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Abstract

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Free-Radical Addition of Alcohols to Acrylic Acid and Its Methyl Ester

Synthesis of γ-Lactones

Many natural organic compounds containing a γ-lactone group exert a strong physiological action on microorganisms and macroorganisms, and alkyl-γ-lactones possess valuable fragrance properties. In a number of works (^{1}-^{3}) it was shown that γ-lactones (γ-alkylparaconic acids) can be obtained by the interaction of isopropanol, 2-octanol, and ethanol with maleic acid

$$\mathrm{R{-}CH(OH)CH_3 + CHCOOH \rightarrow R{-}C(CH_3)(O){-}CHCOOH{-}CH_2{-}C(=O) + H_2O.}$$

Reactions are carried out in the presence of benzophenone under prolonged (18-25 h) irradiation with ultraviolet light; the yields of lactones in most cases are 18-38%.

In the present work we set ourselves the task of studying the reaction of the addition of alcohols to acrylic acid and its methyl ester using tert-butyl peroxide as the initiator. It was established that both in the case of acrylic acid and in the case of methyl acrylate γ-lactones are formed. The reaction of acrylic acid with alcohols proceeds by a free-radical chain mechanism, which may be represented by the following series of equations:

$$\mathrm{(CH_3)_3COOC(CH_3)_3 \rightarrow 2(CH_3)_3CO\cdot \rightarrow 2CH_3\cdot + 2CH_3COCH_3;} \tag{a}$$

$$\mathrm{(CH_3)_3CO\cdot + RCH_2OH \rightarrow R\dot{C}HOH + (CH_3)_3COH;} \tag{b}$$

$$\mathrm{R\dot{C}HOH + CH_2{=}CH{-}COOH \rightarrow R{-}CH(OH)CH_2\dot{C}H{-}COOH;} \tag{c}$$

$$\mathrm{R{-}CH(OH)CH_2\dot{C}H{-}COOH + RCH_2OH \rightarrow R{-}CH{-}CH_2CH_2C{=}O + R{-}\dot{C}HOH + H_2O.} \tag{d}$$

In the last equation, the fragment R—CH—CH_2CH_2C=O is closed through oxygen to form the γ-lactone ring.

Abstraction of a hydrogen atom from the alcohol molecule can also be effected by a methyl radical. The reaction with methyl acrylate proceeds analogously. In this case, evidently, methyl esters of γ-hydroxy acids are formed initially, which then are converted into γ-lactones as a result of intramolecular transesterification. The conditions of individual experiments, the amounts of reaction components and peroxide, the yields of 1:1 adducts, and the amounts of the high-boiling products formed are presented in Table 1. Table 3 gives the properties of the lactones obtained.

Table 1

Experiment No.	Reaction components A	Reaction components B	Taken into reaction, g-mol A	Taken into reaction, g-mol B	Taken into reaction, g-mol peroxide	Temp., °C	Duration, h	Yield of 1:1 adduct, g	Yield of 1:1 adduct, %	Residue, g
1	Heptanol-1	Acrylic acid	3	0.3	0.045	160—170	6.5	36	70.5	21
2	Heptanol-1	Methyl acrylate	3	0.3	0.045	160—170	6.5	36.5	71.5	17.4
3	Octanol-2	Acrylic acid	3	0.3	0.045	160—170	6.5	33.5	60.6	18.8
4	2-Ethylhexanol-1	Acrylic acid	2.6	0.26	0.039	160—170	6	19.8	41.5	25
5	Cyclohexanol	Acrylic acid	3	0.3	0.045	156—163	6.5	40	86.5	3.2
6	Benzyl alcohol	Acrylic acid	3	0.3	0.045	160—170	6	27	56	21
7	Nonanol-1	Methyl acrylate	3	0.15	0.075	155—165	3	26	87	17.4

Table 2

Reaction of nonanol-1 (A) with acrylic acid (B)

Experiment No.	Taken into reaction, g-mol A	Taken into reaction, g-mol B	Taken into reaction, g-mol peroxide	Temp., °C	Duration, h	Yield of 1:1 adduct, g	Yield of 1:1 adduct, %	Residue, %
8	3	0.3	0.09	160–170	6.5	43	72.3	20.5
9	3	0.3	0.045	160–170	6.5	38.8	65	20
10	3	0.3	0.0225	160–170	6.5	26.5	45	29.5
11	3	0.3	0.0075	160–170	6.5	15	25	40

In the reaction with acrylic acid, heptyl, nonyl, secondary-octyl, 2-ethylhexyl, cyclohexyl, benzyl, and γ-phenylpropyl alcohols were studied (experiments Nos. 1, 3–6, 8–11); in the reaction with methyl ester of acrylic acid, heptyl and nonyl alcohols were studied (experiments Nos. 2 and 7). Only with γ-phenylpropanol was it not possible to obtain a lactone–only high-molecular products of polymerization and telomerization were formed, which were not investigated. With the other alcohols, γ-lactones were obtained in fairly high yields at a molar ratio alcohol : acid : peroxide of 10 : 1 : 0.15. The comparatively low yield (41.5%) of lactone from 2-ethylhexanol is evidently explained by the ease of abstraction of the hydrogen atom from the tertiary carbon atom of this alcohol and by the low reactivity of the free radical formed, which is prone to dimerization and disproportionation. Even with benzyl alcohol it was possible to obtain γ-phenylbutyrolactone in a yield of 56%, despite the fact that benzyl radicals are characterized by low reactivity (4).

In order to study the influence of the amount of peroxide on the yield of γ-octylbutyrolactone, a series of experiments was carried out at different molar ratios of nonanol-1 : acrylic acid : peroxide (Table 2). The properties of the lactone obtained are given in Table 3. Figure 1 gives a graphical expression of the dependence of the lactone yield on the amount of tert-butyl peroxide, calculated with respect to peroxide and acrylic acid.

When the reaction of nonyl alcohol with acrylic acid was initiated with benzoyl peroxide, γ-octylbutyrolactone was obtained in negligible yield.

Table 3

Experiment No.	γ-Lactone (1:1 adduct)	Mol. wt., found[1]	Mol. wt., calc.	B.p., °C (mm Hg)	d_4^{20}	n_D^{20}	MRD, found	MRD, calc.	Elemental analysis, found, % C	Elemental analysis, found, % H	Elemental analysis, calc., % C	Elemental analysis, calc., % H
1[3]	$C_6H_{13}CH-CH_2CH_2C{=}O$ $\vert$ O $\vert$	166,9	170,25	97–100(1)	0,9482	1,4482	48,09	48,07	–	–	–	–
2	$C_6H_{13}CH-CH_2CH_2C{=}O$ $\vert$ O $\vert$			95–97(1)	0,9478	1,4485	48,13	48,07	70,61 [illegible]	[illegible]	70,56	10,66
3	$(C_6H_{13})(CH_3)C-CH_2CH_2C{=}O$ $\vert$ O $\vert$	183,6	184,28	97–98(1)	0,9433	1,4496	52,46	52,72	71,73 [illegible]	[illegible]	71,69	10,94
4	$C_4H_9-CH-CH-CH_2CH_2C{=}O$ C_2H_5 O	185,1	184,28	100–101(1)	0,9488	1,4545	52,65	52,72				
5	$(CH_3)_3C-CH_2CH_2C{=}O$ $\vert$ O $\vert$	152,3	154,21	90–92(1,5)	1,0735	1,4817	40,93	41,53	70,20 70,35	9,34 9,15	70,09	9,15
6[3]	$C_8H_5CH-CH_2CH_2C{=}O$ $\vert$ O $\vert$			125–127[2](1,5)	–	–	–	–	74,24 74,16	6,16 6,13	74,06	6,21
7[3]	$C_8H_{11}CH-CH_2CH_2C{=}O$ $\vert$ O $\vert$	162,0	162,19	130–132(1,5)	0,9342	1,4521	57,27	57,37	–	–	–	–
9	$C_8H_{17}CH-CH_2CH_2C{=}O$ $\vert$ O $\vert$	195,4	198,30	120–121(1)	0,9334	1,4520	57,32	57,37	72,96 [illegible]	[illegible]	[illegible]	11,18

Figure 1

Figure 1: Figure 1

[1] Molecular weight determined from the ester number.
[2] M.p. 36,5—37° (from acetone and from heptane).
[3] Literature data: experiment No. 1—b.p. 281° (5); No. 6—m.p. 37° (6); b.p. 130—130,3° (1,5 mm); m.p. 45,5—46° (7); No. 7—b.p. 130° (0,5 mm); d_4^{20} 0,9383; n_D^{20} 1,4522 (8).

Experimental Part

All experiments listed in Tables 1 and 2 were carried out by a single procedure. A solution was prepared of the calculated amounts of acrylic acid (or its methyl ester) and tert-butyl peroxide in a portion of the alcohol taken from the total calculated amount of alcohol indicated in Tables 1 and 2. We give the experiment numbers and, in parentheses, the amounts of alcohol in moles taken for preparation of the solution: 1, 2 (1.3); 3(1.1); 4—6, 8—11 (1); 7 (0.2). The solution was added dropwise, uniformly, to the alcohol placed in a 0.75-liter flask and heated to the required temperature. All experiments were carried out with stirring. The solution was added over the time indicated in the tables, after which the reaction mixture was heated at the specified temperature for another 1—1.5 hours. The water liberated in the reaction was condensed in a condenser, after which it was removed from the reaction zone through a special outlet. From the reaction mass the decomposition products of the peroxide, excess initial alcohol, and the 1 : 1 adduct were distilled off. The yield of lactone (the 1 : 1 adduct) was determined after its repeated distillation. The total amount of high-boiling products remaining in the flask after distillation of the 1 : 1 adduct and after its repeated distillation is indicated in Tables 1 and 2.

Fig. 1. Yield of γ-octylbutyrolactone, calculated with respect to peroxide and to acid, as a function of the molar ratio peroxide : acrylic acid. Molar ratio nonanol-1 : acrylic acid = 10 : 1, reaction temperature 160—170°, reaction duration 6.5 h.

The molecular weights of the lactones were determined from the saponification number; for this purpose a sample of the lactone was boiled for 2 h with 0.6 N KOH solution and then titrated with 0.1 N HCl solution. To determine the purity of one of the reaction products—γ-octylbutyrolactone—the latter was converted by boiling with 10% KOH into the sodium salt of γ-oxylauric acid, which, after treatment with hydrochloric acid and distillation, was again converted into the lactone. In this process the properties of the lactone did not change.

γ-Phenylbutyrolactone (experiment 6), by the method described earlier (^{7}), was converted into γ-phenyl-γ-oxybutyric acid, which after recrystallization from warm water had m.p. 75—76°; literature m.p. 75° (^{6}), 111—112° (^{7}).

The amide of γ-phenyl-γ-oxybutyric acid, after recrystallization from a benzene–heptane solution, had m.p. 85–86°; literature m.p. 85.5–86.5° (7); 86° (9).

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