TRANSESTERIFICATION OF ESTERS OF CARBONIC ACID

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Esters of carbonic acid are now produced by the alcoholysis of phosgene [1] or of chloroformates [2], by the alkylation with alkyl halides of alkali metal carbonates and salts of acid esters of carbonic acid, produced by acylation of alcoholates of the alkali metals with carbon dioxide [4]. Cyclic esters of carbonic acid and glycols [5] are produced by the transesterification reaction. It has been shown for the example of esters of malonic and oxalic acids that the transesterification of esters by alcoholysis in the presence of alkaline or acid catalysts is a convenient preparative method for the production of esters of various alcohols from lower esters [6-10]. The ease of alkaline transesterification can be explained by the stabilizing influence of the neighboring carbonyl groups of oxalic ester [9] and by enolization of malonic esters, while in the case of acid transesterification it can be explained by the formation of cyclic transition compounds [8-10]. The mechanism of alkaline transesterification of carbonic ester (S_N2) can be represented by the scheme

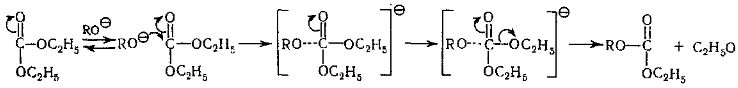

TABLE 1. Conditions of Transesterification of the Ethyl Ester of Carbonic Acid

R	Catalyst	Initial diethyl ester of carbonic acid, M	Mole ratio of reagents carbonic ester: alcohol:catalyst, M	Yield, %	Duration of transesterification, h
n-C_1H_9	NaOH	0,127	1 : 3,937 : 0,0354	74,6	10
n-C_4H_9	NaOH + Ca (OH)$_2$	0,254	1 : 3,937 : 0,0394 + 0,0512	67,8	12
$C_2H_5OCH_2CH_2$	KOH	0,127	1 : 3,150 : 0,0276	79,4—83,4*	2,0
n-C_5H_{11}	NaOH	0,127	1 : 1,968 : 0,0236	71	24,5
n-C_5H_{11}	NaOH	0,127	1 : 6,441 : 0,0354	74,5	4,0
n-C_6H_{13}	NaOH	0,127	1 : 3,937 : 0,0354	65,3	3,0
n-C_6H_{13}	NaOH	0,127	1 : 3,937 : 0,0354	78,8	8,5
cyclo-C_6H_{11}	KOH	0,127	1 : 3,307 : 0,0512	71,2	3,17
n-C_7H_{15}	NaOH	0,127	1 : 3,937 : 0,0354	74,2	3
n-C_7H_{15}	Ca (OH)$_2$	0,127	1 : 3,937 : 0,0512	77,2	2,5
n-C_8H_{17}	NaOH	0,127	1 : 3,937 : 0,0354	73,0	8,5
n-C_8H_{17}	LiOH	0,127	1 : 3,937 : 0,0984	68,8	6
n-C_8H_{17}	LiOH	0,127	1 : 3,937 : 0,162	73,5	4
n-C_9H_{19}	NaOH	0,127	1 : 3,937 : 0,0354	76	4,5
n-C_9H_{19}	LiOH	0,127	1 : 3,937 : 0,0392	66,8	9
n-$C_{10}H_{21}$	NaOH	0,127	1 : 3,937 : 0,0354	84,1	5,5

*The yield is cited after 4 - 5 h of exposure: after mixing of the reagents and heating to boiling, the mixture was allowed to cool for 5 h, after which it was heated, as usual, distilling off the ethanol formed; without such exposure the yield is reduced to 50 - 60%.

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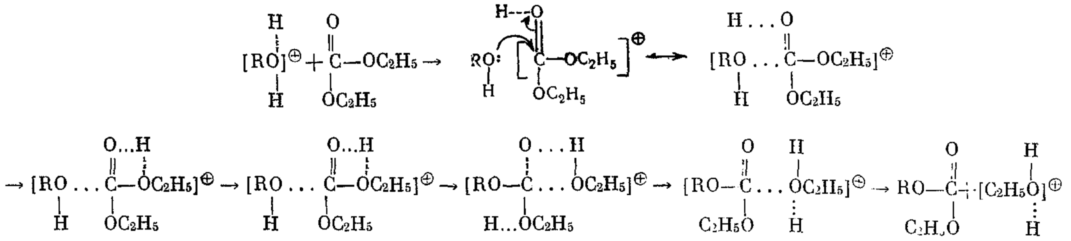
TABLE 2. Esters of Carbonic Acid Produced by Transesterification of $CO(OR)_2$

R	Bp, °C (p, mm Hg)	Mp, °C	n_D^t	d_4^t	Viscosity			MR		Literature data				
					kinematic ν_t, cSt	absolute, η_t, cP	t, °C	found	calculated	bp, °C (p, mm Hg)	n_D^t	d_4^t	t, °C	absolute viscosity, $\eta_{.5}$, cP
n-C H$_9$	118—122 (40)	—	1,4108	0,9236	1,774	1,652	20	46,81	47,069	98—99 (17) [12]	1,4117 [13]	0,9238 [13]	20	1,7634 [12]
			1,4069	0,9156	1,551	1,420	30	46,84						
			1,3988	0,8978			50	46,91						
C_2H_5O—CH_2CH_2	132—134 (18)	—86	1,4236	1,0397	4,395	4,569	20	50,58	50,345	112—113 (5) [14]	1,4227 [14]	1,0439 [14[	20	2,5158 [12]
			1,4194				30							
			1,4111	1,0117	1,988	1,992	50							
n-C_5H_{11}	120—122 (10) 143—145 (40)	—	1,4198	0,9120	2,655	2,421	20	56,08	56,541	126,7—127 (15) [12]	1,41887 [12]	0,9109 [12]	25	2,5158 [12]
			1,4159	0,9033	2,198	1,985	30	56,19						
			1,4078	0,8869			50	56,24						
n-C_6H_{13}	147—149 (10) 177—179 (50)	—39	1,4260	0,9026	3,771	3,403	20	65,37	65,541	152—154 (20) [12]	1,4274 [15]		20	
			1,4222	0,8945	2,979	2,664	30	65,45				0,9002 [12]	25	3,5691 [12]
			1,4142	0,8898			50	65,51						
Cyclo-C_6H_{11}	173—174 (26)	+39—39,5	1,4600	1,0079	14,491	14,606	50	61,50	61,131	Т. пл. 41—42 [16]	—	—	—	—
			1,4556	1,0004	10,509	10,513	60	61,45						
n-C_7H_{15}	170—172 (10) 201—203 (41)	—26	1,4312	0,8974	5,333	4,786	20	74,56	74,777	142—144 (5) [15]	1,4329 [15]	—	20	—
			1,4274	0,8897	3,983	3,543	30	74,73						
			1,4193	0,8744			50	74,67						
n-C_8H_{17}	194—195,5 (10) 211—213 (26)	—15	1,4350	0,8921	7,586	6,768	20	83,90	84,013	168—170 (5) [15]	1,4384 [15]	—	20	—
			1,4320	0,8847	5,556	4,915	30	83,97						
			1,4241	0,8698			50	84,03						
n-C_9H_{19}	212—214 (10) 246—248 (40)	—4,9	1,4391	0,8878	9,929	8,815	20	93,26	93,249	187—189 (5) [15]	1,4415 [15]	—	20	—
			1,4356	0,8804	7,140	6,286	30	93,30						
			1,4280	0,8660			50	93,46						
n-$C_{10}H_{21}$	228—230 (10)	—3,3	1,4420	0,8853	13,153	11,644	20	102,4	102,48	202—204 (5) [15]	1,4432 [15]	—	20	—
			1,4380	0,8788	9,471	8,324	30	102,3						
			1,4308	0,8642			50	102,6						

The multicenter mechanism of acid transesterification proceeds as follows



Exchange of the corresponding alkoxy group of carbonic ester proceeds successively according to the mechanisms cited. Transesterification of carbonic esters, catalyzed by bases, is facilitated by the stabilizing electron-repelling influence of the carbonyl oxygen, while transesterification catalyzed by acids is facilitated by the formation of a cyclic transition state [11], but in the latter case the cyclic transition state is substantially more stressed and energetically less profitable than in the case of malonic and oxalic esters [8, 9], since it is four-membered. As a result of this, in the alcoholysis of carbonic esters, acid catalysts should be relatively ineffective. It has been shown experimentally that p-toluenesulfonyl chloride is little suited as an acid catalyst for the alcoholysis of carbonic ester. Therefore, only the alkaline catalysts LiOH, NaOH, $Ca(OH)_2$, and KOH were used for the transesterification of carbonic ester. An excess of alcohol above the stoichiometric amount promotes exchange of both alkoxyl groups, since it is evident from the mechanisms cited that transesterification proceeds successively at the reaction center.

This work presents the transesterification of the ethyl ester of carbonic acid by alcoholysis with higher alcohols, cyclohexanol, and 2-ethoxyethanol in the presence of alkaline catalysts. Transesterification was conducted with an excess of alcohol (usually 87%) in the presence of 2.8-5.1 mole % KOH, 3.5 mole % NaOH, 3.3-10.2 mole % LiOH, or 5 mole % $Ca(OH)_2$. On the average, the yield of products of transesterification is: 70-80% in the presence of KOH, 65-84% for NaOH, 66-77.5% for LiOH, and 67-77% in the presence of $Ca(OH)_2$. Consequently, the most active catalysts are KOH and NaOH. The optimum time of the reaction is 2-5.5 h. Treatment of the reaction product consists of filtration of the mixture, removal of the excess alcohol, and purification of the ester of carbonic acid obtained by fractional redistillation. The boiling points, melting points, indices of refraction, density, and viscosities at various temperatures were determined for the compounds obtained, higher esters of carbonic acid, and the molecular refraction was found.

EXPERIMENTAL

The catalyst was dissolved with heating in the corresponding alcohol, the solution cooled to 20-40°C, the diethyl ester of carbonic acid added, and the mixture heated, simultaneously distilling off the ethanol formed. After the formation of ethanol ceased, the mixture was cooled, filtered to remove the catalyst, the excess of alcohol taken distilled off under vacuum, and the higher ester of carbonic acid purified by fractional redistillation under vacuum. The conditions of transesterification are cited in Table 1; the esters of carbonic acid obtained and their constants are cited in Table 2.

CONCLUSIONS

1. The corresponding higher esters were obtained in yields of 65-84% by transesterification by alcoholysis of the diethyl ester of carbonic acid with higher alcohols in the presence of alkaline catalysts.

2. The best catalysts are KOH and NaOH in amounts of 3-5 mole %. Acid catalysts are relatively ineffective.

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