FREE-RADICAL ADDITION OF DICARBOXYLIC ACID ESTERS TO α -OLEFINE AND THE SYNTHESIS OF α -ALKYLDICARBOXYLIC ACID ESTERS

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N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR Translated from Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk, No. 7, pp. 1326-1330, July, 1961 Original article submitted July 14, 1960

We have previously studied the addition of carboxylic acids and their methyl esters of α -olefins [1]:

$$R-CH_{2}COOH+CH_{2}+CH-R' \xrightarrow{} R'-CH_{2}CH_{2}-CH-COOH$$

This reaction proceeds by a free-radical mechanism, the initiator being tert-butyl peroxide between 135 and 200°. Further detailed studies showed that the reaction may be regarded as a new preparative method for dialkylacetic acids. It has a number of advantages over the sodiomalonic and sodioacetoacetic ester syntheses usually employed. The chief advantage is the simplicity of the experimental technique required and the fact that the process takes place in one stage.

The aim of the present work was to extend the applicability of this reaction (free-radical addition of acids to multiple bonds) and to use it for the synthesis of α -alkyldicarboxylic acid esters. It was established that malonic, succinic, adipic, azelaic, and sebacic acid esters add on the α -olefins with the formation of the corresponding α -alkyldicarboxylic acid esters:

ROOC-
$$(CH_2)_n$$
-COOR+ CH_2 = $CH-R' \rightarrow ROOC-CH-(CH_2)_{n-1}COOR$,
 CH_2
 CH_2
 CH_2
 CH_2
 R'
where $n = 1, 2, 4, 7, 8; R=CH_3-; C_2H_5-$

The reactions were carried out at atmospheric pressure in the presence of tert-butyl peroxide. The conditions employed in the various experiments, the proportions of the reagents and of the peroxide, and the yields of the 1:1 adducts are given in Table 1, and the properties of the 1:1 adducts in Table 2. All the experiments were carried out under comparatively similar conditions – duration 4-6 hr, at 155-165°, and with ester: olefin: peroxide ratios of 7.7-10:1:0.25-0.26. The 1:1 adducts with the exception of those of α - olefins and methyl adipate (experiments 4 and 5), were obtained in high yields (52-75%). In the case of methyl adipate the yields were much lower. To confirm the structure postulated for the 1:1 adducts (experiments 4-7), dimethyl α -octyladipate (experiment 4) was hydrolyzed to the free acid (m. p. 74.5-75°), which was then converted to the amide (m. p. 186.2-186.8°). Published data [2]: α -octyladipic acid, m. p. 75°; α -octyladipamide, m. p. 186.7°.

The data obtained here and in previous work [1] may thus be regarded as proof that the addition of dibasic acid esters to α -olefins takes place at the α -carbon atom of the former. We have already reported that only those acids or esters which have the CH₂ or CH group in the acid radical can¹add on readily to α -olefins. Methyl acetate could not be added to 1-decene, i.e., it was impossible to convert the olefin to an acid having two additional carbon atoms in the molecule. This was successfully accomplished in another way. By adding dimethyl malonate to 1-decene, diethyl decylmalonate was obtained. The latter, after hydrolysis and decarboxylation, yielded lauric acid:

a de la compañía de l	Residue, g	22899999999999999999999999999999999999
: 1 adduct	0/0	22 3 4 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5
Yield of 1	50	49,33 49,57,77 49,37,77,76 49,37,77 49,37,77 40,37 40,37 40,37 40,37 40,0000000000
	Time. hr	ຉ୶ໞຉຉ୶ຉຉຉ <mark>ຉ</mark> ຉຉ
	Temp., °C	$\begin{array}{c} 155 \\ 155 \\ 155 \\ 155 \\ 152 \\ 152 \\ 152 \\ 152 \\ 153 \\ 160 \\ 165 \\ 155 \\ 162 \\ 156 \\ 162 \\ 157 \\ 162 \\ 162 \\ 157 \\ 162 \\ 162 \\ 155 \\ 162 \\ 165 \\ 155 \\ 162 \\ 165 \\ 155 \\ 162 \\ 165 \\$
action, mole	tert-butyl peroxide	0,04 0,05 0,051 0,041 0,041 0,041 0,041 0,05 0,05 0,05
ss used in re	<u>م</u>	$\begin{array}{c} 0,16\\ 0,16\\ 0,156\\ 0,156\\ 0,156\\ 0,143\\ 0,22\\ 0,143\\ 0,143\\ 0,12\\$
Quantitie	A .	404444467004 00080100004
	unsaturated com- pound B	1-Decene 4-Methyldec-1-ene 1-Octene 1-Octene 1-Decene 1-Octene 1-Octene Methyl acrylate Methyl acrylate Methyl acrylate Methyl acrylate Methyl acrylate
Reactant	Ester or acid A	CH ₃ (COOC ₂ H ₃) ² CH ₂ (COOC ₂ H ₃) ² CH ₃ OOC(CH ₃) ² COOCH ₃ CH ₃ OOC(CH ₃) ² COOCH ₃ CH ₃ OOC(CH ₃) ₄ COOCH ₃ CH ₃ OOC(CH ₃) ₄ COOCH ₃ CH ₃ OOC(CH ₃) ₆ COOCH ₃ CH ₃ OOC(CH ₃) ₈ COOCH ₃ n.C ₆ H ₁₃ COOH n.C ₆ H ₁₃ COOH n.C ₆ H ₁₃ COOH n.C ₆ H ₁₃ COOCH ₃
	Expt. No.	400400000000000000000000000000000000000

$$\begin{array}{c} C_8H_{17}-CH=CH_2+CH_3\ (COOC_2H_5)_2-\cdots-C_{10}H_{21}CH\ (COOC_2H_5)_2-\cdots-C_{10}H_{21}\cdots-CH_2COOH\end{array}$$

The esters of α -alkyl dicarboxylic acids can also be obtained by the addition of monobasic acids or their esters to unsaturated acids or their esters:

 $\begin{array}{c} R-CH_{2}COOH+CH_{2}=CH (CH_{2})nCOOR' \rightarrow \\ \hline \\ ---- \rightarrow HOOC--CH--CH_{2}CH_{2}-- \\ | \\ R \\ (--CH_{2})nCOOR' \end{array}$

The reaction was carried out in three cases (experiments 8-11). Enanthic acid and methyl caprate were added to methyl acrylate (n = 0), and valeric acid was added to methyl undecenoate (n = 8). A high yield of the 1:1 adduct with methyl acrylate could not be obtained. This is obviously due to the ease of polymerization and telomerization under the reaction conditions, since, in addition to the small yield of the 1:1 adduct, a large quantity of macromolecular products is obtained (see column headed "residue" in Table 1). To increase the yield of the 1:1 adduct of methyl acrylate and enanthic acid, a 20:1:0.5 acid: methyl acrylate: peroxide ratio was employed in experiment 9 instead of the usual 10:1:0.25 (experiment 8). However, the yield was not much improved. The yield of the addition product of valeric acid and methyl undecenoate is close to those of the 1:1 adducts of monobasic acids and α -olefins under analogous conditions. The appropriate melting points, or more correctly the temperatures of the appearance of liquid phase, of α -alkyldicarboxylic acid esters, which are liquid at room temperature, were determined. The determinations were made in a test tube 20 mm in diameter mounted in another vessel ("jacket"). Seven ml of ester was placed in the test tube and a thermometer was inserted. On cooling the esters turned into a crystalline mass; the cooling was then terminated and the temperature at which liquid phase appeared in the test tube, inclined at 45°, was noted. The following results were obtained: dimethyl ester of α -octylsuccinic acid, -9 to -10° ; dimethyl ester of α -octylazelaic acid, 1.5°; dimethyl ester of α octylsebacic acid, 1 to 0°; dimethyl ester of α -decyladipic acid, 7.5°; diethyl ester of decylmalonic acid, -10° .

For compounds of the type $CH_3OOCCH(C_8H_{17})(CH_2)_{III}COOCH_3)$ (Experiments, 3, 4, 6, 7, and 10) exaltation of molecular refraction (ΔMR_D) was observed, the average value of ΔMR_D being -0.6.

Kharasch and Gladstone [3] converted monobasic acids to the dibasic under the influence of acetyl peroxide; they showed that decomposition of acetyl peroxide in acetic, isobutyric, and chloroacetic acids leads to condensation of the α -carbon atom with the formation of succinic, tetramethylsuccinic, and dichlorosuccinic acids, respectively, in 42-45% yields, based on the peroxide. The present investigation established that a condensation of this type takes place readily also under the influence of tert-butyl peroxide. The methyl ester of enanthic acid yielded the dimethyl ester of α , α '-dipentyl-succinic acid in 36% yield, based on the peroxide:

TABLE

TABLE	3 2			.			-					
1		Mol. W	rt.	B. p., °C,	20	-20	W	R	Found	. Ho	Calc.	8
No.	T: T Adduct	found*	calc.	mm Hg	4 4		found	calc.	v	н	с С	H
1	C ₁₀ H ₂₁ CH(COOC ₂ H ₆) ₂	•		148-150	0,9373	1,4377	84,09	84,58				
24	C ₆ H ₁₃ CH(CH ₂),CH(COOC ₂ H ₅),			132-135 1,5	0,9337	1,4392	88,62	89,22	68,51 68,40	10,90	68,75	10,90
ŝ	CH ₃ 00C-CH-CH ₂ COOCH ₃	253,7	258,35	133-135 1,5	0,9679	1,4392	70,23	70,62	64,95 64,80	10,01 9,82	65,08	10,15
4	СН ₃ ООССН(СН ₂) ₃ СООСН ₂ Д	281	286,4	153-154 1,5	0,9576	1,4431	79,30	79,93	66,83 66,63	10,50	61,09	10,56
ŝ	Сн ₃ 00С—СН—(СН ₂) ₃ СООСН ₃			170-172	0,9446	1,4461	88,79	89,22				
9	С ₁₀ Н ₂₁ СН ₃ ООССН(СН ₂),сООСН ₃			159-159,5	0,9406	1,4462	93,17	93,87	69,24 69,35	$11,10\\10,90$	69,46	11,05
2	CH300C-CH-(CH2)7C00CH3	- 	ىرىنى ئۆلەردىكەن. سەر ئىرىنى ئەر ئ	169,5-170	0,9363	1,4472	97,78	98,42	69,96 69,75	10,98 10,83	70,13	11.18
ø	CH300C-CH3CH3-CH-COOH	220,7	216,27	155-157 1,0	1,0281	1,4482	56,33	56,57	61,06 61,08	$9,10 \\ 9,38$	61,08	9,32
10	CH ₃ OOCCH ₂ CH ₂ -CH-COOCH ₃			128—130 1,0	0,9666	1,4435	74,78	75,28	66,35 66,35	10,50 10,20	64,14	10,36
11	CH300C-(CH2)10-CH-COOH** CH300C-(CH2)10-CH-COOH** C3H,	300,9	300,43	190-192					67,93 68,00	10,59 10,53	67,96	10,74
			-									

• The molecular weights were calculated from acid and ester numbers. • * M_{\bullet} p. 36.5-37.5° (recrystallized from acetone).

$\begin{array}{c} C_5H_{11}CH_2COOCH_3+(CH_3)_3COOC\ (CH_3)_3 \longrightarrow \\ \rightarrow CH_3OOC-CH-CH-COOCH_3+2\ (CH_3)_3COH\ (\texttt{M}\ CH_3COCH_3+CH_4) \\ | & | \\ CH_{11}\ C_5H_{11} \end{array}$

EXPERIMENTAL

All the experiments described in Table 1 were carried out by the same method. The ester or the acid itself (component A) was placed in a flask provided with a thermometer, a dropping funnel, a reflux condenser, and a stirrer. A solution of tert-butyl peroxide and of the unsaturated compound (component B) in approximately 1/4 to 1/3 of the total quantity of component A calculated for the reaction was added dropwise to the main bulk of the ester, which had been heated to 155-165°; the time of the addition is given in the table. After the addition had been completed, the mixture was stirred for a further hour at the reaction temperature and then distilled. Broad fractions of 1:1 adducts were separated and further purified by fractional distillation. The residue in the distillation flask consisted of higher-boiling products (see column headed "residue" in Table 1).

Experiment 1. Diethyl decylmalonate was converted to the decylmalonic acid by being boiled with 50% KOH and subsequent treatment with concentrated hydrochloric acid. The free acid decarboxylated on heating, yielding lauric acid; $m, p, 43.5-44^{\circ}$.

Experiment 2. Similarly, diethyl 4-methyldecylmalonate was converted to 6-methyldodecanoic acid: m. p. 156-158° (1.5 mm); d^{20}_{4} 0.8926, π^{20} D 1.4442; MR found 63.81; MR calc. 63.91. Found: C 72.86, 72.95; H 12.08, 12.20%; mole wt, 215.2 (from the acid number). $C_{13}H_{26}O_{2}$. Calculated: C 72.84; H 12.23%; mole wt. 214.35. The yields of the acids in experiments 1 and 2 were approximately 80%.

Experiment 4. Hydrolysis under the conditions of experiment 1 of 9 g of dimethyl α -octyladipate gave 5.6 g (yield 75%) of α -octyladipic acid melting at 74.5-75.0° (after 3 recrystallizations from acetone). A mixture of 1 g of the acid and 10 ml of thionyl chloride was heated to boiling for approximately 1 hr; the excess thionyl chloride was then distilled off, and the residue was treated with aqueous ammonia. The diamide of α -octyladipic acid formed melted at 186.2-186.8° after recrystallization from 70% alcohol. Published data [2]: m. p. of acid 74.5-75°; m. p. of the amide 186.7°.

Recomposition of tert-Butyl Peroxide in Methyl Enanthate

A solution of 20 g (0.137 mole) of the peroxide in 50 g of the ester was added, over 5 hr, to 80 g of the enanthic acid ester heated to 145-155°. Yield 14 g (36%) of the dimethyl ester of $\alpha_{,\alpha}$ '-dipentyl succinic acid; b, p. 108-110° (1 mm); d²⁰₄ 0.9527, n²⁰D 1.4420; found MR 79.54; calc. MR 79.93. Found: C 66.76, 66.89; H 10.30, 10.31%. C₁₆H₃₀O₄. Calculated: C 67.10; H 10.56%.

SUMMARY

1. Free-radical addition of dicarboxylic acid esters to α -olefins leads to the formation, in high yields, of α -alkyldicarboxylic acid esters. The reaction may be employed for the preparative synthesis of α -alkyldicarboxylic acids.

2. Carboxylic acids (or their esters) add on to esters of unsaturated acids with the formation of dicarboxylic acid esters.

LITERATURE CITED

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