6-Benzal-2-phenylcyclohexanone was cyanoethylated and also converted into a Mannich base.

The preparation of 2-phenyl-2-cyclohexenone is described.

Six Mannich salts were prepared from four 2-arylcyclohexanones. The Mannich base from 2-phenylcyclohexanone was converted into 2-oxo-3-phenylcyclohexanepropionic acid, which was synthesized also by another method.

ANN ARBOR, MICH. RECEIVED JANUARY 23, 1950

[CONTRIBUTION NO. 272 FROM THE CHEMICAL DEPARTMENT, EXPERIMENTAL STATION, E. I. DU PONT DE NEMOURS AND COMPANY]

Synthesis of 2,2-Dimethylalkanoic Acids from Ethylene

BY DONALD D. COFFMAN AND J. R. ROLAND

The free radical-initiated polymerization of styrene in the presence of carbon tetrachloride has been found to yield products presumed to be terminated by $-Cl$ and $-CCl_3$ end-groups.[1] Also, the polymerization of ethylene in the presence of halogenated methanes has been described. Carbon tetrachloride as a chain transfer agent gave a series of $\alpha,\alpha,\alpha,\omega$-tetrachloroalkanes, $Cl(CH_2CH_2)_nCCl_3$, among which members having n values of 1 to 4, inclusive, have been identified.[2] Chloroform gave the α,α,α-trichloroalkanes, $H(CH_2CH_2)_nCCl_3$, ranging in n values from 1 to 6.[3]

This type of free radical-initiated reaction has now been extended to the synthesis of 2,2-dimethylalkanoic acids from ethylene and isobutyric acid. The reaction proceeds smoothly without perceptible formation of products other than the mixed carboxylic acids. This is the first known example of a chain reaction in which an alkanoic acid as transfer agent has been utilized with ethylene to obtain a family of carboxylic acids the identities of which indicate the course of reaction.

The reaction of ethylene with isobutyric acid has been brought about under a variety of conditions. It proceeds readily at 250° with benzalazine catalyst, employing high pressures of ethylene containing up to 100 parts per million of oxygen. At lower concentrations (*e. g.*, 2–5 ppm.), oxygen alone also induced the reaction. The structure of the products was demonstrated to be that of 2,2-dimethylalkanoic acids, $H(CH_2CH_2)_nC(CH_3)_2COOH$, by the identification of 2,2-dimethylbutanoic acid (6–13%), 2,2-dimethylhexanoic acid (4–8%), 2,2-dimethyloctanoic acid (3–5%) and 2,2-dimethyldecanoic acid (2%) isolated in the proportions indicated from the reaction of 200 g. of isobutyric acid with ethylene at 700 atm. pressure. The proportions of the individual dimethylalkanoic acids that comprise the whole product depend on the concentration of ethylene relative to that of isobutyric acid, and are subject to some control by adjustment in the ethylene pressure or the amount of isobutyric acid employed. Mixtures of acids having neutral equivalents from 132 to 728 have been prepared in this way. The low iodine numbers (less than 4) indicate the nearly complete absence of higher olefinic products.

It appears likely that the 2,2-dimethylalkanoic acids originate by the following mechanism in which R· is the initiating free radical.

$$(1)\quad R\cdot + HC(CH_3)_2COOH \longrightarrow RH + \cdot C(CH_3)_2COOH$$

$$(2)\quad \cdot C(CH_3)_2COOH + C_2H_4 \longrightarrow HOOCC(CH_3)_2(CH_2CH_2)\cdot$$

$$(3)\quad HOOCC(CH_3)_2(CH_2CH_2)\cdot + nC_2H_4 \longrightarrow HOOCC(CH_3)_2(CH_2CH_2)^{\cdot}_{n+1}$$

$$(4)\quad HOOCC(CH_3)_2(CH_2CH_2)^{\cdot}_{n+1} + HC(CH_3)_2COOH \longrightarrow HOOCC(CH_3)_2(CH_2CH_2)_{n+1}H + \cdot C(CH_3)_2COOH$$

This is analogous to the mechanism proposed by Joyce[2] and Kharasch[4] for the synthesis of α,α,α-trichloroalkanes.

Experimental

Reaction of Ethylene with Isobutyric Acid.[5]—A silver-lined pressure vessel of 400-ml. capacity was purged with nitrogen and charged with 200 g. of isobutyric acid. The vessel was closed, evacuated, and connected to a reservoir of ethylene containing 2–5 parts per million of oxygen. Ethylene at 300 atm. pressure was introduced, and the tube and its contents were heated and agitated. During a reaction time of fourteen hours, the temperature was maintained at 247–251° and the pressure at 850–980 atm. by periodic addition of ethylene. The cumulative absorption of ethylene amounted to 735 atm. After cooling the vessel to room temperature, the pressure was released, the vessel was opened, and the contents discharged. Distillation of this reaction mixture gave 155 g. of isobutyric acid and 64 g. of alkali-soluble higher boiling acids. The mixed monobasic acids had a neutral equivalent of 328. The iodine number was 2.9, and the molecular weight determined ebullioscopically was 364.

By operation in the foregoing manner employing benzalazine catalyst (0.2 g.) and ethylene containing about 10 parts per million of oxygen, a series of reactions were carried out under different conditions of pressure and temperature with various ratios of reactants in order to determine the effects of these variables. As shown in Table I,

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(1) (a) Price, *Ann. N. Y., Acad. Sci.*, **44**, 351 (1943); (b) Suess, Pilch and Rudorfer, *Z. physik. Chem.*, **A179**, 361 (1937); **A181**, 81 (1937); (c) Breitenbach, Springer and Abrahamczik, *Oesterr. Chem. Ztg.*, **41**, 182 (1938); (d) Springer, *Kautschuk*, **14**, 212 (1938); (e) Breitenbach and Maschin, *Z. physik. Chem.*, **A187**, 175 (1940).

(2) Joyce, Hanford and Harman, THIS JOURNAL, **70**, 2529 (1948).

(3) Harmon, Ford, Hanford and Joyce, *ibid.*, **72**, 2213 (1950).

(4) Kharasch, Jensen and Urry, *ibid.*, **69**, 1100 (1947).

(5) Roland and Harmon, U. S. Patent 2,433,015 (December 23, 1947); Coffman, U. S. Patent 2,433,016 (December 23, 1947).

the neutral equivalents of the products formed at 250° increased with increasing pressure and with increasing ratios of ethylene to isobutyric acid charged.

TABLE I

VARIABLES IN THE REACTION OF ETHYLENE WITH ISOBUTYRIC ACID

Isobutyric acid, g.	Pressure, atm.	Temp., °C.	Wt. ratio, ethylene/acid	Product g.	Product Neut. equiv.
200	200–300	250	0.37	114	137
200	500–600	250	0.37	43	280
200	850–950	250	0.37	133	(346)[a]
200	850–950	265	0.37	102	290
200	850–950	275	0.37	114	278
100	850–950	250	1.12	97	728
300	850–950	250	0.12	53	132

[a] Calcd. from the neutral equivalents and weights of fractions listed in Table II.

TABLE II

MOLECULAR WEIGHT DISTRIBUTION OF ACIDS FORMED IN THE REACTION OF ETHYLENE WITH ISOBUTYRIC ACID

Fraction no.	Temp., °C.	Pressure, mm.	Weight, g.	Neutral equiv.	Average no. C's	% of product
1	50–68	12	132[a]	..	..	..
2	77–117	14	13.3	141	7.8	10.2
3	123–143	14	12.4	174	10.2	9.3
4	126–158	3.5	15.5	221	13.5	11.7
5	150–160	1.5	12.3	287	18.2	9.3
6	160–175	1.25	6.1	323	20.8	4.6
7	184–202	0.5–0.75	7.7	359	23.4	5.8
8	202–225	0.75–1.0	7.9	426	28.1	5.9
Residue	.....	....	57.4	1237	88	43.2

[a] Recovered isobutyric acid.

TABLE III

Properties of 2,2-dimethylalkanoic acids, $H(CH_2CH_2)_nC(CH_3)_2COOH$, and their derivatives

n	B. p. of acid °C.	B. p. of acid Mm.	B. p. of acid chloride, °C.	M. p. of anilide, °C.	M. p. of amide, °C.	N Analyses of amides $H(CH_2CH_2)_nC(CH_3)_2CONH_2$ Formula	Calcd.	Found
1	184–185[a]		131–134[b]	90.5–91[d]	101.5–102[c]	$C_6H_{13}ON$	12.15	11.79
2	119–122	18[e]	176–178[f]	88	92–92.5[g]	$C_8H_{17}ON$	9.77	9.51
3	139–141.5	13	210–212[h]	66.5–67	102.5–103[i]	$C_{10}H_{12}ON$	8.17	7.89
4	....	...	139 (24)	35–40[j]	87–88	$C_{12}H_{25}ON$	7.03	6.81

[a] Wyschenegradsky, *Ann.*, **174**, 561 (1874) gives 187°. Haller, *Compt. rend.*, **148**, 127 (1909) gives 184–185°. [b] Wyschenegradsky, *Ann.*, **178**, 105 (1875) gives 132°. [c] Haller, *Compt. rend.*, **148**, 129 (1909) gives 103–104°. [d] Hommelen, *Bull. soc. chim. Belg.*, **42**, 243 (1933), gives 91.4°. [e] Meerwein, *Ann.*, **419**, 149 (1919) gives 120–122° (15 mm.). [f] 76–77° (25 mm.); Locquin, *Compt. rend.*, **178**, 2097 (1924) gives 55° (10 mm.). [g] Locquin, *ibid.*, gives 92°. [h] 108–109° (23 mm.); 115–117° (30 mm.). [i] Buu-Hoi and Cagniant, *Rec. trav. chim.*, **45**, 246 (1946), gives 103°. [j] This anilide was analyzed. Calcd. for $C_{18}H_{29}ON$: N, 5.08. Found: N, 5.21.

Molecular Weight Distribution of Mixed Acids.—The molecular weight distribution of the products synthesized in a typical run is indicated in Table II. These data are based on the neutral equivalents of products obtained by fractional distillation of the mixed acids prepared at 250° and 850–950 atm. employing 200 g. of isobutyric acid and 0.2 g. of benzalazine catalyst. About half of the product distilled at pressures of 0.5–14 mm. and comprised 2,2-dimethylalkanoic acids ranging in average chain length from C_8 to about C_{28}.

The Identity of the Acids Synthesized.—In order to provide a supply of the lower mixed 2,2-dimethylalkanoic acids for characterization, the synthesis was carried out in a bomb at autogenous pressure. The silver-lined pressure vessel of 400-ml. capacity was swept with nitrogen, and charged with 200 g. of isobutyric acid. The reactor was closed, evacuated and charged with 75 g. of ethylene containing about 5 parts per million of oxygen. When agitated and heated at 275°, the reactor was under an initial pressure of 700 atm. During the eighteen hours, the pressure dropped to 90 atm. The vessel was cooled, the pressure released, and the contents (219 g.) discharged. Distillation of the reaction mixture through a column packed with Fenske rings gave 113 g. of isobutyric acid and 104 g. of higher acids. During distillation some degradation occurred. A rough separation of a composite of acids obtained in this manner showed the mixture to contain 13% 2,2-dimethylbutanoic acid, 8.4% 2,2-dimethylhexanoic acid, 4.8% 2,2-dimethyloctanoic acid and 2.2% 2,2-dimethyldecanoic acid. A composite of these acids was converted to the acyl chlorides by reaction with a slight excess of thionyl chloride at room temperature. The mixture of acyl chlorides was separated into its individual components by distillation employing a 1 × 30″ column packed with Fenske rings and a reflux ratio of 20:1. The following were taken as pure compounds: 2,2-dimethylbutanoyl chloride, b. p. 131–134°; 2,2-dimethylhexanoyl chloride, b. p. 76–77° (25 mm.); 2,2-dimethyloctanoyl chloride, b. p. 108–109° (23 mm.); and 2,2-dimethyldecanoyl chloride, b. p. 139° (24 mm.).

The acid chlorides were converted to their corresponding amides and anilides for identification. The amides were prepared[6] by adding the chlorides to ice-cold, concentrated ammonia. The product was filtered and recrystallized from ethanol. The anilides were obtained by treating the acid chlorides with a benzene solution of freshly distilled aniline. The benzene solution was extracted in turn with water, dilute aqueous hydrochloric acid, 5% aqueous sodium hydroxide solution, water and was then evaporated to dryness. The anilides were recrystallized from ethanol. The data which confirm the identity of these products are listed in Table III.

Acknowledgment.—The authors are indebted to Dr. H. S. Rothrock and Dr. J. Harmon for suggestions and to Mr. H. S. Young and staff for supervision of the experiments carried out at high pressure.

Summary

The free radical-initiated reaction of ethylene with isobutyric acid at elevated temperatures and pressures yields a mixture of 2,2-dimethylalkanoic acids. This is believed to be the first example of a chain reaction in which an alkanoic acid as transfer agent and ethylene have given a series of acids that clearly demonstrate a chain transfer mechanism.

WILMINGTON, DEL. RECEIVED NOVEMBER 16, 1949

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[6] Shriner and Fuson, "Identification of Organic Compounds," 2nd ed., John Wiley and Sons, Inc., New York, N. Y., 1940, p. 132.