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Abstract

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FREE-RADICAL ADDITION OF MONOBASIC ACIDS AND THEIR METHYL ESTERS TO α-OLEFINS

It was shown earlier that at a temperature of 250° and a pressure of 850–950 atm ethylene enters into a telomerization reaction with isobutyric acid, as a result of which a mixture of telomer homologs of α,α-dimethylcarboxylic acids is formed (^{1}). Other acids having a C—H bond at the α-carbon atom may also be used in this reaction (^{2}).

In the present communication we give a description of the synthesis of dialkylsuccinic acids by the method of free-radical addition of acids of normal structure to α-olefins. The reactions studied by us of propionic, butyric, enanthic, and capric acids (or their methyl esters) with hexene-1, octene-1, decene-1, and tridecene-1 proceed according to the scheme

$$\mathrm{R-CH_2-COOH+CH_2=CH-R'\rightarrow R'-CH_2-CH_2-CH(R)-COOH.}$$

Using the addition of isobutyric acid to decene as an example, it was shown that this method can also be applied to the synthesis of trialkylsuccinic acids. The reactions were carried out under atmospheric pressure, in the temperature range 135–180°; tert-butyl peroxide served as the initiator. Table 1 gives the experimental conditions, the amounts and molar ratios of the reaction components and peroxide, the structures and yields of the addition products (1 : 1 adducts). The properties of the products obtained—acids and esters—are given in Table 2. Experiments I–VII and IX were carried out under standard conditions: to the initial acid (or its methyl ester), placed in a flask, the olefin and peroxide were added dropwise over the course of 5–7.5 hr. The acids were taken in a 5–8-fold excess relative to the olefin. In experiment VIII the peroxide was added in portions. As can be seen from the data presented, in almost all cases 1 : 1 adducts are formed in fairly high yields (36–69%). The low yield of dimethylhexylsuccinic acid (experiment III) is explained by the insufficiently high reaction temperature. The methyl esters of acids (experiments VI and IX) form 1 : 1 adducts in yields somewhat lower than the acids (experiments IV and V). The amount of peroxide has a substantial effect on the yield of the addition products. In two experiments (VI and VII), carried out under the same conditions, with molar ratios methyl enanthate : octene-1 : peroxide of 7.7 : 1 : 0.26

and 7.7 : 1 : 0.13, the yield of methyl amyloctylsuccinate was 56.5% in the first case and 40% in the second. Replacement of continuous feeding of peroxide into the reaction zone by portionwise feeding also leads to a decrease in the yield of the 1 : 1 adduct from 56.5% (experiment VI) to 42.4% (experiment VIII). In all experiments, in addition to 1 : 1 adducts, more highly molecular products are formed.

When tert-butyl peroxide is used as the initiator, free-radical reactions are usually carried out at temperatures not below 120°. In the experiments described above such temperatures were achieved by virtue of the sufficiently high boiling temperature of the starting acids or esters. The addition reactions of methyl esters of propionic, butyric, and isobutyric acids (which have insufficiently high boiling temperatures) to α-olefins could be carried out only in an autoclave. Table 1 gives the conditions of the autoclave experiments (Nos. X–XIV); Table 2 gives the properties of the 1 : 1 adducts obtained, whose yields were 17–31%. In these experiments the peroxide was introduced in three portions into a solution of olefin in the acid ester. The attempts we made to carry out the addition reaction

Table 1

Experiment No.	Reaction product	Reaction component: acid or ester A	Reaction component: olefin B	A, g	A, mol	B, g	B, mol	Peroxide, g	Peroxide, mol	Temperature, °C	Time, h	Yield based on olefin, %: charged	Yield based on olefin, %: consumed
Experiments at atmospheric pressure													
I	n-$C_{13}H_{27}CH(CH_3)COOH$	C_2H_5COOH	Tridecene	92,5	1,25	45,5	0,25	6,0	0,041	136–140	6,5	38,3	46,5
II	n-$C_{10}H_{21}C(CH_3)_2COOH$	$(CH_3)_2CHCOOH$	Decene	211	2,4	44,5	0,317	12,0	0,082	142–144	5,0	36,2	44,0
III	n-$C_6H_{13}C(CH_3)_2COOH$	$(CH_3)_2CHCOOH$	Hexene	211	2,4	26,5	0,315	12,0	0,082	120–130	5,0	12,1	24

Experiment No.	Reaction product	Reaction component: acid or ester A	Reaction component: olefin B	A, g	A, mol	B, g	B, mol	Peroxide, g	Peroxide, mol	Temperature, °C	Time, h	Yield based on olefin, %: charged	Yield based on olefin, %: consumed
IV	n-$C_6H_{13}CH(C_2H_5)COOH$	n-C_3H_7COOH	Hexene	211	2,4	26,5	0,315	12,0	0,082	136 – 150	5,5	69,5	–
V	n-$C_8H_{17}CH(C_5H_{11})COOH$	n-$C_6H_{13}COOH$	Octene	312	2,4	35,0	0,312	12,0	0,082	167 – 180	5,7	65	–
VI	n-$C_8H_{17}CH(C_5H_{11})COOCH_3$	n-$C_6H_{13}COOCH_3$	Octene	174	1,2	17,5	0,156	6,0	0,041	150 – 152	5,0	56,5	–
VII	n-$C_8H_{17}CH(C_5H_{11})COOCH_3$	n-$C_6H_{13}COOCH_3$	Octene	174	1,2	17,5	0,156	3,0	0,02	156 – 165	5,0	40	–
VIII	n-$C_8H_{17}CH(C_5H_{11})COOCH_3$	n-$C_6H_{13}COOCH_3$	Octene	174	1,2	17,5	0,156	7,0	0,048	140 – 150	7,5	42,4	–
IX	(n-$C_8H_{17})_2CHCOOCH_3$	n-$C_9H_{19}COOCH_3$	Octene	447	2,4	35	0,312	12,0	0,082	143 – 149	6	53,7	–
Experiments in an autoclave													
X	n-$C_6H_{13}CH(CH_3)COOCH_3$	$C_2H_5COOCH_3$	Hexene	130	1,48	18,4	0,218	7,5	0,052	160 – 165	9,5	31,4	–
XI	n-$C_{10}H_{21}CH(CH_3)COOCH_3$	$C_2H_5COOCH_3$	Decene	130	1,48	20,7	0,148	7,2	0,049	160 – 170	22	30,8	37,2
XII	n-$C_{10}H_{21}C(CH_3)_2COOCH_3$	$(CH_3)_2CHCOOCH_3$	Decene	130	1,28	18	0,128	6,3	0,043	160 – 170	24	26,2	36
XIII	n-$C_6H_{13}CH(C_2H_5)COOCH_3$	n-$C_3H_7COOCH_3$	Hexene	153	1,5	13	0,15	7,5	0,052	155 – 160	23	34	

Experiment No.	Reaction product	Reaction component: acid or ester A	Reaction component: olefin B	A, g	A, mol	B, g	B, mol	Peroxide, g	Peroxide, mol	Temperature, °C	Time, h	Yield based on olefin, %: charged	Yield based on olefin, %: consumed
XIV	n-$C_6H_{13}CH(C_2H_5)COOCH_3$	n-$C_3H_7COOCH_3$	Hexene	160	1,57	13	0,15	7,5	0,052	118–150	9	17,7	

Table 2

No.	Addition products	Mol. wt. found**	Mol. wt. calc.	B.p., °C/mm	d_4^{20}	n_D^{20}	MR_D found	MR_D calc.	Found, % C	Found, % H	Calculated, % C	Calculated, % H	M.p. of acid, amide, °C
1*	n-$C_{13}H_{27}CH(CH_3)COOH$	258,5	256,42	173–174/3***					74,92	12,61	74,94	12,58	
2*	n-$C_{10}H_{21}C(CH_3)_2COOH$	229,5	228,37	142–144/3****									94–95
3*	n-$C_8H_{13}C(CH_3)_2COOH$	171,9	172,26	102–103/3,5	0,9022	1,4350	49,82	50,17					102–103
4	n-$C_6H_{13}CH(C_2H_5)COOH$	174,9	172,26	107–108/4	0,8481	1,4344	49,99	50,17					
5*	n-$C_8H_{17}CH(C_5H_{11})COOH$	244,8	242,4	170–171/4	0,8845	1,4457	73,03	73,41	73,93	12,21	74,32	12,48	
6	n-$C_8H_{17}CH(C_5H_{11})COOCH_3$	258,2	256,42	94,5–95/1	0,8642	1,4370	77,73	78,18	74,93	12,20	74,94	12,58	
7*	$(n$-$C_8H_{17})_2CHCOOCH_3$	294,6	298,5	150–151/4	0,8619	1,4422	91,67	92,12	76,95	12,71	76,45	12,83	123–123,5
8	n-$C_6H_{13}CH(CH_3)COOCH_3$	174,0	172,26	60–62/5	0,8703	1,4210	50,19	50,29					

No.	Addition products	Mol. wt. found	Mol. wt. calc.**	B.p., °C/mm	d_4^{20}	n_D^{20}	MR_D found	MR_D calc.	Found, % C	Found, % H	Calculated, % C	Calculated, % H	M.p. of acid amide, °C
9*	n-$C_{10}H_{21}CH(CH_3)COOCH_3$	229,1	228,38	86,5–90/1	0,8661	1,4332	68,56	68,88					75,5–76
10	n-$C_{10}H_{21}C(CH_3)_2COOCH_3$	243,2	243,41	97–98/3	0,8708	1,4378	73,40	73,40					
11*	n-$C_6H_{13}CH(C_2H_5)COOCH_3$	186,4	186,3	68–72/6	0,8660	1,4248	54,98	54,94					100–101

* Literature data: 1) b.p. 172–173° (2.5 mm), m.p. 24° (3); 2) b.p. 184° (12 mm), m.p. 27°, amide m.p. 95–96° (4); 3) amide m.p. 103° (5); 5) b.p. 161–164 (2–3 mm) (6); 7) amide m.p. 122.5–123.5 (7); 9) amide m.p. 77° (8); 11) amide m.p. is given in the present article.

** Molecular weights were calculated from saponification and neutralization numbers.

*** M.p. 37–38°.

**** M.p. 26–27°.

the addition of methyl acetate to decene-1 ended without result. The experiments were carried out at different ratios of decene-1 : methyl acetate : peroxide, in the temperature range 160-240°. Consequently, only those acids (and their esters) that have CH_2 and CH groups can add to olefins. However, when several methylene groups are present in the acid molecule, it might have been expected that its addition to the olefin would occur not only at the expense of the α-C—H bonds. To clarify this, the product of the addition of methyl butyrate to hexene-1 was saponified to an acid with b.p. 93-95° (2 mm), n_D^{20} 1.4336, and the acid was converted into an amide with m.p. 100.5-101° C. By independent synthesis

$$C_6H_{13}CHO + C_2H_5MgBr \xrightarrow{H_2O} C_6H_{13}CH(OH)C_2H_5 \xrightarrow{HBr}$$

$$\rightarrow C_6H_{13}CHBrC_2H_5 \xrightarrow[2.\ CO_2]{1.\ Mg} C_6H_{13}CH(C_2H_5)COOH$$

ethylhexylacetic acid was obtained, with b.p. 126-128° (5 mm), d_4^{20} 0.8957; n_D^{20} 1.4332. Its amide had m.p. 100-101°, and a mixed melting-point test with the amide of the adduct showed no depression. If methyl butyrate had added to hexene through the β-carbon atom, 3-methylnonanoic acid would have been formed. The amide of 3-methylnonanoic acid, obtained by us from 2-bromooctane by malonic ester synthesis, had m.p. 79°, which corresponds to the melting point of the amide reported in the literature (8). Thus, the free radicals arising upon decomposition of the peroxide abstract a hydrogen atom only from the α-carbon atom of the acid, which leads to the formation of the radical $R-\dot{C}H-COOH$, which then adds to the olefin. The reaction proceeds by a chain mechanism. Experiments I–VII and IX were carried out under identical conditions. We shall confine ourselves to describing one of them.

Experiment V. To 240 g of enanthic acid, heated to 180° with vigorous stirring for 5 hr 40 min, a mixture of 72 g of enanthic acid, 35 g of octene-1, and 12 g of peroxide was added dropwise, after which the reaction mixture was heated for another hour. Owing to the formation of low-boiling decomposition products of the peroxide, the temperature of the mixture by the end of the experiment had fallen to 167°. On distillation, 7.6 g of low-boiling products, 280 g of enanthic acid, 49 g of amyloctylacetic acid (yield 65%), and 19.5 g of high-boiling residue were obtained. In experiment I, methyltridecylacetic acid was obtained from propionic acid and tridecene-1, and on distillation of the high-boiling residue an acid with m.p. 51–53° was isolated, apparently having the structure:

$$C_{13}H_{27}CH(C_{11}H_{23})CH_2CH(CH_3)COOH \quad \text{(adduct 2 : 1)}$$

Found % : C 79.60; 79.64; H 13.04; 13.32
$C_{29}H_{58}O_2$. Calculated % : C 79.38; H 13.32

In experiment VIII, 174 g of the acid ester, 13.5 g of octene-1, and 2 g of peroxide were heated in a flask at 150° for 1 hr; then the remaining peroxide and olefin were added to it in five equal portions at equal time intervals.

Experiments X–XIV were carried out in a stationary steel autoclave of 200 ml capacity, into which the acid ester and olefin were charged; tert-butyl peroxide was added in three equal portions: $^1/_3$ at the beginning of the experiment and $^2/_3$ at approximately equal intervals of time (~8 hr in XI–XIII, ~3 hr in experiments X and XIV). In experiments XI–XIII the peroxide was introduced three times into the cold autoclave; in X and XIV, $^1/_3$ of the peroxide was introduced into the cold autoclave, and $^2/_3$ in a solution of the ester was injected into the autoclave at the reaction temperature.

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Note: Figure translations are in progress. See original paper for figures.

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