SovietRxiv

Soviet-era science, translated into English

Corresponding Member of the Academy of Sciences of the USSR R. Kh. FREIDLINA, S. N. AMINOV,

A. B. TERENT' EV

1964

SovietRxiv

View the original and related papers at https://sovietrxiv.org/items/ru-196401.56645

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.

SovietRxiv

Abstract

Full Text

CHEMISTRY

Corresponding Member of the Academy of Sciences of the USSR R. Kh. FREIDLINA, S. N. AMINOV,
A. B. TERENT' EV

REARRANGEMENT OF RADICALS IN THE PROCESS OF TELOMERIZATION OF ETHYLENE WITH ACETIC ACID

The telomerization of ethylene with acetic acid is of interest as a route to the synthesis of saturated carboxylic acids of an even-numbered series. This reaction has been mentioned only in a patent (^1). The patent describes an experiment in carrying out this reaction in the presence of tert-butyl peroxide at 145° and a pressure of 57 atm; a mixture of liquid acids was obtained, from which fractions corresponding to butyric, caproic, a mixture of caprylic and isooctanoic acids, and capric and isodecanoic acids were isolated. Determination of the acid numbers showed that the fractions obtained contained from 66 to 90% of the indicated acids. The structure of the iso acids was not established, and the yields of the individual fractions were not reported.

We initiated the telomerization of ethylene with glacial acetic acid by heating with tert-butyl peroxide at 140° and a pressure of 15–40 atm. Under these conditions, in four hours the conversion of acetic acid did not exceed 2%. Such a low conversion excluded the possibility of initiation of the reaction of ethylene with acids formed in the telomerization process. On distillation of the reaction mixture in vacuo, fractions of acids containing up to 10 carbon atoms in the molecule were obtained, together with a residue containing higher acids. The fractions were analyzed by gas–liquid chromatography (GLC). The data obtained are summarized in Tables 1 and 2. It turned out that the distilled fractions contained only the following acids: butyric, caproic, caprylic, one isooctanoic acid, capric, and one isodecanoic acid; moreover, the yield of iso acids was considerably greater than the yield of normal acids with the same number of carbon atoms in the molecule. It is of interest to emphasize the practical absence of isohexanoic acid among the reaction products. By repeated distillation of the higher fractions, both isooctanoic and isodecanoic acids were isolated in nearly pure form. The first of these acids proved to be α-ethylcaproic acid; it was identified with an authentic acid by GLC and by determination of the melting point of a mixed sample of benzylisothiuronium salts obtained from both acid samples. Authentic α-ethylcaproic acid was obtained by oxidation of 2-ethylhexanol.

Isodecanoic acid was identified with authentic α, n-butylcaproic acid by GLC;

SovietRxiv

the latter acid was obtained by the reaction of caproic acid with butene-1, initiated by tert-butyl peroxide.

For the telomerization of ethylene with acids, the following scheme has been proposed (^1):

$$[(CH_3)_3CO]_2 \rightarrow 2(CH_3)_3CO\cdot;$$

$$RCH_2COOH + (CH_3)_3CO\cdot \rightarrow R\dot{C}HCOOH + (CH_3)_3COH,$$

$$R\dot{C}HCOOH + n(CH_2CH_2) \rightarrow \dot{C}H_2CH_2(CH_2CH_2)_{n-1}CHRCOOH,$$

$$\dot{C}H_2CH_2(CH_2CH_2)_{n-1}CHRCOOH + RCH_2COOH \rightarrow$$

$$\rightarrow CH_3CH_2(CH_2CH_2)_{n-1}CHRCOOH + R\dot{C}HCOOH.$$

This scheme well describes the formation from acetic acid (R = H) of carboxylic acids of normal structure. The formation of α-ethylcaproic

and α, n-butylcaproic acids by the interaction of ethylene with caproic acid according to this scheme in the present case, as it seems to us, is excluded not only because of the low concentration ($< 1\%$) of caproic acid in the solution, but also because the yield of isooctanoic acid is greater than the yield of caproic acid, which requires the assumption of an improbably large conversion of caproic acid; moreover, by this mechanism isohexanoic acid should also have been formed by the reaction of ethylene with butyric acid, which is not confirmed by experiment. We assume that the formation of α-ethylcaproic and α, n-butylcaproic acids is a consequence of rearrangement of the primary radicals A into the more stable secondary radicals B with 1–5 migration of a hydrogen atom according to the scheme:

$$\dot{C}H_2(CH_2)_3CH_2CO_2H\ (A) \rightarrow CH_3(CH_2)_3\dot{C}HCO_2H\ (B).$$

The practical absence of isohexanoic acid in the reaction mixture shows that under our conditions the radicals $\dot{C}H_2CH_2CH_2CO_2H$ (B) do not undergo rearrangement. This difference in the behavior of radicals A and B is probably connected with the possibility, in the case of A, of achieving a conformation favorable for rearrangement:

It may be thought that rearrangement of radicals in the process of telomerization of ethylene with ineffective telogens at a sufficiently high temperature must play an important role.

SovietRxiv

schematic conformation showing HOOC, H, and CH2 groups connected by a dashed H-transfer line

Figure 1: schematic conformation showing HOOC, H, and CH2 groups connected by a dashed H-transfer line

An analogous rearrangement was proposed to explain the formation of isomeric alkyltrichlorosilanes during the thermal telomerization of ethylene with trichlorosilane ([2]). For a review of the literature on 1,5 migration of hydrogen in radicals, see ([3]).

Experimental Part

Telomerization of ethylene with acetic acid.

The experiments were carried out in a half-liter enamelled rocking autoclave with a jacket for heating by liquid from a thermostat, at a temperature of 140°. The ratio of the starting products and some results of the experiments are given in Tables 1 and 2.

Table 1

No. of experiment	Loaded, mol: acetic acid	Loaded, mol: tert-butyl peroxide	Ethylene pressure, atm	Consumption: ethylene, mol	Consumption: acetic acid, mol	Consumption: acetic acid, mol per mol peroxide	Consumption: ethylene, mol per mol acid	Conversion of acetic acid, %
1	5	0.055	15	0.40	0.10	1.8	4	2.0
2	5	0.055	30	0.64	0.08	1.4	8	1.6
3	5	0.055	40	0.80	0.10	1.8	8	2.0
4	5	0.027	40	0.50	0.06	2.2	8	1.2
5	5	0.027	30	0.46	0.07	2.5	7	1.4

The pressure in all experiments was maintained constant by introducing ethylene as it was absorbed. The end of the reaction was determined by the cessation of ethylene absorption.

Acetic acid and low-boiling products were distilled off from the liquid reaction mixture, and the residue was fractionated: fraction I: 90-130° (50 mm); fraction II: 130° (50 mm)–125° (13 mm); fraction III: 125° (13 mm)–150° (10 mm); residue $> 150^{\circ}$ (10 mm).

SovietRxiv

Analysis of the telomers in each fraction was carried out by gas-liquid chromatography. For analysis of the fatty acids, a chromatograph with a flame-ionization detector was used. For quantitative calcu-

To take into account the composition of the mixture of telomers, calibration had first been carried out and correction factors for each telomer relative to the standard substance (reference), valeric acid, were found.

In each analysis a definite amount of the reference was added to a weighed portion of the fraction, after which the correction factors taken from the graphs were introduced into the calculation of the chromatogram. The results of the quantitative determination are given in Table 2.

Table 2

Amount of acid (in percent) of the sum of the reaction products

Experiment Nos.	Butyric	Caproic	Isooctanoic	Caprylic	Isodecanoic	Capric	Higher acids
1	7.5	6	12	traces	7	traces	67
2	6.7	6	10	2.5	6	4	66
3	3.0	5	6	2	4	6	73
4	2.0	4	6	4	8.5	4	75
5	4.0	6	13	4	8	4	61

Identification of the telomers was carried out by retention time. The results are given in Table 3.

From the second fraction of the telomerization product a substance was isolated with b.p. 120° (13 mm); n_D^{20} 1.4290, d_4^{20} 0.9014. Found MR 41.24; for $C_8H_{16}O_2$ calculated MR 40.68. According to the literature data ([4]), for α-ethylcaproic acid: b.p. 120° (13 mm); n_D^{25} 1.4229, d_4^{25} 0.9031. The S-benzylisothiuronium salt of this product was obtained, m.p. 127–128°, which gave no melting-point depression in a mixed sample with an authentic specimen of the S-benzylisothiuronium salt of α-ethylcaproic acid.

Found, %: C 61.85, 62.00; H 8.41, 8.59

$C_{16}H_{26}N_2O_2S$. Calculated, %: C 61.90; H 8.44

Authentic α-ethylcaproic acid was synthesized by oxidation of 39 g (0.3 mole) of 2-ethylhexanol with 63 g (0.4 mole) of $KMnO_4$ in acetone;

Table 3*

SovietRxiv

Substance tested	Substance tested	Temperature, °C	Gas flow rate, l/h	Retention time	Retention time
from experiment	authentic			from experiment	authentic
Butyric	Butyric	125	0.5	1 min 23 s	1 min 22 s
—	Valerianic	125	0.5	—	2 min 11 s
Caproic	Caproic	125	0.5	3 min 06 s	3 min 05 s
Isooctanoic	α-Ethylcaproic	150	0.5	1 min 36 s	1 min 36 s
Caprylic	Caprylic	150	0.5	1 min 55 s	1 min 59 s
Isodecanoic	α-*n*-Butylcaproic	150	0.5	2 min 17 s	2 min 17 s
Capric	Capric	150	0.5	3 min 53 s	4 min 01 s

* Glass column 2 m long; solid phase—glass; stationary phase—silicone elastomer, 0.2%; carrier gas—nitrogen.

23 g (53% of theory) of product was obtained, b.p. 120-121° (13 mm); n_D^{20} 1.4260, d_4^{20} 0.9067; found MR 40.75; for $C_8H_{16}O_2$, calculated MR 40.68.

From the third fraction of the telomerization products a substance was isolated with b.p. 137-138° (12 mm); n_D^{20} 1.4459, d_4^{20} 0.9216; found MR 49.84; for $C_{10}H_{20}O_2$, calculated 49.22. Literature data for α-*n*-butylcaproic acid ([5]): b.p. 137 (12 mm); n_D^{20} 1.4330, d_4^{20} 0.8848.

Found, %: C 70.13, 70.24; H 11.25, 11.24

$C_{10}H_{20}O_2$. Calculated, %: C 69.72; H 11.70

The product obtained is identical, by GLC, with authentic α, n-butylcaproic acid.

Investigation of the high-boiling products of the telomerization reaction. The undistilled residues from a number of experiments were combined. The product is readily soluble in alkalis and in petroleum ether. The acid number is 210; the average molecular weight, calculated on the basis of the acid number obtained, is 263. Elemental analysis of the residue shows that there are 2 oxygen atoms per 16-18 carbon atoms; i.e., the residue consists mainly of monocarboxylic acids with an average number of carbon atoms of 16-18, which is also confirmed by the average molecular weight found for the residue. The IR spectrum showed the absence of compounds containing a double bond.

SovietRxiv

Institute of Organoelement Compounds
Academy of Sciences of the USSR

Received
11 III 1964

REFERENCES

1. F. W. Banes, Wm. Fitz Gerald, I. F. Nelson, U.S. Pat. 2 585 723; Chem. Abstr. **47**, 9767 (1953).

2. R. Kh. Freidlina, Yu. P. Egorov et al., Izv. AN SSSR, OKhN, 1961, 1256.

3. R. Kh. Freidlina, V. N. Kost, M. Ya. Khorlina, Usp. khim., **31**, 3 (1962).

4. Chem. Abstr. **30**, 8177 (1936).

5. Chem. Abstr. **49**, 5281 (1955).

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

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.