TABLE II

4-ALKEN-1-OLS, R—CH=CH—$CH_2$—$CH_2$—$CH_2OH$

| R group | B. p., °C. (760 mm.) | $d^{20}_4$ | $n^{20}_D$ | Yield,[a] % | Over-all[b] yield, % | Carbon, % Calcd. | Carbon, % Found | Hydrogen, % Calcd. | Hydrogen, % Found |
|---|---|---|---|---|---|---|---|---|---|
| Methyl | 159.0–159.4 | 0.8513 | 1.4407 | 45 | 30 | 71.95 | 71.28 | 12.07 | 12.01 |
| Ethyl | 176.0–176.4 | .8452 | 1.4433 | 29 | 16 | 73.64 | 73.22 | 12.35 | 12.30 |
| *n*-Propyl | 194.1–194.6 | .8452 | 1.4460 | 36 | 18 | 74.94 | 74.36 | 12.57 | 12.58 |
| *n*-Butyl | 211.9–212.2 | .8454 | 1.4478 | 60 | 26 | 75.99 | 75.83 | 12.76 | 12.78 |
| *n*-Amyl | 228.0–228.5 | .8433 | 1.4499 | 60 | 22 | 76.86 | 77.04 | 12.90 | 12.77 |
| Isopropyl | 185.8–186.3 | .8365 | 1.4419 | 20 | 5 | 74.94 | 74.40 | 12.57 | 12.56 |
| Isobutyl | 203.5–204.0 | .8426 | 1.4454 | 59 | 19 | 75.99 | 75.65 | 12.76 | 12.61 |
| Isoamyl | 220.0–221.0 | .8445 | 1.4492 | 67 | 23 | 76.86 | 76.72 | 12.90 | 12.69 |

[a] From 2-alkyl-3-bromotetrahydropyrans. [b] From 3,4-dihydro-1,2-pyran.

the β-bromoether was added at such a rate as to maintain gentle reflux; in some cases the reaction mixture became very viscous and it was necessary to add more di-isopropyl ether in order to maintain stirring. The reaction mixtures were allowed to stand at room temperature for two days, after which they were hydrolyzed with small portions of cold water (caution). The ether layers were thoroughly washed, dried over lime and fractionated through the same column as were the 2-alkyl-3-bromotetrahydropyrans; the higher boiling alkenols were distilled under reduced pressure. Each of the alkenols was redistilled before the physical properties and yields listed in Table II were determined. The products were colorless liquids having characteristic odors, those of the lower boiling members being stronger and less pleasant.

**Proof of Structure.**—Since all of the alkenols were prepared by the same procedure, two, 4-hexen-1-ol and 4-octen-1-ol, were picked as representative products, and their carbon skeletons were demonstrated by hydrogenation to the corresponding saturated alcohols which are well known.

The procedure followed in hydrogenating 4-hexen-1-ol and 4-octen-1-ol over platinic oxide catalyst has been described in the literature.[8] Absolute alcohol was used as the solvent, and in each case approximately the theoretical amount of hydrogen was absorbed. The hydrogenates were distilled through a 20-cm. Vigreux column to obtain a 78% yield of 1-hexanol (b. p. 155 to 156° (744 mm.)) and an 85% yield of 1-octanol (b. p. 191 to 192° (742 mm.)). The compounds were identified by the melting points of their phenyl urethans and dinitrobenzoates.

To fix the position of the double bond, a sample of 4-hexen-1-ol was treated in the cold with a slight excess of aqueous potassium permanganate. (A similar reaction with this alcohol had been described previously,[9] but no physical properties were given.) The manganese dioxide was removed by filtration and the acidified (sulfuric acid) solution was distilled rapidly. The distillate was neutralized with dilute sodium hydroxide and evaporated to dryness. Gray crystals remained and when treated with concd. sulfuric acid, gave a distinct odor of acetic acid; addition of alcohol to the acidified portion gave the characteristic odor of ethyl acetate. The crystals were identified as sodium acetate by conversion to the corresponding *p*-bromophenacyl ester which melted at 83 to 84° (literature,[10] 85°). Identification of the acetate radical showed that the double bond was, as expected, in the 4-position.

## Summary

A method has been devised whereby unsaturated primary alcohols of more than five carbon atoms can be prepared from the commercially available 3,4-dihydro-1,2-pyran by a new modification of the β-bromoether synthesis of olefins.

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[8] (a) Adams and Vorhees, *Organic Syntheses*, **8**, 10 (1928); (b) Adams, Vorhees and Shriner, *ibid.*, **8**, 92 (1928).

[9] Fischer and Wiedemann, *Ann.*, **522**, 1 (1936).

[10] Judefind and Reid, THIS JOURNAL, **42**, 1048 (1920).

COLUMBUS, OHIO RECEIVED NOVEMBER 23, 1949

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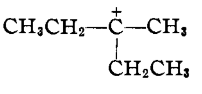
[CONTRIBUTION NO. 270 FROM THE CHEMICAL DEPARTMENT, EXPERIMENTAL STATION, E. I. DU PONT DE NEMOURS & COMPANY]

# Synthesis of Ethyl α-Ethyl-α-methylbutyrate from Ethylene and Carbon Monoxide

BY J. R. ROLAND, J. D. C. WILSON, II, AND W. E. HANFORD[1]

In an exploration of carbon monoxide reactions, ethyl α-ethyl-α-methylbutyrate was the principal and unexpected product obtained from ethylene and carbon monoxide with boron fluoride hydrate catalyst at 115° and 1,000 atmospheres total pressure. This unusual reaction can be explained as proceeding through carbonium ions, and the present paper offers evidence in support of such a mechanism.

From a consideration of the various mechanisms by which this highly branched ester might have been formed, it seemed likely that the precursor of the ester was a carbonium ion that on carboxylation and esterification gave ethyl α-ethyl-α-methylbutyrate. The carbonium ion VI


$$CH_3CH_2—\overset{+}{\underset{\displaystyle CH_2CH_3}{C}}—CH_3 \quad VI$$

may arise from the conversion of ethylene to ethyl carbonium ion by addition of a proton[2] from the boron fluoride hydrate, followed by a sequence of additions to ethylene as represented in equations 1, 2 and 3.

$$(1)\quad C_2H_4 + H^+ \rightleftharpoons CH_3CH_2^+ \qquad I$$

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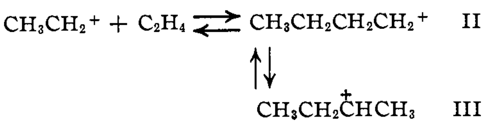
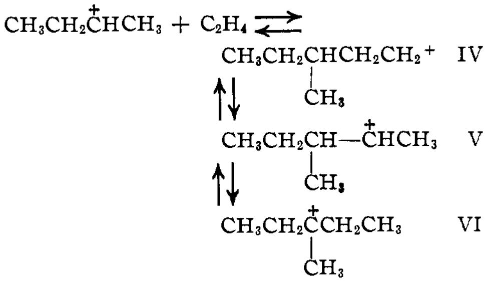
[1] Present address: M. W. Kellogg Company, 225 Broadway, New York 7, N. Y.

[2] Whitmore, *Chem. Eng. News*, **26**, 668 (1948).

(2)


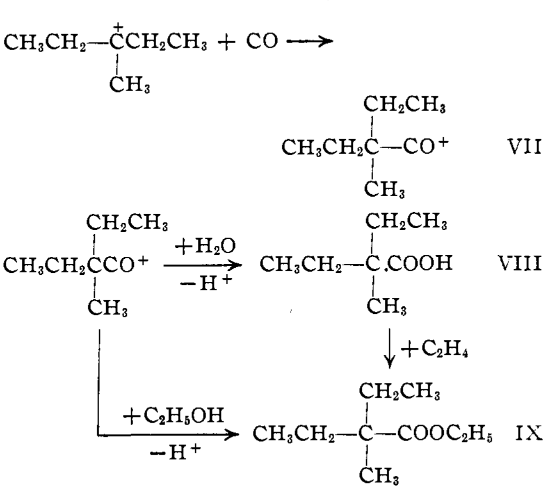
$$\begin{array}{ll} CH_3CH_2^+ + C_2H_4 \rightleftarrows CH_3CH_2CH_2CH_2^+ & II \\ \qquad\qquad\qquad\quad \upharpoonleft\downharpoonright & \\ \qquad\qquad\qquad\quad CH_3CH_2\overset{+}{C}HCH_3 & III \end{array}$$

(3)


$$\begin{array}{ll} CH_3CH_2\overset{+}{C}HCH_3 + C_2H_4 \rightleftarrows & \\ \qquad CH_3CH_2\underset{CH_3}{\underset{|}{C}H}CH_2CH_2^+ & IV \\ \qquad \upharpoonleft\downharpoonright & \\ \qquad CH_3CH_2\underset{CH_3}{\underset{|}{C}H}—\overset{+}{C}HCH_3 & V \\ \qquad \upharpoonleft\downharpoonright & \\ \qquad CH_3CH_2\underset{CH_3}{\underset{|}{\overset{+}{C}}}CH_2CH_3 & VI \end{array}$$

The relatively stable carbonium ion VI can react in turn with carbon monoxide, water, and finally ethylene to form the ester IX (equations 4 and 5).

(4)

(5)


$$CH_3CH_2—\underset{CH_3}{\underset{|}{\overset{+}{C}}}CH_2CH_3 + CO \longrightarrow CH_3CH_2\underset{CH_3}{\underset{|}{\overset{CH_2CH_3}{\overset{|}{C}}}}—CO^+ \quad VII$$

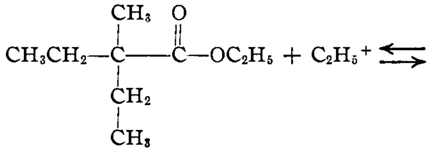
$$CH_3CH_2\underset{CH_3}{\underset{|}{\overset{CH_2CH_3}{\overset{|}{C}}}}CO^+ \xrightarrow[-H^+]{+H_2O} CH_3CH_2—\underset{CH_3}{\underset{|}{\overset{CH_2CH_3}{\overset{|}{C}}}}.COOH \quad VIII$$

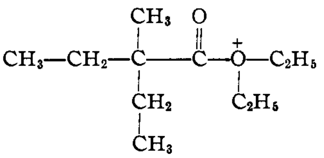
$$\downarrow +C_2H_4$$

$$\xrightarrow[-H^+]{+C_2H_5OH} CH_3CH_2—\underset{CH_3}{\underset{|}{\overset{CH_2CH_3}{\overset{|}{C}}}}—COOC_2H_5 \quad IX$$

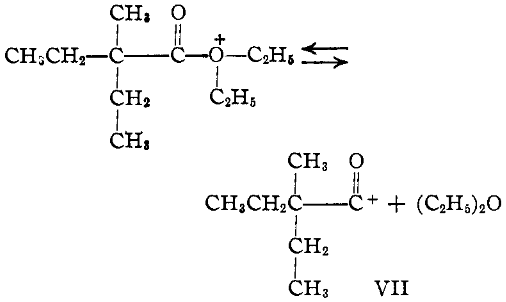
The tendency of the intermediate carbonium ions to satisfy the electron deficiencies of the carbon atoms by rearrangement to stabler forms, *i. e.*, from primary to secondary to tertiary, must be very large since products corresponding to intermediates II, IV, and V were not found. The distillation curve of the reaction mixture showed slight breaks at the boiling points of ethyl propionate and ethyl α-methylbutyrate, which compounds would be obtained from I and III, respectively, by carboxylation and esterification.

The ethyl α-ethyl-α-methylbutyrate was accompanied by an appreciable amount of diethyl ether and partially saponifiable material. Diethyl ether was not formed in the absence of carbon monoxide. It is likely that it originated by reaction of the strongly acidic ethyl carbonium ions with the ester present in the reaction mixture (equations 6 and 7).

(6)




$$CH_3CH_2—\underset{\underset{CH_3}{\underset{|}{CH_2}}}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}——\overset{O}{\overset{\|}{C}}—OC_2H_5 + C_2H_5^+ \rightleftarrows CH_3—CH_2—\underset{\underset{CH_3}{\underset{|}{CH_2}}}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}——\overset{O}{\overset{\|}{C}}—\underset{C_2H_5}{\underset{|}{\overset{+}{O}}}—C_2H_5$$

(7)


$$CH_3CH_2—\underset{\underset{CH_3}{\underset{|}{CH_2}}}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}——\overset{O}{\overset{\|}{C}}—\underset{C_2H_5}{\underset{|}{\overset{+}{O}}}—C_2H_5 \rightleftarrows CH_3CH_2\underset{\underset{CH_3}{\underset{|}{CH_2}}}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}——\overset{O}{\overset{\|}{C}}{}^+ + (C_2H_5)_2O \quad VII$$

Ether was also formed when ethyl propionate or propionic acid was heated with ethylene and boron fluoride hydrate. Such ester cleavage to ether is strictly analogous to that induced by reaction with anhydrous aluminum chloride.[3,4,5]

The alternative mechanisms considered were carboxylation of a branched-chain hexene corresponding to VI followed by esterification, and ethylation of the alpha carbon of propionic acid which is known to be formed when ethylene reacts with excess carbon monoxide in the presence of boron fluoride hydrate.[6] The absence of olefins in the reaction mixture made the first alternative appear unlikely, and the second was eliminated since under the same reaction conditions carbon alkylation did not occur with ethyl propionate or propionic acid.

## Experimental

**The Preparation of Ethyl α-Ethyl-α-methylbutyrate.[7,8]**—A silver-lined steel high-pressure tube of 400-ml. capacity was charged with 100 g. of boron fluoride hydrate of 1:1.7 mole ratio. The tube was closed, placed in a shaker and connected to a source of ethylene. Ethylene was passed into the tube to a pressure of 300 atm. Carbon monoxide was then passed in to obtain a total pressure of 500 atm. Heating and agitation were started. During a reaction time of 14.25 hours, throughout which the temperature was maintained at 109–110° and the pressure at 840–990 atm. by the periodic addition of carbon monoxide, the total observed pressure drop was 815 atmospheres. In a similar experiment, carried out to check the calculations of gas concentrations, the initial ethylene charge weighed 126 g., and the carbon monoxide 26 g. The carbon monoxide added amounted to 86 g. The vessel was cooled, the pressure released, and the reaction mixture discharged. The recovered gas contained 52.6% ethylene and 43.5% carbon monoxide. A mass spectrometer analysis to detect butenes or higher olefins showed less than 0.05% of material having a molecular weight above 28.

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[3] Norris and Sturgis, THIS JOURNAL, **61**, 1413 (1939).

[4] Norris and Arthur, *ibid.*, **62**, 874 (1940).

[5] C. A. Thomas, "Anhydrous Aluminum Chloride in Organic Chemistry," Reinhold Publishing Corp., New York, N. Y., 1941, pp. 673–678.

[6] Loder, U. S. Patent 2,135,459.

[7] The authors are indebted to Dr. T. A. Ford of this laboratory for the precise definition of reaction conditions and consequent improvement in yield.

[8] Hanford and Roland, U. S. Patent 2,378,009.

The liquid reaction mixture was diluted with water and steam distilled. The organic layer (79.5 g.) was separated from the distillate and distilled through a $^1/_2''$ × 12″ Fenske ring-packed column. The following fractions were obtained.

| | | |
|---|---|---|
| 1 | 35–40° | 14.1 g. |
| 2 | 40–161° | 7.6 g. |
| 3 | 163–165° | 48.5 g. |
| 4 | Residue | 6.3 g. |
| 5 | Distillation loss | 3.0 g. |

Fraction 1 was diethyl ether.

Fraction 2 was a complex mixture soluble in cold concentrated sulfuric acid and insoluble in 85% phosphoric acid. The material was partially saponifiable.

Fraction 3, subsequently shown to be ethyl α-ethyl-α-methylbutyrate, was soluble in cold concentrated sulfuric acid and insoluble in 85% phosphoric acid. No ketone reaction was shown by tests with *m*-dinitrobenzene plus alcoholic potassium hydroxide, and no hydrazone was formed with 2,4-dinitrophenylhydrazine. Reaction did not occur with bromine in carbon tetrachloride or with potassium permanganate in the presence of 5% sodium carbonate.

A composite of Fraction 3 from several runs was precision distilled through a 30-plate Fenske ring-packed column. The pure ester had a distinctive camphoraceous odor. It had the following properties: b. p., 166–166.5°; $n^{25}_{D}$ 1.4100; $d^{25}_{4}$ 0.8687.

*Anal.* Calcd. for $C_9H_{18}O_2$: C, 68.30; H, 11.39; *MR*D, 45.41. Found: C, 68.5; H, 10.71; *MR*D, 45.01.

The ester was hydrolyzed less than 10% in two days refluxing with 0.25 *N* alcoholic potassium hydroxide. On refluxing with 48% hydrobromic acid, ethyl bromide was evolved. This was identified by its boiling point, 38–40°, and refractive index, $n^{20}_{D}$ 1.4238. The residual organic layer was separated and distilled. After a small foreshot, the acid was found to boil at 198–203°. The acid contained some neutral material and was consequently purified by solution in alkali, extraction of the neutral bodies with ether and reacidification. The acid was converted to the acid chloride by reaction with phosphorus pentachloride, and the amide and anilide were prepared from the acid chloride. After two crystallizations from benzene, the amide was found to melt at 73–74° and the anilide at 87–88°. These melting points agree with those reported by Hardy[9] for the amide and anilide of α-ethyl-α-methylbutyric acid.

The aqueous layer of the steam distillate was exactly neutralized with sodium hydroxide, evaporated to dryness (0.5 g.) and treated with *p*-phenylphenacyl bromide. Even after three recrystallizations from alcohol, the *p*-phenylphenacyl ester melted over the range of 80 to 90° and hence could not be taken as indicative of any compound.

Approximately two liters of organic material was composited from several runs and precision distilled through a $^3/_4''$ × 20″ Fenske ring-packed column. The distillation curve showed a flat at 99°, indicating the presence of about 1% of ethyl propionate, and a slight break between 130 and 140° which might indicate the presence of ethyl α-methylbutyrate (b. p., 130–131°).

**Attempted Alkylation of Ethyl Propionate.**—The 400-ml. high pressure vessel was charged with 100 g. of boron fluoride hydrate, and 50 g. of ethyl propionate. Reaction with ethylene was carried out at 110–114° and 760–940 atmospheres pressure. The reaction mixture was diluted with water and steam distilled. The organic layer of the steam distillate was separated, dried and distilled. This yielded

| | | |
|---|---|---|
| 1 | 35–50° | 4 ml. |
| 2 | 50–95° | 2 ml. |
| 3 | 95–100° | 22 ml. |
| 4 | 100–160° | 16.4 ml. |
| 5 | 160–170° | 6 ml. |

Fraction 1 was diethyl ether and supports the view that reactions 6 and 7 occur as postulated.

Fraction 3 was shown to be ethyl propionate by boiling point and saponification equivalent.

Fractions 4 and 5 resembled the intermediate fraction obtained in the preparation of ethyl α-ethyl-α-methylbutyrate in giving no clear indication of a single compound present in amount sufficient for isolation. No single reaction predominated, and it was concluded that boron fluoride hydrate did not induce the simple alkylation of ethyl propionate.

**Alkylation of Propionic Acid.**—The above experiment was repeated with substitution of 50 g. of propionic acid for the ethyl propionate. Isolation in the same manner gave an organic layer which was separated into fractions.

| | | |
|---|---|---|
| 1 | 35–90° | 3.5 ml. |
| 2 | 95–98° | 18.8 g. |
| 3 | 100–170° | 2.0 g. |
| 4 | Residue | 8.2 g. |

Fraction 1 contained diethyl ether which could be formed by reactions like 6 and 7.

Fraction 2 had a refractive index $n^{23}_{D}$ 1.3842. Ethyl propionate boils at 99° and has an index $n^{20.2}_{D}$ 1.3819. The chief reaction was clearly esterification of the carboxyl group.

The low recovery of ethyl propionate in this and the preceding experiment was caused by large losses of this volatile material when the ethylene pressure in the reactor was released.

**Acknowledgment.**—The authors are indebted to Mr. Harold M. Kelley of the Polychemicals Department, E. I. du Pont de Nemours & Co., Wilmington, Delaware, for the mass spectrometer analysis, and to Mr. Howard S. Young and Staff for supervision of the experiments carried out at high pressure.

## Summary

Ethyl α-ethyl-α-methylbutyrate has been synthesized by a boron fluoride hydrate-catalyzed reaction of ethylene and carbon monoxide.

A mechanism based on reactions of carbonium ions is proposed for this reaction.

WILMINGTON, DEL. RECEIVED NOVEMBER 29, 1949

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[9] Hardy, *J. Chem. Soc.*, 464 (1938).