CHEMISTRY

G. N. NIKISHIN, Yu. N. OGIBIN, and Corresponding Member of the Academy of Sciences of the USSR A. D. PETROV

1961

SovietRxiv

Abstract

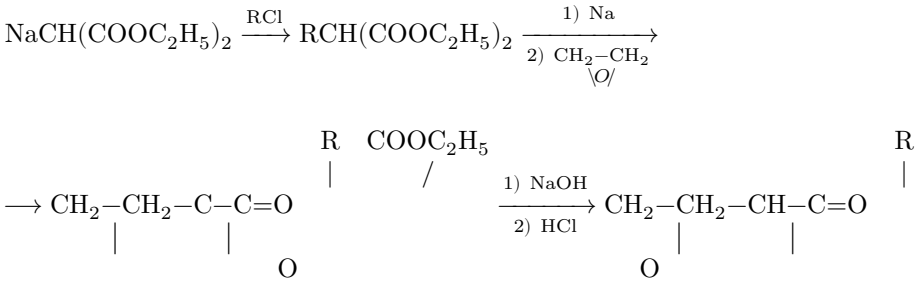
Full Text

CHEMISTRY

G. N. NIKISHIN, Yu. N. OGIBIN, and Corresponding Member of the Academy of Sciences of the USSR A. D. PETROV

FREE-RADICAL ADDITION OF CARBOXYLIC ACIDS TO VINYL AND ALLYL ACETATES

In order to study the relationship between structure and odor, Rothestein in 1935 carried out the synthesis of a series of homologs of α-alkyl-γ-butyrolactones according to the scheme ([1])



He found that these lactones possess a pleasant odor valuable for perfumery, provided that R (an aliphatic radical of normal structure) has the composition C_6-C_{12}. A study analogous in its aim and synthetic method was carried out by Brown ([2]). The latter prepared a series of α-alkyl-γ-valerolactones, using allyl bromide instead of ethylene oxide in the scheme given above. Among the compounds he obtained, α-hexyl-γ-valerolactone had the strongest odor, the intensity of which decreased with an increase or decrease in the number of carbon atoms in the alkyl radical. There are indications that δ-lactones also possess a pleasant odor ([3]). However, the preparation of most of the indicated lactones is associated with a number of difficulties, one of the chief among them being the two-stage malonic ester synthesis.

In one of our works it was established that carboxylic acids are capable of adding to α-olefins when the reaction is initiated by tert-butyl peroxide ([4]). At 140-160° and with a ratio acid : olefin : peroxide of 10 : 1 : 0.25, the yield of the resulting dialkylacetic acids (1 : 1 adducts) was 60–70%.

In the present communication we give the results of our study of the addition reaction of acids and their methyl esters to vinyl and allyl esters of acetic and formic acids, as well as the results of the synthesis, from the esters obtained, of α-alkyl-γ- and δ-hydroxy acids and the corresponding γ- and δ-lactones. The

synthesis of α-alkyl-γ-butyrolactones was carried out according to the following general scheme:

$$CH_3COOCH{=}CH_2 + R{-}CH_2COOH \longrightarrow CH_3COOCH_2CH_2{-}\overset{R}{C}H{-}COOH \longrightarrow$$

$$\xrightarrow[2)\ HCl]{1)\ NaOH} CH_2{-}CH_2{-}CH(R){-}C{=}O \quad (O)$$

When vinyl acetate was replaced by allyl acetate, α-alkyl-δ-valerolactones were similarly obtained. The conditions of individual addition-reaction experiments, the amounts of the components and peroxide, and the yield of 1:1 adducts are given in Table 1; the properties of the adducts obtained are given in Table 3, and the properties of the lactones in Table 2. Comparison of the results of experiments 1–6 with experiments on the addition of carboxylic acids (or their methyl esters) to α-olefins gives grounds for the following conclusion: under standard conditions, aliphatic monobasic acids form 1:1 adducts with unsaturated acid esters in yields 10–20% lower than in the case of α-olefins.

Table 1

Free-radical addition reaction

Experiment No.	Reaction components: A	Reaction components: B	Amounts taken in the reaction, A, g	Amounts taken in the reaction, A, mol	Amounts taken in the reaction, B, g	Amounts taken in the reaction, B, mol	Peroxide, g	Peroxide, mol	Temperature, °C	Duration, h	1:1 adduct, yield, g	1:1 adduct, yield, %	Residue, g
1	$C_4H_9CH{=}CH_2$	$CH_2{=}CHOCOCH_3$	50	0.5	43	0.5	18.3	0.125	158–160	5	42.5	45	36
2	$C_7H_{15}CH{=}CH_2$	$CH_2{=}CHOCOCH_3$	56	0.5	17.2	0.2	7.3	0.05	160–163	6	24	52	16
3	$C_6H_{13}CH{=}CH_2$	$CH_2{=}CHOCOCH_3$	28	0.25	16.2	0.2	7.3	0.05	158–160	5	17	37	22
4	$C_4H_9CH{=}CH_2$	$CH_2{=}CH{-}CH_2OCOCH_3$	30	0.3	30	0.3	11	0.075	157–164	5	28.5	47	22

Experiment No.	Reaction components: A	Reaction components: B	Amounts taken in the reaction, A, g	Amounts taken in the reaction, A, mol	Amounts taken in the reaction, B, g	Amounts taken in the reaction, B, mol	Peroxide, g	Peroxide, mol	Temp., °C	Duration, h	1:1 adduct yield, g	1:1 adduct yield, %	Residue, g
5	C_7H_{15}—CH(OH)—CH_2OCOCH_3	CH_2=CH—CH_2OCOCH_3	7.2	0.05	25	0.25	9.2	0.063	159–163	5.5	28	46	19
6	C_9H_{19}—CH(OH)—CH_2OCHO	CH_2=CH—CH_2OCHO	2	17.2	0.2	7.3	0.05	155–157	5	20	37	28	

Table 3

γ- and δ-lactones

Experiment No.	Lactone	Yield, %	b.p., °C (mm Hg)	d_4^{20}	n_D^{20}	MR_D, found	MR_D, calc.	Elemental composition, found C, %	Elemental composition, found H, %	Elemental composition, calc. C, %	Elemental composition, calc. H, %
7	CH_2—CH_2—CH_2—CH(C_3H_7)—O—C=O *	91	107–108 (15)	1.0016	1.4410	33.79	34.29	65.42; 65.21	9.42; 9.64	65.59	9.44
8	CH_2—CH_2—CH_2—CH(C_8H_{13})—O—C=O **	84	87–88 (1)	0.9561	1.4490	47.76	48.23	69.66; 69.86	10.55; 10.53	69.64	10.66
9	CH_2—CH_2—CH_2—CH(C_5H_{11})—O—C=O	85	92.5–93 (2)	0.9681	1.4470	43.12	43.58	69.01; 68.91	10.13; 10.25	69.19	10.32
10	CH_2—CH_2—CH_2—CH(C_3H_7)—O—C=O	81	71–72 (1)	1.0080	1.4568	38.40	38.93	67.52; 67.74	9.99; 10.17	67.57	9.93

Experiment No.	Lactone	Yield, %	b.p., °C (mm Hg)	d_4^{20}	n_D^{20}	MR_D, found	MR_D, calc.	Elemental composition, found C, %	Elemental composition, found H, %	Elemental composition, calc. C, %	Elemental composition, calc. H, %
11	$CH_2-CH_2-CH_2-CH(C_6H_{13})-O-C(=O)$ (1)	87	107–108 (1)	0.9623	1.4590	52.35	52.88				
12	$CH_2-CH_2-CH_2-CH(C_8H_{17})-O-C(=O)$ (0.5)	91	120–122 (0.5)	0.9438	1.4602	61.64	62.18	73.60; 73.40	11.46; 11.31	73.53	11.40

* b.p. 107° (15 mm), d_4^{20} 1.0021, n_D^{20} 1.4410, mint odor (1).

** b.p. 146° (16 mm), d_4^{21} 0.9551, n_D^{21} 1.4480; odor of apricots and ambergris (1).

At the same time, the amounts of high-boiling products formed through polymerization and telomerization of the unsaturated esters increase considerably. Increasing the acid:vinyl(allyl) acetate ratio from 10:1 (experiments 1, 4) to 20:1 (experiments 2, 5) has almost no effect

on the yield of 1:1 adducts; an insignificant decrease in yield is observed when the acids are replaced by their methyl esters (experiments 3, 6). Lactonization of the esters of γ- and δ-hydroxycarboxylic acids was carried out by the usual procedure. In calculating the molecular refraction of the lactones from bond increments [5], an exaltation (ΔMR_D) is observed, the average value of which is +0.5.

The preparation of γ- and δ-acetoxycarboxylic acids and their methyl esters (experiments 1-6). The quantitative characteristics of the experiments are given in Table 1; the procedure for carrying them out was the same.

About $\sim$ 2/3 of the acid (in experiments 2 and 6, the methyl ester of the acid), taken from the total calculated amount (component A), was placed in a four-necked flask equipped with a stirrer, a thermometer with reflux condenser, and a calibrated dropping funnel. After the acid had been heated to the required temperature, a solution of tert-butyl peroxide and the unsaturated ester (component B) in the remaining $\sim$ 1/3 of the acid was added to it uniformly, dropwise. The time of addition of the solution is indicated in Table 1. After the addition was complete, the reaction mixture was heated for another $\sim$ 1 hour at the same temperature, and then the decomposition products of the peroxide

and the excess acid (methyl ester of the acid) were distilled off from it. The γ- and δ-acetoxycarboxylic acids and their methyl esters—the 1:1 adducts—were isolated from the high-boiling reaction products by fractional distillation. The quantities of substances boiling higher than the 1:1 adducts are indicated in Table 1. These residues are resin-like, very viscous liquids.

Table 3

No. of experiment	1:1 adduct	Molecular weight found*	Molecular weight calc.	B.p., °C (mm Hg)	d_4^{20}	n_D^{20}	MR_D found	MR_D calc.	C found, %	H found, %	C calc., %	H calc., %
1	$CH_3COOCH_2CH_2CH(C_2H_5)CH_2COOH$	190	188	109 (0.5)	1.0572	1.4394	46.86	47.27	57.48	8.27	57.43	8.57
2	$CH_3COOCH_2CH_2CH(C_6H_{13})CH_2COOH$	230	230	139 (0.5)	1.0070	1.4486	60.96	61.21	62.39	9.32	62.58	9.63
3	$CH_3COOCH_2CH_2CH(C_6H_{13})CH_2COOCH_3$	238	244	89 (1)	1.0037	1.4420	61.49	61.31	62.58	9.78	62.58	9.63
4	$CH_3COOCH_2CH_2CH(C_2H_5)CH_2CH_2COOH$	208	202	118 (0.5)	1.0365	1.4460	51.92	51.92	59.10	8.88	59.38	8.98
5	$CH_3COOCH_2CH_2CH(C_6H_{13})CH_2CH_2COOH$	246	244	149 (1)	1.0036	1.4483	65.60	65.86	64.20	10.41	63.90	9.90
6	$HCOOCH_2CH_2CH(C_8H_{17})CH_2CH_2COOH$	271	272	113 (0.5)	0.9652	1.4407	70.06	75.26	66.38	10.68	66.13	10.36

* Molecular weight determined by the ebullioscopic method.

Preparation of α-alkyl γ- and δ-lactones (experiments 7-12). A weighed portion (15-30 g) of γ-(δ-) acetoxycarboxylic acid or its methyl ester was boiled for 4-6 h with a 5-7-fold molar excess of 25% aqueous NaOH solution. The reaction mixture was then treated with conc. HCl until the medium was strongly acidic and was boiled for another ~30 min in experiments 7-9, and for 4 h in experiments 10-12. The organic layer was separated from the aqueous layer; the aqueous layer was extracted with ether; the organic layer and the ethereal extracts from the aqueous layer were combined and dried over Na_2SO_4 in experiments 7 and 8, and by azeotropic removal of water with benzene in the remaining experiments. After removal of ether and benzene, the residue was distilled in vacuo. From δ-hydroxy acids, along with the formation of lactones, formation of polycondensation products also occurred; however, upon heating

during distillation (a wide temperature interval of boiling), the polymer slowly decomposed with liberation of δ-lactone. At the same time, the hydroxy acid that had not entered into the reaction also distilled over; it was then washed with 10% sodium carbonate solution, and the resulting α-alkyl-δ-lactone was distilled again. The yields of lactones are given in Table 3. Judging from the titration results, the δ-lactones contain a small impurity (~3%) of acids.

N. D. Zelinsky Institute of Organic Chemistry
Academy of Sciences of the USSR

Received
12 II 1961

REFERENCES CITED

1. V. Rothstein, Bull. Soc. chim. France, 2, 80 (1935).
2. J. Braun, Ber., 70, 1250 (1939).
3. L. Ruzicka, Helv. chem. acta, 26, 673 (1943).
4. A. D. Petrov, G. I. Nikishin, Yu. N. Ogibin, DAN, 131, 580 (1960).
5. A. J. Vogel, W. T. Greswell, G. J. Jeffery, J. Leicester, J. Chem. Soc., 1952, 514; J. Phys. Chem., 58, 174 (1954).

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