TRANSESTERIFICATION OF ESTERS OF ADIPIC ACID

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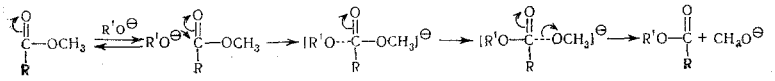
Esters of adipic acid are produced by esterification of adipic acid without a catalyst [1] and in the presence of acid [2] or alkaline catalysts [3], as well as by alcoholysis of the chloride of adipic acid [4], acidolysis of the diphenyl ester of carbonic acid [5], and alkylation of salts of adipic acid with alkyl bromides [6]. The production of the dicyclohexyl ester of adipic acid by transesterification of the dimethyl ester with cyclohexanol is also known [7].

We have shown for the example of esters of oxalic and malonic acids that the transesterification of esters by alcoholysis in the presence of alkaline and acid catalysts is a convenient preparative method for the production of esters of varied alcohols from lower esters [8-11]. The S_N2-mechanism of the alkaline transesterification of adipic ester can be represented as follows



The multicenter mechanism of acid transesterification can be represented as follows

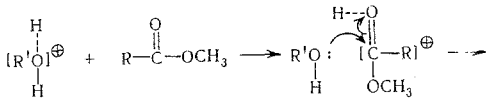


TABLE 1. Conditions of Transesterification of Esters of Adipic Acids

R	R′	Catalyst	Initial adipic ester, M	Ratio adipic ester:alcohol :catalyst, M	Yield, %		Time of transesterification, h
					transesterification	esterification	
n-C_3H_7	CH_3	NaOH	0,2	1 : 4,35 : 0,125	82,0	—	20
n-C_3H_7	CH_3	PTSC*	0,115	1 : 3,00 : 0,003	91,4	—	8,0
n-C_4H_9	CH_3	NaOH	0,2	1 : 3,62 : 0,125	80,3	—	1,0
n-C_4H_9	CH_3	PTSC	0,059	1 : 2,66 : 0,02	91,8	—	2,0
n-C_5H_{11}	CH_3	NaOH	0,2	1 : 2,78 : 0,125	84,3	91,5	10
n-C_5H_{11}	CH_3	PTSC	0,15	1 : 2,67 : 0,02	91,6		3,5
n-C_6H_{13}	CH_3	NaOH	0,2	1 : 2,81 : 0,125	84,3	92	7
Cyclo-C_6H_{11}	CH_3	PTSC	0,15	1 : 2,67 : 0,02	98,1		6
n-C_7H_{15}	CH_3	NaOH	0,2	1 : 2,13 : 0,1	72,6	91,5	5
n-C_7H_{15}	CH_3	PTSC	0,15	1 : 2,67 : 0,02	98		4,5
n-C_7H_{15}	CH_3	PTSC	0,12	1 : 3,53 : 0,045	84,6		
n-C_8H_{17}	CH_3	NaOH	0,15	1 : 2,67 : 0,167	66,9	92,5	12
n-C_8H_{17}	CH_3	PTSC	0,059	1 : 2,67 : 0,02	90,3		2
n-C_8H_{17}	CH_3	PTSC	0,059	1 : 5,20 : 0,043	87,4		8,5
n-C_9H_{19}	CH_3	PTSC	0,060	1 : 3,80 : 0,079	99,0	95,8	5
n-C_9H_{19}	n-C_3H_7	PTSC	0,090	1 : 3,46 : 0,017	91,3		3,58
n-$C_{10}H_{21}$	CH_3	PTSC	0,060	1 : 3,20 : 0,026	91,4	96,0	2
n-$C_{10}H_{21}$	CH_3	PTSC	0,09	1 : 3,00 : 0,04	98		5
n-$C_{10}H_{21}$	CH_3	PTSC	0,181	1 : 3,00 : 0,083	Quantitative		3

* PTSC) para-toluenesulfonyl chloride.

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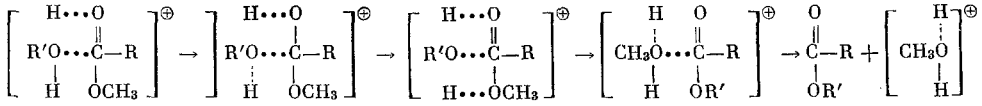
TABLE 2. Esters of Adipic Acid Produced by Transesterification of $ROOC(CH_2)COOR$

R	Bp, °C (p, mm Hg)	Mp, °C	n_D^t	d_4^t	Viscosity: kinematic ν_t, cSt	Viscosity: absolute η_t, cP	t, °C	MR: found	MR: calculated	Literature data: bp, °C (p, mm Hg)	Literature data: mp, °C	Literature data: n_D^t (t)	Literature data: d_4^t (t)
n-C_3H_7	138—140 (11)	—22,5	1,4304		4,2115		20		60,924	145—146 (9)	—20,25	1,43109	0,9810
	113—114 (2)		1,4288	0,98382			25	60,32		[12]	[13]	(20)	(20)
			1,4265	0,97144	3,006	2,921	30	60,81				[14]	[12]
			1,4230				40						
			1,4183	0,95424	1,570	1,498	50	60,83					
n-C_4H_9	153—155 (6)	—24,0	1,4360		5,514		20		70,160	158—159 (7)	—23	1,43526	0,9563
	150—152 (4)		1,4329	0,9573			25	70,13		[12]	[15]	(20)	(25)
			1,4320	0,95405	3,849	3,672	30	70,14				[14]	[15]
			1,4281				40						
			1,4243	0,93473	1,980	1,851	50	70,57					
n-C_5H_{11}	152—153 (2)	—11,0	1,4378		6,883		20		79,396	185—186 (10)	—14,0	1,4389	0,9433
	163—168 (3)		1,4372	0,94608			25	79,34		[12]	[16]	[15]	(25)
	177—178 (6)		1,4340	0,93837	4,803	4,507	30	79,49					[15]
			1,4301				40						
			1,4263	0,92487	2,810	2,598	50	79,40					
n-C_6H_{13}	195—196 (6)	—17,5	1,4402		9,746		20		88,632	164 (3)	—13,8	1,4406	0,9323
			1,4389	0,9351			25	88,44		[15]	[15]	[15]	(25)
			1,4365	0,93158	5,784	5,389	30	88,35					[15]
			1,4327				40						
			1,4290	0,91436	3,035	2,775	50	88,66					
Cyclo-C_6H_{11}	181—182 (2)	33,0	1,4719 *				20			212—219 (9)	36	1,4720	1,030
			1,4711 *	1,03004 *			25			[7]	[17]	(20)	(15)
			1,4681 *				30			212 (12)		[18]	[15]
			1,4639				40			[15]			1,037
			1,4602	1,01017	10,767	10,875	50	84,19	84,232				(20)
n-C_7H_{15}	185—187 (3)	2,0	1,4440		12,812		20		97,868	--	3,8—4,5	—	—
	213—215 (5)		1,4418	0,92461			25	97,98			[16]		
	219—221 (7)		1,4402	0,92338	7,553	6,974	30	97,80					
			1,4364				40						
			1,4326	0,90632	3,996	3,622	50	98,14					
n-C_8H_{17}	232 (6)	7,5	1,4457		15,363		20	107,25	107,104	—	9 5—9,8	—	—
			1,4447	0,91903			25				[16]		
			1,4419		9,131		30						
			1,4380				40						
			1,4343	0,90005	4,353	3,918	50	107,31					
n-C_9H_{19}	211—212 (2)	18,5	1,4478	0,91369	19,053	17,408	20	116,75	116,340	—	17—18,5	—	—
	226—228 (3)		1,4464				25				[19]		
			1,4440	0,90944	11,219	10,203	30	116,54					
			1,4402				40						
			1,4367	0,89418	5,762	5,152	50	116,72					
n-$C_{10}H_{21}$	244—245 (3)	25,4	1,4456	0,90465	14,082	12,740	30	125,68	125,576	—	26,8—27,2	—	—
			1,4420				40				[20]		
			1,4383	0,89077	6,360	5,665	50	125,82					

* Supercooled liquid.



The exchange of alkoxy groups of adipic esters proceeds successively at both carbalkoxyl groups according to the mechanism cited. In contrast to oxalic and malonic esters [8-11], in the transesterification of adipic esters there are no supplementary factors promoting this process. To shift the equilibrium in the direction of higher esters, an excess of the alcohol is taken, while the alcohol displaced is distilled off from the reaction mixture as completely as possible, as it is formed. These conditions are very important for the transesterification by lower alcohols. In the alcoholysis of esters of adipic acid, acid catalysts are more effective than alkaline catalysts.

This work presents the transesterification of the dimethyl ester of adipic acid by alcoholysis with alcohols from n-propyl to n-decyl and with cyclohexanol, taken in excess, as well as transesterification

of the diisopropyl ester of adipic acid by n-nonyl alcohol in the presence of sodium hydroxide or p-toluenesulfonyl chloride. The production of esters of adipic acid by azeotropic acid esterification is cited for comparison. The melting and boiling points, index of refraction, density and viscosity at various temperatures, and the molecular refraction were determined for the esters obtained.

EXPERIMENTAL METHOD

Transesterification by Alcoholysis. The catalyst was dissolved in the corresponding alcohol, the lower ester of adipic acid was added, and the mixture was heated, simultaneously distilling off the lower alcohol formed. After completion of the reaction, the mixture was cooled, washed with water, with a solution of Na_2CO_3 or acid to neutralize the catalyst, and again with water. The aqueous layer was extracted with benzene, the extract added to the ester obtained, and the benzene distilled off (water is removed simultaneously). The excess alcohol was distilled off under vacuum and the residue fractionated under vacuum. The conditions of transesterification are cited in Table 1. Table 2 presents esters of adipic acid and their constants.

Azeotropic Esterification. A mixture of adipic acid, alcohol, p-toluenesulfonyl chloride, and an azeotroping solvent, for example, benzene, in a 1 : 3.65 : 0.0192 : 0.84 mole ratio was heated at boiling until the formation of water ceased entirely (1-2 h), then boiled for 4-5 h, after which the mixture was cooled, washed with a 2% solution of Na_2CO_3, and with water. To the organic layer we added 20 ml of benzene, and distilled off the mixture of benzene and water. Alcohol was removed under vacuum and the residue fractionated. The yields of the esters of adipic acid obtained are cited in Table 1.

CONCLUSIONS

The corresponding higher esters were produced in good yields by transesterification of lower esters of adipic acid by alcoholysis with alcohols in the presence of an alkaline or acid catalyst. Acid catalysts (p-toluenesulfonyl chloride) are more effective than alkaline catalysts (KOH).

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