymethyl-1,3-dioxane.—In a similar saponification experiment there was obtained from 40 g. (0.23 mole) of 2-carbethoxymethyl-1,3-dioxane, 7 g. (66%) of ethanol and 16 g. (48%) of the 1,3-dioxane acid, b. p. 100–125° (2 mm.), which crystallized in the receiver, m. p. 60.5–62.5°. *Anal.* Calcd. for $\mathrm{C_6H_{10}O_4}$: C, 49.27; H, 6.89; neutral equivalent, 146. Found: C, 49.55; H, 6.80; neutral equivalent, 147.

2-Methyl-1,3-dioxane.—Distillation of the above acid (0.1 mole) at atmospheric pressure gave 0.1 mole of carbon dioxide and 9 g. (0.09 mole) of the dioxane, b. p. 105–111°; $n^{20}\mathrm{D}$ 1.4130.[4]

2-Carbethoxy-2-carbethoxymethyl-1,3-dioxolane.—Distillation of a mixture consisting of 262 g. (1.0 mole) of ethyl α,α-diethoxysuccinate, 62 g. (1.0 mole) of ethylene glycol and 3 ml. of a 1:1 acetic acid–boron trifluoride complex gave 88 g. (95.6%) of ethanol. The cooled residue after washing with water and drying over anhydrous potassium carbonate gave 83 g. (36%) of the 1,3-dioxolane, b. p. 110–116° (0.3 mm.), $n^{20}\mathrm{D}$ 1.4441. *Anal.* Calcd. for $\mathrm{C_{10}H_{16}O_6}$: C, 51.72; H, 6.95. Found: C, 52.41; H, 7.10.

If the above washing procedure was eliminated the yield was 55%. Substitution of aluminum chloride for the boron trifluoride complex gave an 85% yield when the latter procedure was employed.

2-Carbomethoxy-2-carbomethoxymethyl-1,3-dioxane.—From one mole of methyl α,α-dimethoxysuccinate, one mole of trimethylene glycol and 2 g. of sodium bisulfate there was obtained 71 g. of ethanol and 88 g. (33%) of the 1,3-dioxane, b. p. 109–110° (0.5 mm.), $n^{20}\mathrm{D}$ 1.4550. *Anal.* Calcd. for $\mathrm{C_9H_{14}O_6}$: C, 49.54; H, 6.42; saponification equivalent, 109. Found: C, 49.62; H, 6.45; saponification equivalent, 110.

2-Carbethoxy-2-carbethoxymethyl-1,3-dioxane.—This dioxane was obtained in 65% yield using ethyl α,α-diethoxysuccinate and ether–boron trifluoride as catalyst, b. p. 116–125° (0.1 mm.), $n^{20}\mathrm{D}$ 1.4570. *Anal.* Calcd. for $\mathrm{C_{11}H_{18}O_6}$: C, 53.66; H, 7.33; saponification equivalent, 123. Found: C, 54.25; H, 7.46; saponification equivalent, 123.

Saponification of the dioxane gave ethanol (79%) and 1,3-dioxo-2,6,10-trioxaspiro[5.4]decane (23%), b. p. 88–100° (1 mm.); neutral equivalent, 86 (calcd. 87).

3-Carbomethoxymethylene-2-oxo-1,4-dioxane (I).—Distillation of 206 g. (1 mole) of methyl α,α-dimethoxysuccinate, 62 g. (1.0 mole) of ethylene glycol and 2 g. of sodium bisulfate gave 86 g. (2.7 moles) of methanol, 54 g. of a fraction, b. p. 128–178° (8 mm.), and 46 g. of the dioxane (I), b. p. 178–186° (8 mm.), which solidified in the receiver; m. p. 105.5–106.5° (from benzene). *Anal.* Calcd. for $\mathrm{C_7H_8O_5}$: C, 48.85; H, 4.68; saponification equivalent, 86. Found: C, 48.81; H, 4.59; saponification equivalent, 87. The intermediate fraction was not purified; it is probably a mixture of the succinate and dioxolane.

Summary

1. Ethyl β-ethoxyacrylate or ethyl β,β-diethoxypropionate react with certain glycols to produce 2-carbethoxymethyl-1,3-dioxolanes and 2-carbethoxymethyl-1,3-dioxanes.

2. Extension of this reaction to ethyl α,α-diethoxysuccinate yields 2-carbethoxy-2-carbethoxymethyl-1,3-dioxolanes and 2-carbethoxy-2-carbethoxymethyl-1,3-dioxanes, respectively.

PHILADELPHIA, PA. RECEIVED MARCH 29, 1949

---

[3] Croxall, Glavis and Neher, THIS JOURNAL, **70**, 2805 (1948).

[4] M. M. Otto, *ibid.*, **59**, 1590 (1937).