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# Reactions of Allenes. I. The Synthesis of Unsaturated Monocarboxylic Esters by the Carboxylation Reaction of Allenes; Reaction Conditions and Products*1

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The carboxylation reaction of propadiene and 1, 2-hexadiene with carbon monoxide and methanol in the presence of a catalyst was studied. Propadiene was carboxylated to give methyl methacrylate in a fairly good yield (62% based on the propadiene consumed) by the use of a catalyst composed of nickel carbonyl and methacrylic acid or water under a relatively low pressure. A small amount of methyl vinylacetate was also present. The predominant side reaction was a polymer formation reaction. The carboxylation of 1, 2-hexadiene, however, did not proceed smoothly, and a great amount of tarry materials was obtained. The carboxylation products obtained in low yields (max. 15%) were exclusively the materials formed by a carbonyl attack on the central carbon of the allenic structure, that is, methyl *trans*-2-methyl-2-hexenoate and methyl 2-butyl-2-propenoate.

The synthesis of unsaturated monocarboxylic esters by the carboxylation reaction of acetylenes is well known, and its application to the industry has already been established. The carboxylation reaction of monoolefins is also investigated widely. Concerning the carboxylation reaction of allenes, which have a character intermediate between acetylenes and olefins with regard to the chemical structure, however, very little has been published.

One patent and one article have described the synthesis of methyl methacrylate in up to a 50% yield by the carboxylation of propadiene with carbon monoxide and methanol under a high pressure in the presence of a catalyst composed of tin or germanium salt and a salt of a noble metal in Group VIII of the periodic table1) or in the presence of diruthenium nonacarbonyl or iron pentacarbonyl.2) Recently, Tsuji and Susuki3) have reported the synthesis of diethyl itaconate from propadiene, carbon monoxide, and ethanol in the presence of palladium chloride.

The present investigation has aimed at the synthesis of unsaturated monocarboxylic esters by the carboxylation of propadiene and 1, 2-hexadiene under a relatively low pressure of carbon monoxide and at obtaining some information about the reactivities of allenes.

$$\mathrm{CH_2{=}C{=}CH_2} \xrightarrow[\text{cat.}]{\text{CO-CH}_3\text{OH}} \begin{array}{c}\mathrm{CH_3C(COOCH_3){=}CH_2}\\ +\\ \mathrm{CH_2{=}CHCH_2COOCH_3}\end{array}$$

$$\mathrm{C_3H_7CH{=}C{=}CH_2} \xrightarrow[\text{cat.}]{\text{CO-CH}_3\text{OH}} \begin{array}{l}\text{C}_7\text{-unsaturated mono-}\\ \text{carboxylic esters}\end{array}$$

It was found that methyl methacrylate was obtained in a 62% yield from propadiene, carbon monoxide, and methanol at 140°C in the presence of nickel carbonyl and methacrylic acid. The reaction, however, was much more difficult for 1, 2-hexadiene.

## Experimental

**Materials.** Propadiene was obtained commercially and purified by fractional distillation through a Podbielniak-type low-temperature column; bp −33°C. The purity was higher than 99.3%; propylene was shown by gas chromatography to be the principal impurity.

The hexadiene was prepared from propyl magnesium bromide and propargyl bromide according to the procedure of Serratosa.4) The crude 1, 2-hexadiene was purified by fractional distillation through a Podbielniak-type column; bp 75.4—75.6°C. The purity was over 99.7%; hexane was found to be the principal impurity by analysis with gas chromatography.

Carbon monoxide was obtained commercially (99.7% pure).

Metal carbonyls such as nickel tetracarbonyl,5) chromium hexacarbonyl,6) and dicobalt octacarbonyl7) were prepared by the usual methods.

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*1 Presented at the 19th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1966.

1) E. L. Jenner and R. V. Lindsey, Jr., U. S. Pat. 2876254, March 3 (1959); *Chem. Abstr.*, **53**, 17906 (1959).

2) R. E. Benson and T. J. Kealy, *J. Org. Chem.*, **26**, 3126 (1961).

3) J. Tsuji and T. Susuki, *Tetrahedron Letters*, **34**, 3027 (1965).

4) F. Serratosa, *ibid.*, **16**, 895 (1964).

5) W. Reppe and coworkers, *Ann.*, **582**, 116 (1953).

6) G. Brauer, "Handbuch der Präparativen Anorganischen Chemie," Ferdinand Enke Verlag, Stuttgart (1954), p. 1340.

7) A. A. Blanchard and P. Gilmont, *J. Am. Chem. Soc.*, **62**, 1192 (1940).

TABLE 1. RETENTION TIMES OF PRODUCTS FROM PROPADIENE

| Column and condition | | Retention time, min | | | |
|---|---|---|---|---|---|
| | | Methyl methacrylate | Methyl vinylacetate | Methacrylic acid | Standard substance |
| 30% Polyethyleneglycol 1000 on C-22 2.5 m | 70°C<br>50 m*l*/min<br>(of $H_2$) | 13.1 | 18.2 | | Butyl acetate<br>23.0 |
| 21% Dioctyl sebacate +4% sebacic acid on Celite 545 2.5 m | 70°C<br>50 m*l*/min | 17.3 | 18.9 | | |
| | 140°C<br>100 m*l*/min | | | 8.3 | Chlorobenzene<br>4.5 |

Bis(triphenylphosphine) nickel dibromide was prepared according to the directions of Yamamoto.[8]

**Carboxylation.** *Carboxylation of Propadiene.* A stainless steel autoclave, the type and capacity being described in each table, was charged under nitrogen with methanol, hydroquinone, and a catalyst. The vessel was then cooled to about −50°C, and the air was replaced completely by nitrogen. After evacuation, propadiene and carbon monoxide were added by the three different ways described below, and then the vessel was heated to the specified temperature.

(A) The Batch Process: Propadiene was added initially by distillation; carbon monoxide was also charged initially, and repeatedly in some cases.

(B) The Constant Pressure Process: Propadiene was added as A, and carbon monoxide was fed continuously from the gas storage at a constant pressure.

(C) The Semicontinuous Process: Propadiene and carbon monoxide were fed continuously at a constant pressure.

*Carboxylation of 1, 2-Hexadiene.* The procedure was substantially identical with that described for propadiene, but 1, 2-hexadiene and carbon monoxide were added according to Process B.

**The Separation of Reaction Products.** After the absorption of carbon monoxide had ceased practically, the mixture was cooled to room temperature. Then, the remaining gas was discharged through a trap cooled with dry ice and acetone in the case of propadiene, and with ice water in the case of 1, 2-hexadiene. The condensed liquid in the former trap was vaporized and submitted to analysis with gas chromatography in order to determine the unreacted propadiene.

The undecomposed nickel carbonyl was removed thoroughly from the reaction mixture by passing nitrogen through the mixture at about 50°C and measured by a slight modification of the method of Jones *et al.*[9] The decomposed nickel carbonyl was determined by analyzing the nickel in the aqueous layer resulting from the following extraction procedure.

A small portion of the reaction mixture was sampled out for analysis of the products with gas chromatography. The remaining portion was poured into a dilute sulfuric acid and extracted with methylene chloride. The extract was condensed and flash-distilled to give an ester fraction (bp≃60°C/100 mmHg), a higher-boiling fraction (bp 60°C/100 mmHg—90°C/30 mmHg), and a residue for the products from propadiene, and an ester fraction (bp≃90°C/30 mmHg) and a residue for the products from 1, 2-hexadiene.

**The Identification and Analysis of the Reaction Products.** The products from propadiene were identified and determined by gas chromatography using the columns and conditions listed in Table 1. The were methyl methacrylate and a small amount of methyl vinylacetate. When water existed in the reaction system, methacrylic acid was also produced. Gas chromatographic analysis for the products from 1, 2-hexadiene showed that only two of the possible six isomers were present. They were isolated by preparative gas chromatography using a 1-m column of 30% dioctyl phthalate. Their infrared spectra were identical with those of methyl *trans*-2-methyl-2-hexenoate (I) and methyl 2-butyl-2-propenoate (II) prepared by a method similar to that of Cason *et al.*[10]

I: bp 83.8—84.0°C/30 mmHg, $n_D^{25}$ 1.4425, $d_4^{20}$ 0.932 (lit. bp 81.5—82.0°C/30 mmHg, $n_D^{25}$ 1.4418—1.4421). $\nu$ 1718, 1649, 1423, 1280, 1096, and 740 cm$^{-1}$.

Found: C, 67.80; H, 9.82%. Calcd for $C_8H_{14}O_2$: C, 67.57; H, 9.93%.

II: bp 82.0—83.0°C/30 mmHg, $n_D^{25}$ 1.4286, $d_4^{20}$ 0.915. $\nu$ 1727, 1630, 1438, 1210, and 816 cm$^{-1}$.

Found: C, 67.85; H, 10.03%. Calcd for $C_8H_{14}O_2$: C, 67.57; H, 9.93%.

The carboxylation products from 1, 2-hexadiene were analyzed by gas chromatography using a 2.4-m column of 30% Silicone DC 703 on Celite 545 at 140°C.

## Results and Discussion

**Carboxylation Reaction of Propadiene.** *Experiments with Various Catalysts.* At the beginning of this study, the catalytic effects of some compounds were examined by Process A; the results are summarized in Table 2.

A catalyst composed of platinum salt and stannous chloride or germanic chloride, with which Lindsey *et al.*[1] obtained a maximum 40% yield of methyl methacrylate from propadiene under a carbon monoxide pressure of 400—1000 atm, failed to give methyl methacrylate under our experimental

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[8] K. Yamamoto, K. Sato and M. Oku, This Bulletin, **27**, 491 (1954).

[9] E. R. H. Jones, T. Y. Shen and M. C. Whiting, *J. Chem. Soc.*, **1951**, 766.

[10] J. Cason and M. J. Kalm, *J. Org. Chem.*, **19**, 1947 (1954).

TABLE 2. THE CARBOXYLATION OF PROPADIENE WITH VARIOUS CATALYSTS

Autoclave: 100 *ml* electromagnetic stirring-type; Process A; Hydroquinone, 0.05 g

| Run No. | $C_3H_4$ g | $CH_3OH$ *ml* | Catalyst | g | CO[a] atm | Reaction temp. °C | Reaction period hr | Recovered $C_3H_4$ % | Product yield[b] | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | | MMA % | MAA % | $CH_3COCH_3$ % | HBM+Rd g |
| 1 | 7.9 | 20 | $H_2PtCl_6$<br>$SnCl_22H_2O$ | 0.5<br>1.9 | 126—125(84) | 172—176 | 9.4 | 2.5 | 3.6 | 0 | 6.1 | 4.4 |
| 2 | 7.9 | 20 | $PtCl_2$<br>$GeCl_4$ | 0.3<br>0.8 | 93—90 (68) | 140—144 | 9.2 | 1.3 | 2.5 | 0 | 7.9 | 5.1 |
| 3 | 7.5 | 20 | $(Ph_3P)_2NiBr_2$ | 1.4 | 65—40 (25) | 172—176 | 14.5 | 8.0 | 2.7 | 0 | 0.9 | 6.6 |
| 4 | 9.1 | 18 | $NiBr_2$<br>$H_2O$ | 1.3<br>2.0 | 73—51 (20) | 172—175 | 14.6 | 4.4 | 11.0 | 3.6 | trace | 8.1 |
| 5 | 8.2 | 25 | $Ni(CO)_4$<br>HCl-Acid | 7.8<br>10.0 | — (0) | 70—96 | 2.0 | 26.8 | 2.0 | 0 | 0 | 8.5 |
| 6 | 7.5 | 20 | $Ni(CO)_4$ | 2.0 | 136—92 (50) | 220—225 | 8.7 | 0 | 4.8 | trace | trace | 8.7 |
| 10 | 8.2 | 15 | $Ni(CO)_4$<br>$H_2O$ | 2.0<br>5.0 | 150—66 (56) | 210—215 | 2.4 | 0 | 23.5 | 7.5 | 0.8 | 7.2 |
| 11 | 8.9 | 15 | $Co_2(CO)_8$<br>$H_2O$ | 1.8<br>5.0 | 72—44 (29) | 200—210 | 3.4 | 0 | 0 | — | trace | 7.2 |
| 12 | 8.6 | 15 | $Cr(CO)_6$<br>$H_2O$ | 1.5<br>5.0 | 145—88 (55) | (210—220<br>245—255 | 10.2)<br>5.7 | 3.5 | 0.5 | (unreacted)<br>— | 1.6 | 8.4 |
| 13* | 8.2 | 50 | $Ni(CO)_4$<br>HC-Gas | 2.0<br>1.6 | 43—42 (5) | 144—146 | 2.0 | 71.5 | 1.4 | 0 | trace | 1.6 |

* A 200 *ml* magnet-rotating-type autoclave was used.

a) The range of total pressure during the reaction period is shown. The value in parenthesis shows the initial pressure of carbon monoxide at room temperature.

b) MMA=methyl methacrylate, MAA=methacrylic acid, HBM=higher-boiling materials (containing MAA), Rd=residue. The values were calculated on the basis of the propadiene used.

TABLE 3. INFLUENCE OF REACTION CONDITIONS FOR THE CARBOXYLATION OF PROPADIENE

Autoclave: 300 m*l* shaking-type; Process B; Nickel carbonyl, 2.0 g, hydroquinone, 0.05 g

| Run | $C_3H_4$ | $CH_3OH$ | Cocatalyst | | CO | | Reaction temp. | Reaction period | Decomposed[b)] $Ni(CO)_4$ | Recovered $C_3H_4$ | Product yield | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| No. | g | m*l* | | g | Pressure atm | Absorption[a)] amount, % | °C | hr | % | % | MMA % | MAA % | MVA[c)] % | HBM g | Rd g |
| 17* | 8.5 | 70 | $H_2O$ | 10.0 | 87—54(26) | 57 | 198—203 | 4.9 | 10 | 0 | 35.8 | 7.1 | 1.8 | 1.2 | 4.8 |
| 18* | 8.4 | 70 | $H_2O$ | 20.0 | 80—47(26) | 62 | (180—185<br>190—194 | 2.8)<br>4.8 | 22 | 0 | 32.7 | 14.0 | (unreacted)<br>1.7 | 2.1 | 4.5 |
| 22 | 8.3 | 140 | $H_2O$ | 20.0 | 33—32 (7) | 58 | 163—166 | 4.3 | 31(54) | 0 | 35.7 | 9.6 | 1.3 | 1.1 | 4.0 |
| 21 | 8.2 | 140 | $H_2O$ | 20.0 | 50—47(12) | 66 | 177—180 | 5.5 | 16(68) | 0 | 38.1 | 9.7 | — | 1.1 | 3.6 |
| 23 | 8.1 | 140 | $H_2O$ | 20.0 | 88—83(26) | 66 | 205—207 | 5.8 | 9(80) | 0 | 35.1 | 8.6 | 2.6 | 1.1 | 4.6 |
| 24 | 18.8 | 105 | $H_2O$ | 15.0 | 67—47(14) | 62 | 176—180 | 5.9 | 64(22) | 0 | 34.8 | 7.9 | 1.5 | 3.4 | 15.6 |
| 25 | 29.8 | 90 | $H_2O$ | 13.0 | 91—61(20) | 60 | 185—188 | 9.0 | 70(19) | trace | 22.4 | 3.0 | 1.2 | 3.1[d)] | 28.2 |
| 26 | 9.1 | 120 | $H_2O$<br>MAA | 35.0<br>5.0 | 22—21 (6) | 17 | 135—145 | 4.2 | 84 (0) | 26.4 | 22.0 | 2.3 | — | 2.4[d)] | |
| 27 | 9.6 | 120 | $H_2O$<br>MAA | 35.0<br>5.0 | 28—27 (8) | 18 | 142—154 | 3.0 | 78 (0) | 30.2 | 25.0 | 2.7 | — | 0.6[d)] | 2.1 |
| 39† | 7.7 | 50 | MAA | 2.0 | 50—45(12) | 24 | 148—154 | 2.6 | 33(49) | 44.1 | 22.0 | — | trace | 1.6 | 1.5 |

* The reaction was performed by the Process A.

† A 200 m*l* magnet-rotating-type autoclave was used.

a) Percentage of theoretical amount based on the propadiene used.

b) Based on the nickel carbonyl used. The value in parenthesis shows the undecomposed nickel carbonyl.

c) MVA=methyl vinylacetate.

d) Methacrylic acid was removed by $NaHCO_3$-extraction.

TABLE 4. THE CARBOXYLATION OF PROPADIENE BY PROCESS C

Autoclave: 200 m$l$ magnet-rotating-type; Nickel carbonyl, 2.0 g, hydroquinone, 0.05 g

| Run | $C_3H_4$ | $CH_3OH$ | Cocatalyst | | CO | | Reaction temp. | Reaction period | Decomposed $Ni(CO)_4$ | Recovered $C_3H_4$ | Product yield | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| No. | g | m$l$ | | g | Pressure atm | Absorption amount, % | °C | hr | % | % | MMA % | MAA % | MVA % | HBM g | Rd g |
| 28* | 8.2 | 20 | $H_2O$ | 6.0 | 43—39(15) | 57 | 178—181 | 3.7(3.2)[a] | 73(8) | 5.0 | 32.7 | 19.3 | 0.7 | 2.6 | 4.0 |
| 29* | 10.3 | 30 | $H_2O$ | 10.0 | 43—40(15) | 54 | 179—182 | 3.9(3.4) | 90(2) | 10.0 | 31.9 | 17.2 | 0.4 | 2.2 | 4.0 |
| 36 | 7.7 | 48 | MAA | 2.0 | 16 (4) | 32 | 134—128 | 4.0(3.2) | 75(5) | 19.4 | 45.0 | — | 0 | 2.0 | 3.0 |
| 38 | 5.2 | 50 | MAA | 2.0 | 24—23 (8) | 53 | 140—141 | 3.8(3.7) | 75 | 0 | 62.0 | — | 1.4 | 1.5 | 1.4 |
| 41 | 7.4 | 50 | MAA | 2.0 | 24—23 (8) | 48 | 140—144 | 4.1(2.1) | 60 | 24.0 | 48.0 | — | 1.1 | 1.9 | 2.3 |

* A 100 m$l$ electromagnetic stirring-type autoclave was used.

a) The value shows the period of feed of propadiene.

TABLE 5. THE CARBOXYLATION OF 1,2-HEXADIENE BY PROCESS B

Autoclave: 200 m$l$ magnet-rotating-type; Nickel carbonyl, 2.0 g, hydroquinone, 0.1 g

| Run | $C_6H_{10}$ | $CH_3OH$ | Cocatalyst | | CO | | Reaction temp. | Reaction period | Decomposed $Ni(CO)_4$ | Recovered[a)] $C_6H_{10}$ | Product yield[b)] | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| No. | g | m$l$ | | g | Pressure atm | Absorption amount, % | °C | hr | % | | MMH % | MBP % | Rd g | Ply |
| 2 | 12.0 | 50 | $CH_3COOH$<br>$H_2O$ | 3.0<br>2.0 | 47—27(10) | 9 | 140—192 | 4.7 | 43 | × | 3.2 | 0.5 | — | ○ |
| 3 | 12.0 | 45 | $H_2O$ | 10.0 | 35—30(10) | 6 | 160—180 | 2.0 | 32 | × | trace | 0 | — | ○ |
| 4 | 3.0 | 45 | $H_2O$ | 10.0 | 15 (2) | 0 | —152 | 5.2 | — | × | 0 | 0 | — | ○ |
| 5 | 3.0 | 50 | $CH_3COOH$<br>$H_2O$ | 3.0<br>2.0 | 24 (9) | (74) | 151—153 | 3.6 | 61(36) | ○ | 12.8 | 2.7 | 2.2 | × |
| 8* | 6.0 | 50 | $CH_3COOH$<br>$H_2O$ | 3.0<br>2.0 | 28(10) | (48) | 153—155 | 3.5 | 57(29) | ○ | 12.0 | 2.6 | 5.3 | × |
| 10† | 6.0 | 50 | $CH_3COOH$<br>$H_2O$ | 3.0<br>2.0 | 19—20(15) | 0 | 150—154 | 3.4 | 53 | × | 6.6 | 1.5 | — | ○ |
| 11 | 6.0 | 50 | $H_2O$<br>Pyridine | 2.0<br>0.8 | 20—22(10) | 6 | 150—156 | 3.0 | 49 | × | 1.3 | 0.4 | — | ○ |

* Methyl acetylene (3.0 g) was added.

† A large amount of hydroquinone (3.0 g) was used.

a) ×: None, ○: Remained.

b) MMH = methyl 2-methyl-2-hexenoate, MBP = methyl 2-butyl-2-propenoate, Rd = residue, soluble polymer in the reaction medium. Ply = insoluble polymer in the reaction medium; ×: None, ○: Formed.

conditions; rather, a considerable amount of acetone, which might be produced by the hydration of propadiene, was obtained (Runs 1 and 2).

$$CH_2{=}C{=}CH_2 \xrightarrow{H^+} CH_3C^+{=}CH_2 \xrightarrow{OH^-}$$
$$[CH_3C(OH){=}CH_2] \longrightarrow CH_3COCH_3$$

Bis(triphenylphosphine) nickel dibromide, an effective catalyst for the catalytic carboxylation of acetylene, was also ineffective (Run 3). The nickel bromide-water system had some effect, but it was not very good (Run 4). Both the stoichiometric process with nickel carbonyl and hydrochloric acid (Run 5) and the catalytic process with nickel carbonyl only (Run 6) gave only a little methyl methacrylate. In the above runs, considerable amounts of higher-boiling materials were obtained as by-products. The catalytic process with nickel carbonyl-hydrogen chloride could give neither methyl methacrylate nor higher-boiling materials (Run 13). In this case, over 70% of the propadiene was recovered. In the presence of water (Run 10), however, nickel carbonyl was found to be a good catalyst for the carboxylation of propadiene under a much lower pressure of carbon monoxide than that reported by Benson *et al.*[2] (300—900 atm) or Lindsey *et al.*[1] (400—1000 atm), who used the other catalysts described above.

Other metal carbonyls, such as dicobalt octacarbonyl (Run 11) and chromium hexacarbonyl (Run 12), were ineffective even in the presence of water.

It is interesting thatnickel carbonyl - water could catalyze the carboxylation of propadiene, while nickel carbonyl - hydrogen chloride, which is a more well known catalyst for the semicatalytic carboxylation of acetylene than nickel carbonyl and water, could not catalyze the reaction. As will be described below, however, nickel carbonyl and methacrylic acid could catalyze the reaction more effectively than nickel carbonyl and water (Run 39 in Table 3).

Thus, with nickel carbonyl and water, and/or methacrylic acid, as the catalyst, the reaction was further investigated.

*Carboxylation using Nickel Carbonyl and Water, and/or Methacrylic Acid.* The effects of the reaction conditions on the reaction rates and products were examined by Process B. The results are summarized in Table 3.

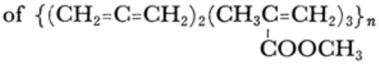
The reaction temperature: the temperature at which the reaction proceeded smoothly depended on the pressure of carbon monoxide and the amount of water added. The reaction temperature rose with an increase in the pressure of carbon monoxide, varying from 165°C for an initial pressure of 7 atm (Run 22) to 205°C for 26 atm (Run 23). On the other hand, the increase in the amount of water lowered the reaction temperature, though the influence of this was small compared with the pressure of carbon monoxide (Runs 17 and 18).

An organic acid, such as methacrylic acid, could be substituted for water, whereupon the reaction proceeded at a lower temperature of 150°C at 12 atm (Run 39). The lowest reaction temperature (140°C) was attained using a catalyst composed of nickel carbonyl, water, and methacrylic acid at an initial charge of 6 atm of carbon monoxide (Run 26). The decomposition of nickel carbonyl, however, increased when the reaction proceeded at a low temperature.

Yield and product distribution: methyl methacrylate and methacrylic acid were obtained in a total yield of 48%, together with a small amount of methyl vinylacetate, when the reaction was carried out at a total pressure of about 50 atm (a 12 atm initial charge of carbon monoxide at room temperature) at 180°C in the presence of nickel carbonyl and water (Run 21). The ratio of methyl vinylacetate to methyl methacrylate was 0—0.07 (Run 23). With a decrease in the reaction temperature, this ratio seemed to decrease. This fact indicates that the –COOR group is almost exclusively combined with the central carbon of propadiene. The yield of methacrylic acid depended linearly on the ratio of water to methanol, regardless of other reaction conditions, provided nickel carbonyl-water was used as the catalyst (Runs 17, 18, and 29 (Table 4)).

At a higher concentration of propadiene, the yield of methyl methacrylate and methacrylic acid decreased, while the amount of the polymer, the sum of the higher boiling materials (HBM) and the residue (Rd), increased (Runs 24 and 25). On gas chromatographic analysis, the higher-boiling materials in these runs appeared mainly to consist of three kinds of $C_7$-esters (and methacrylic acid in the case of Run 24). The richest one of the esters was separated by preparative gas chromatography and identified as methyl 1-methyl-3-methylene-cyclobutane carboxylate by elemental (Found: C, 68.77; H, 8.75%) and NMR analysis (a quintet, 5.23 $\tau$, terminal methylene protons; a singlet, 6.38 $\tau$, methoxy protons; two doublets, 6.91 and 7.62 $\tau$, ring methylene protons; a singlet, 8.62 $\tau$, methyl protons). The other two esters, with almost the same percentage composition of elements and boiling points as the above compound, will be reported later in detail.

The residues of Runs 24 and 25 were precipitated from an acetone solution with petroleum ether. The analytical data (Found: C, 66.26; H, 7.97%) suggest that this polymer has roughly the composition of



$$\{(CH_2{=}C{=}CH_2)_2(CH_3\underset{\displaystyle COOCH_3}{\underset{|}{C}}{=}CH_2)_3\}_n.$$

This would explain the difference between the amount of carbon monoxide absorbed and the yield of carbonyl compounds detected. It was clear that the polymerization reaction was the predominant side reaction. In view of this fact, it would be expected that the carboxylation reaction by Process C, in which propadiene was fed in continuously so as to prevent a higher concentration of propadiene, would give a better yield.

*Carboxylation by Process C.* The results are shown in Table 4. As expected, the yield was increased by this process. The best yield, 62% methyl methacrylate, was obtained in the presence of a catalyst composed of nickel carbonyl (2.0 g) and methacrylic acid (2.0 g) at 140°C a, total pressure of 24 atm (8 atm initial charge of carbon monoxide at room temperature), and a feed rate of 1.4 g of propadiene per hour (Run 38). In Runs 36, 38 and 41, where an efficient stirring autoclave (rotational speed: 800 rpm) was used, the amount of higher-boiling materials and residue decreased as expected, and the amount of carbonyl in the methyl methacrylate and methacrylic acid formed approached the total available amount from the absorbed carbon monoxide and from the decomposed nickel carbonyl. However, in the case of a 100-m*l* autoclave equipped with a weak electromagnetic-stirring (up-down stirring; max. 130 times per min), relatively large amounts of higher-boiling materials and the residue were found (Runs 28 and 29). In addition, in these two cases, most of the nickel carbonyl was decomposed, though a higher pressure of carbon monoxide of 15 atm was applied.

**Carboxylation Reaction of 1, 2-Hexadiene.** In order to study the characteristics of the carboxylation reaction of allenes, the carboxylation reaction of 1, 2-hexadiene, an allene homologue, was undertaken. The results obtained are shown in Table 5. The reaction of 1, 2-hexadiene was far more difficult than that of propadiene, and the reaction conditions under which propadiene was carboxylated in a considerable yield could give little of the carboxylation products (Runs 2, 3, and 4).

Pyridine, which is known to be an accelerator of the oxo process, was ineffective (Run 11).

In the above runs, much amount of tarry materials was obtained; it appeared to be produced by the polymerization of 1, 2-hexadiene. Thus, 1, 2-hexadiene seemed to be easier to polymerize than propadiene. The addition of methyl acetylene accelerated the reaction (Runs 5 and 8), and in these runs, about 15% of the carboxylation products was obtained. The ratio of methyl *trans*-2-methyl-2-hexenoate (I) to methyl 2-butyl-2-propenoate (II) was roughly 5 under these reaction conditions.

Considering the product distribution of 1, 2-hexadiene and propadiene, it might be concluded that allenes are carboxylated to yield unsaturated monocarboxylic esters with a conjugated structure; that is, the –COOR group combines with the central carbon of the allenic structure. Moreover, the lower reactivity for the carboxylation of 1, 2-hexadiene and the product distribution suggest that the addition of active species, which might be designated as $HNi(CO)_nX$ (X is an anionic fragment of water or methacrylic acid) to the diene is controlled by inductive and steric effects. The ratio of I to II may be controlled by an inductive effect of the propyl group of 1, 2-hexadiene, while the absence of the cis-isomer of I must be due to its steric interference.

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