ADDITION OF TETRAHYDROFURAN TO UNSATURATED ACIDS

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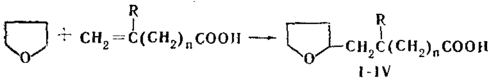
UDC 547.722

The corresponding tetrahydrofurancarboxylic acids were obtained in yields of 25 to 33% by the addition of tetrahydrofuran to acrylic, methacrylic, allylacetic, and undecylenic acids in the presence of tert-butyl peroxide at 200-300 deg C under pressure.

The addition of tetrahydrofuran to a number of unsaturated acids (acrylic, methacrylic, allylacetic, and undecylenic) in the presence of tert-butyl peroxide was investigated in order to synthesize tetrahydrofurancarboxylic acids, which are possible growth stimulators for cotton plants.



I-IV

I n=0, R=H; II n=0, R=CH$_3$; III n=2, R=H; IV n=8, R=H

The study was based on the results of well-known investigations of the alkylation of tetrahydrofuran and other cyclic ethers with olefins [1, 2] and on data on the free-radical addition to unsaturated acids and their derivatives of compounds with a labile hydrogen atom [3, 4].

We have previously accomplished the addition of tetrahydrofuran and dioxane to acrylonitrile [5]. The reaction with unsaturated acids was carried out under similar conditions by heating a mixture of the reagents in a 3-liter steel autoclave. The effect of various factors on the yields of tetrahydrofurancarboxylic acids and on the conversion of the unsaturated acids was investigated. The results are presented in Table 1. It is apparent from Table 1 that the reaction proceeds best at 300 deg; the tetrahydrofuran ring is cleaved at 350 deg; at 200 deg the yield of products decreased; and, while the reaction can be carried out at 300 deg without an initiator, an initiator is required at lower temperatures.

TABLE 1. Carboxyalkylation of Tetrahydrofuran by Unsaturated Acids

Expt. No.	Starting acid	Exptl. conditions			Yield of I-IV, %	
		tetrahydrofuran : acid : tert-butyl peroxide	temp., °C	time, h	based on all of the starting acid	based on acid entering into the reaction
1	Acrylic	100 : 1	300	3	17	
2	The same	100 : 1 : 0,12	300	2	30	
3	" "	100 : 1 : 0,12	300	6	30	
4	" "	60 : 1 : 0,1	300	2	20	
5	" "	100 : 1 : 0,12	300	3	25	
6	Methacrylic	100 : 1	300	3	25	
7	The same	100 : 1 : 0,12	300	3	25	
8	" "	100 : 1 : 0,12	300	6	25	
9	Allylacetic	100 : 1 : 0,1	300	3	30	
10	The same	100 : 1 : 0,1	200	4	20	
11	" "	100 : 1	300	3	25	
12	" "	75 : 1 : 0,1	200	2	9	
13	Undecylenic	100 : 1 : 0,12	300	3	18	70
14	The same	50 : 1 : 0,12	300	3	26	48
15	" "	50 : 1 : 0,12	300	1	26	56
16	" "	50 : 1 : 0,12	300	6	33	67
17	" "	100 : 1	300	1	—	—

Institute of the Chemistry of Plant Substances, Academy of Sciences of the Uzbek SSR, Tashkent. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 2, pp. 147-149, February, 1971. Original article submitted July 25, 1969.

Dilution of the reaction mixture with tetrahydrofuran, particularly in the case of the readily polymerized acrylic and methacrylic acids, has a great effect on the course of the addition; a tetrahydrofuran:unsaturated acid ratio of 100:1 (experiments 2, 3, 7, and 8) was most suitable for them. This ratio may be less with undecylenic acid (experiment 15). It should be noted that part of the starting acids, particularly in the case of allylacetic and undecylenic acids, is recovered unchanged, and changing the reaction conditions does not result in a decrease in their conversion. The maximum yields of the tetrahydrofurancarboxylic acids is 25-30%.

The acids obtained were investigated by IR, NMR, and mass spectroscopic methods.

EXPERIMENTAL

Tetrahydrofuran, the unsaturated acid, and tert-butyl peroxide were charged in an autoclave and heated for 1-6 h. The excess starting materials were removed by distillation, and the residue was vacuum-distilled.

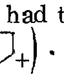
The crude fractions obtained were treated with an ether solution of diazomethane and analyzed by gas-liquid chromatography with a "Shimadzu-GC2B" chromatograph; the column was 2 m long and 4 mm in diameter; the mobile phase was neopentylsuccinate (5%) and polyethylene glycol adipate (1%) on TND–TS–M brick. The column temperature was 190-200 deg, and the hydrogen flow-rate was 20-50 ml min. The purity of the products (70-90% acid) was determined from the gas-liquid chromatographic data, and the yields were calculated from theory. The chief impurities were the products of polymerization of the unsaturated acids (usually dimers) and products of transformation of tetrahydrofuran.

Acids I-IV were isolated and purified repeatedly by reprecipitation from saturated sodium bicarbonate solutions. The IR spectra (obtained with a UR-10 spectrometer) contained absorption bands of the C–O–C grouping of the ring (1070–1085–1180 cm^{-1}) and of the carbonyl groups (1720–1735 cm^{-1}).

The NMR spectra were obtained with a JNM-4H-100 spectrometer with an operating frequency of 100 MHz with CCl_4 as the solvent (10% solution) and hexamethyldisiloxane as the standard.

3-(Tetrahydrofuryl) propionic Acid (I). This was obtained as a colorless liquid with bp 125 deg (5 mm), n_D^{23} 1.4582 (bp 123-124 deg (5 mm), n_D^{22} 1.4480 [6, 7]), and mol. wt. (Rast) 150.8 (calc. 144); it was identified by superimposition of the IR spectra of the synthesized and model samples.

2-Methyl-3-(tetrahydrofuryl)propionic Acid (II). This compound had bp 136 deg (2 mm), d_4^{20} 1.078, and n_D^{20} 1.4550. Found %: C 60.40; H 9.23; MR 39.99. $C_8H_{14}O_3$. Calc. %: C 60.76; H 8.86; MR 40.66. NMR spectra (ppm, ρ scale): doublet centered at 8.8 (CH_3 protons), multiplets centered at 6.25 and 8.1 (α- and β-protons of the tetrahydrofuran ring), multiplets centered at 8.5 and 7.5 (CH_2 and side-chain CH protons), and a singlet at 10.26 (COOH proton).

5-(Tetrahydrofuryl)valeric Acid (III). This compound had bp 148 deg (2 mm), n_D^{20} 1.4640, and d_4^{20} 1.063. Found %: C 63.08; H 9.53; MR 44.49. $C_9H_{16}O_3$. Calc. %: C 62.79; H 9.30; MR 45.13. The mass spectrum of the methyl ester of III (obtained with an MKh-1303 spectrometer) had the following ion peaks (m/e): 186 (M^+), 113 $(M-CH_2COOCH_3)^+$, 85 $(M-CH_2CH_2CH_2COOCH_3)^+$, 71 () . NMR spectrum: 6.1-6.4 (α-protons of the ring and protons of the α-CH_2 group with respect to the ring), 7.7-8 (β-protons of the ring, unresolved multiplet), 8-8.9 (protons of the side chain), 10.64 (carboxyl proton).

11-(Tetrahydrofuryl)undecylenic Acid (IV). This was obtained as white needles with mp 59 deg (ether). Found %: C 69.95; H 11.2. $C_{15}H_{28}O_3$. Calc. %: C 70.31; H 10.93. The NMR spectrum contains the same signals as the NMR spectrum of III. The mass spectrum of the methyl ester contains the following ion peaks (m/e): 270 (M^+), 242 $(M-C_2H_4)^+$, 227 $(M-C_3H_7)^+$, 197 $(M-CH_2COOCH_3)^+$, 185, 166, 124, 85, and 71, metastable ions (235.2* = 270→252; 207.5* = 242→224; 167.5* = 227→195, etc.).

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