leaving 2.3 g. of a brown solid mass, m.p. 140°. A solution of 0.5 g. of the latter was taken up in 10 ml. of benzene and passed through a column containing 15 g. of neutral alumina (Merck) to afford 0.05 g. of crude hydrocarbon (benzene eluent) and 0.30 g. of unchanged ketone (VII) (chloroform eluent). The former was recrystallized from 95% ethanol as pale yellow needles, m.p. 118–120°, unchanged upon further recrystallization.

This hydrocarbon (50 mg.) was dissolved in 2 ml. of benzene-hexane (50:50) and passed through a column containing 5 g. of acidic alumina (Merck). The first fraction (10 mg.) was recrystallized from 95% ethanol to afford VIII as colorless fine needles, m.p. 108–109°, $\lambda_{\text{EtOH}}^{\max}$ (log ϵ) 235 mμ (4.7), 244 (4.9), 256 (4.1), 266 (4.5), 277 (4.7), 313 (4.1), 327 (4.5), 343 (4.6), 357 (3.5), 369 (2.8), and 377 (3.4). (Lit., m.p. 107–108°,[11] 112–113°[12]; the spectra were superimposable in all respects.[12])

The second fraction (20 mg.) was recrystallized from 95% ethanol to afford VI as pale yellow plates, m.p. 123–124°, $\lambda_{\text{EtOH}}^{\max}$ (log ϵ) 218 mμ (4.6), 228 (4.4), 235 (4.5), 269 (4.4), 279 (4.6), 290 (4.7), 311 (3.9), 325 (3.9), 340 (3.8), 356 (3.3), 367 (2.9), 374 (3.2). (Lit.,[10] m.p. 134°.)

Anal. Calcd. for $C_{19}H_{12}$: C, 94.97; H, 5.03. Found: C, 94.80; H, 5.09.

B. Zinc-sodium hydroxide reduction. A mixture of 1.0 g. of ketone (VII) and 8 g. of zinc dust in 60 ml. of 10% sodium hydroxide solution was covered with 10 ml. of 1-hexanol and heated under reflux for 6 hr. The solution was evaporated and acidified with 6*N* hydrochloric acid. The resulting black precipitate was filtered, dried, and pyrolyzed for 15 min. at 280° and 0.5 mm. pressure. The yellow sublimate (0.30 g.) was chromatographed on 10 g. of acidic alumina to afford 0.13 g. of hydrocarbon (VI) and 0.08 g. of unchanged ketone (VII). The former was recrystallized from 95% ethanol as pale yellow plates, m.p. 123–124°, undepressed on admixture with that prepared *via* method A.

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Carboxylation of Propargyl Halides

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The reactions of propargyl halides with nickel carbonyl have been studied. Carboxylation of propargyl bromide at 70° and atmospheric pressure yielded ethyl 3-bromo-3-butenoate (I). Partial reduction of I with $LiAlH_4$ yielded 3-bromo-3-buten-1-ol which upon ozonolysis yielded formaldehyde. A mechanism is given which postulates the formation of an allenic ester, ethyl 2,3-butadienoate (II), intermediate. In the case of propargyl chloride both II and ethyl 3-chloro-3-butenoate (III) were isolated. Lower yields of product were obtained when the reaction was run under carbon monoxide pressure. This result is consistent with the hypothesis of Wender that the first step of the reaction is the formation of an acetylenic-carbonyl complex and carbon monoxide.

In the course of investigations being carried out in our laboratories, propargyl halides were carboxylated with nickel carbonyl. The recent disclosure by Jones, Whitham, Whiting[1] of similar work made it desirable for us to release our findings.

According to Raphael[2] propargylic bromides in ethanol react with nickel carbonyl and water to yield bromine-free allenic acids. In our laboratories when propargyl bromide in ethanol was caused to react with nickel carbonyl at 70° and atmospheric pressure, an evolution of heat took place and instead of a halogen-free allenic acids being formed, ethyl 3-bromo-3-butenoate, $CH_2{=}CBrCH_2CO_2C_2H_5$ (I), was obtained in 21% yield. The characterization of I presented some interesting problems. Due to the presence of the bromine atom, infrared analysis could not distinguish whether the ester contained a terminal methylene group or a double bond conjugated with the carbonyl group. Semimicro hydrogenation revealed that two moles of hydrogen was absorbed per mole of compound. Although the compound did not give a positive halide test when tested directly with alcoholic silver nitrate, it was found to contain approximately 39% bromine when the solution formed by either hydrogenating the sample or heating it one hour with caustic, was analyzed for halide ion. Saponification equivalents of several samples averaged 190. Vapor phase chromatographic analysis indicated the presence of a single compound of 90+% purity. All these data were consistent with the ethyl ester of a monobromobutenoic acid, which would have a molecular weight of 193 and would, under the conditions used, absorb two moles of hydrogen (hydrogenation of the double bond and hydrogenolysis of the bromine atom). The problem of which isomer was present, however, was as yet undecided. Therefore, the hydrogenated solution was saponified and yielded the potassium salt of an acid which was converted to *n*-butyro-*p*-toluide, and the *p*-bromo- and *p*-phenylphenacyl esters of *n*-butyric acid. Thus the carbon skeleton was that of *n*-butane. The location of the halogen atom was assigned to the third carbon atom by the fact that

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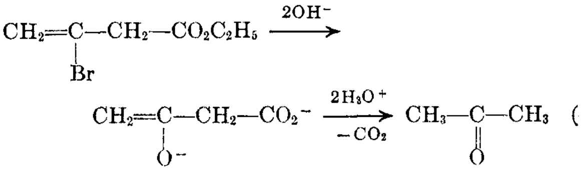
[1] E. R. H. Jones, G. H. Whitham, and M. C. Whiting, *J. Chem. Soc.*, 4628 (1957).

[2] R. A. Raphael, *Acetylene Compounds in Organic Synthesis*, Academic Press, N. Y., 1955, p. 138.

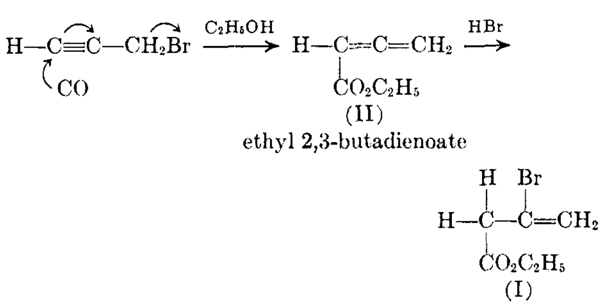
saponification of the ester followed by acidification with further refluxing yielded acetone. The reaction sequence is pictured as in equation (1).



$$CH_2{=}\underset{\substack{|\\Br}}{C}{-}CH_2{-}CO_2C_2H_5 \xrightarrow{2OH^-} CH_2{=}\underset{\substack{|\\O^-}}{C}{-}CH_2{-}CO_2^- \xrightarrow[-CO_2]{2H_3O^+} CH_3{-}\underset{\substack{\|\\O}}{C}{-}CH_3 \quad (1)$$

Despite the fact that infrared analysis suggested a terminal methylene group, this was not confirmed by ozonolysis. The compound was ozonized but attempts to isolate formaldehyde either as the 2,4-dinitrophenylhydrazone or as the dimedone adduct failed. However, the presence of the terminal methylene group was established by the method of Lemieux and Rudloff[3] which consisted of oxidizing the compound with a periodate-permanganate mixture at *p*H 7 and then observing the color formed by the addition of chromotropic acid to the formaldehyde formed. Partial reduction of I with lithium aluminum hydride yielded 3-bromo-3-buten-1-ol which was characterized by infrared analysis, bromine analysis, hydrogen and hydroxyl numbers, and preparation of a derivative. Ozonolysis of this compound in the presence of 2,4-dinitrophenylhydrazine yielded formaldehyde 2,4-dinitrophenylhydrazone.

The mechanism for the formation of I can be visualized as follows:



It was hoped that ethyl 2,3-butadienoate (II) could be isolated from the reaction mixture and caused to react with hydrobromic acid to form I and thus lend support to this mechanism. However, none was isolated from the propargyl bromide carboxylation mixture. Because of the well-known relationship of the rates of addition of hydrobromic acid and hydrochloric acid to double bonds, it was hoped that II (formed from the analogous carboxylation of propargyl chloride) could be isolated before it reacted with the hydrochloric acid present. Consequently, propargyl chloride was carboxylated at atmospheric pressure and small yields of both II and ethyl 3-chloro-3-butenoate (III) were isolated. II was identified by its infrared spectrum, hydrogen number, and saponification equivalent. The index of refraction of II was the same as reported by Eglenton *et al.*,[4] but the boiling point (44°/130 mm.) differed from ours (92–94°/140 mm.). However, hydrolysis of II with dilute sodium hydroxide yielded 2,3-butadienoic acid, m.p. 63–65°, the same melting point reported by them. III, which was not either ethyl β-chlorocrotonate or -isocrotonate reported by Hatch and Perry,[5] was characterized by the same sequence of reactions used to identify I. Some support for the mechanism was gotten from the fact that when hydrochloric acid was caused to react with II, the only products obtained were II and III.

The low yield obtained in the carboxylation of propargyl chloride was believed to be due to the fact that the boiling point (65°) of propargyl chloride was lower than the reaction temperature (70°). The carboxylation, therefore, was carried out in an autoclave and a 30% yield of a mixture of II and III was isolated. No heat was used, an exotherm was avoided, and 88% of the product was II.

This work is comparable to that of Jones, Whitham, and Whiting[2] in which they carboxylated 3-chloro-3-methyl-1-butyne in the presence of sodium acetate buffer to remove the hydrochloric acid formed and obtained a 34% yield of 4-methylpenta-2,3-dienoic acid along with 11% of its ethyl ester. In the case of propargyl chloride they reported a 6% yield of buta-2,3-dienoic acid, but made no mention of an ester fraction.

Several attempts were made to carboxylate propargyl chloride under an elevated carbon monoxide pressure (400–2000 p.s.i.g.) and it was found that considerably less carboxylation took place. These data indicate it is possible that carbon monoxide inhibits the carboxylation. This conclusion is analogous to that of Natta, Ercoli, Castellano, and Barbieri[6] who, in a study of the hydroformylation reaction, found that above carbon monoxide partial pressures of 10 atm. the percent olefin conversion decreased with increasing pressure. They postulated that the first step involved the reaction of the olefin with cobalt carbonyl to form an olefin-carbonyl complex and carbon monoxide. It is possible, therefore, that the first step of the carboxylation of acetylenic compounds with nickel carbonyl involves the reaction of the two compounds to form an acetylenic-carbonyl complex and carbon monoxide. This has been shown[7] to be the case in the reaction of acetylenes and cobalt carbonyl as shown in equation (2). Carboxylations of

$$R{-}C{\equiv}C{-}R' + Co_2(CO)_8 \longrightarrow RC_2R'Co_2(CO)_6 + 2\ CO \quad (2)$$

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(3) R. U. Lemieux and E. von Rudloff, *Can. J. Chem.*, **33**, 1710 (1955).

(4) G. Eglenton, E. R. H. Jones, G. H. Mansfield, and M. C. Whiting, *J. Chem. Soc.*, 3197 (1954).

(5) L. F. Hatch and R. H. Perry, *J. Am. Chem. Soc.*, **77**, 1137 (1955).

(6) G. Natta, R. Ercoli, S. Castellano, and F. H. Barbieri, *J. Am. Chem. Soc.*, **76**, 4049 (1954).

(7) I. Wender, H. W. Sternberg, H. Greenfield, R. A. Friedel, J. Wotiz, and R. Markby, *J. Am. Chem. Soc.*, **76**, 1457 (1954).

propargyl chloride with cobalt carbonyl both in the absence of carbon monoxide and under elevated carbon monoxide pressure were attempted and yielded no carboxylation product.

EXPERIMENTAL

Carboxylation of propargyl bromide. A mixture of freshly distilled propargyl bromide (119 g., 1.0 m.), absolute ethanol (100 ml.), and concentrated hydrochloric acid (59.5 g., 0.6 m.) was placed into a 4-necked flask having a stirrer, thermometer, dropping funnel, and condenser. Nitrogen was swept through the system while the stirred solution was heated to 70°. At this temperature a small portion of a solution of nickel carbonyl (39 g., 0.23 m.) in absolute ethanol (100 ml.) was added to the reaction mixture. After a short induction period an exothermic reaction took place and the solution was kept at 70° (heating mantle removed) by the rate of addition of carbonyl solution. At the end of the reaction (1.5 hr.) the temperature gradually dropped to 45°. Ether was added, the pot was heated, and everything distilling off below 82° was discarded. The contents were cooled, dissolved in ether, and washed with 5% sodium bicarbonate solution. The dried (magnesium sulfate) layer was distilled through a 6-in. Vigreux column and yielded 46 g. (24%) of ethyl 3-bromo-3-butenoate boiling at 82° (23 mm.). The crude product was redistilled through a helix-packed Todd column (900 × 12 mm.) and there was obtained 33.2 g. of product boiling at 85° (25 mm.); n_D^{23} 1.4650. Infrared: 5.75 μ (vs), 6.12 μ (s), 8–9 μ (vs), 11.1 μ (vs).

Anal. Calcd. for $C_6H_9O_2Br$: Br, 41.4; Hydrogen No., 2.0; Sapon. Equiv., 193. Found: Br (hydrogenation), 39.8, Br (caustic), 39.1; Hydrogen No., 1.9; Sapon. Equiv., 191.

The experiment was repeated using acetic acid instead of hydrochloric acid and a 21% yield of the same product was obtained.

Proof of structure of ethyl 3-bromo-3-butenoate. (a) Carbon skeleton. (1) The carboxylation product (13 g., 0.07 m.) was hydrogenated over pre-reduced platinum oxide catalyst at atmospheric pressure and room temperature. The absorption was 1.9 moles of hydrogen per mole of compound. Solid potassium hydroxide (4 g., 0.07 m.) was added to the alcoholic ester solution and the mixture was refluxed 1 hr. The ethanol was removed under reduced pressure to give 5.8 g. of solid. This potassium salt was converted by standard methods into the *p*-bromophenacyl ester, the *p*-phenylphenacyl ester, and the *p*-toluidide. Table I summarizes the results. The acid, therefore, was *n*-butyric acid.

TABLE I

Derivative	Literature Value, M.P., °C.		Observed M.P., °C.
	Isobutyric Acid	*n*-Butyric Acid	
p-Bromophenacyl ester	77[a]	63[a]	62–63[e]
p-Phenylphenacyl ester	89[b]	82[b]	79–80
p-Toluidide	106[c]	73[d]	68–70

[a] W. L. Judefind and E. E. Reid, *J. Am. Chem. Soc.*, **42,** 1055 (1920). [b] P. W. Clutterbuck, H. Raistrick, and F. Reuter, *Biochem. J.*, **29,** 880 (1935). [c] L. F. Fieser, J. L. Hartwell, and A. M. Seligman, *J. Am. Chem. Soc.*, **58,** 1226 (1936). [d] P. W. Robertson, *J. Chem. Soc.*, **115,** 1220 (1919). [e] Authentic sample melted at 61–62°; mixed m.p. with unknown sample, 61–62°.

(2) Carboxylation product (50 g., 0.26 m.) was dissolved in 125 ml. anhydrous ether and over a period of 3 hr. lithium aluminum hydride (9.5 g., 0.25 m.) was added with gentle refluxing. The reaction was stirred overnight and water was added to the mixture at such a rate that there was gentle refluxing. The solution was filtered, the filtrate was dried (magnesium sulfate), distilled under reduced pressure through a 6-in. Vigreux column, and there was isolated 11.6 g. of 3-bromo-3-buten-1-ol boiling at 80–85° (16 mm.); n_D^{30} 1.4949.

Anal. Calcd. for C_4H_7OBr: Br, 53.0; Hydrogen No., 2.0; Hydroxyl No., 1.0. Found: Br, 53.0; Hydrogen No., 2.1; Hydroxyl No., 1.0.

3-Bromo-3-buten-1-ol was converted into its 3,5-dinitrobenzoate which after two recrystallizations (ethanol-water) melted at 57.5–58.0°.

Anal. Calcd. for $C_{11}H_9N_2O_6Br$: C, 38.3; H, 2.6; N, 8.1. Found: C, 39.0; H, 2.7; N, 8.3.

3-Bromo-3-buten-1-ol (1.1 g.) was dissolved in 25 ml. benzene and completely hydrogenated over pre-reduced platinum oxide catalyst at atmospheric pressure and room temperature and 2.0 moles of hydrogen was absorbed per mole of compound. The catalyst was removed by filtration and 1 g. of alpha-naphthyl isocyanate was added. The solution was warmed on the steam bath and the benzene removed by evaporation. *n*-Hexane was added and a high melting solid separated. The filtrate was concentrated and a solid melting at 60–65° separated. Recrystallization three times from *n*-hexane raised the m.p. to 68–69°. The melting point of a mixture of this compound and the alpha-naphthylurethane of *n*-butanol (m.p. 70°) was 68–69°.

(b) *Location of bromine atom.* Ethanol (40 ml.) was added to a mixture of propargyl bromide carboxylation product (10 g., 0.05 m.) and 150 ml. water containing 5 g. (0.13 m.) sodium hydroxide until the solution was homogeneous and the mixture was allowed to stand overnight at room temperature. Concentrated hydrochloric acid (15 ml.) was added and the solution was heated 1 hr. on the steam bath. The solution was cooled and a solution of 10 g. (0.05 m.) of 2,4-dinitrophenylhydrazine in 20 ml. concentrated sulfuric acid and 5 ml. water was added. There was obtained 5 g. (0.02 m.) of acetone 2,4-dinitrophenylhydrazone melting at 125–126°. No depression was observed on the melting point of a mixture of it and authentic acetone 2,4-dinitrophenylhydrazone.

(c) *Location of the double bond. (1) Permanganate-periodate oxidation.* A sample of the compound was oxidized according to the method of Lemieux and Rudloff.[3] Propargyl bromide carboxylation product (10 ml. of a solution made by dissolving 3 drops of compound in 300 ml. water) was adjusted to *p*H 7.0–7.6 with $0.1N$ potassium carbonate. Then 10 ml. of $0.02M$ potassium meta-periodate and 1 ml. of $0.005N$ $KMnO_4$ were added. The solution was made up to 25 ml. and a 5 ml. aliquot was removed and added to a mixture of 2 ml. of $1M$ sodium arsenite and 2 ml. of $2N$ sulfuric acid. The solution was allowed to stand 15 min. and then a 1 ml. aliquot was added to 10 ml. of chromotropic acid reagent (1 g. of acid dissolved in 100 ml. of H_2O and the solution made to 500 ml. with 2:1 v/v sulfuric acid-water mixture) and heated on a boiling water bath for 30 min. An intense violet color appeared signifying the presence of a terminal methylene group.

(2) *Ozonolysis of 3-bromo-3-buten-1-ol.* 3-Bromo-3-buten-1-ol, (1 g.) was dissolved in 100 ml. of methanol and this solution was ozonized (Welsbach Corp. Model T-23 Laboratory Ozonator) at 0° for 100 min. Then 1.5 g. of 2,4-dinitrophenylhydrazine in 5 ml. of concentrated sulfuric acid was added. A small amount of amorphous solid precipitated. The addition of water to the filtrate yielded a yellow compound melting at 140–148°. Recrystallization from ethanol (charcoal) gave a solid melting at 166–168°. The melting point of a mixture of it and acetaldehyde 2,4-dinitrophenylhydrazone (m.p. 167–168°) showed melting point depression, m.p. 130+°; but with authentic formaldehyde 2,4-dinitrophenylhydrazone (m.p. 166–167°) no depression, m.p. 166–167°.

Stoichiometric carboxylation of propargyl chloride with *nickel carbonyl.* Propargyl chloride (50 g., 0.66 m.), acetic acid (30 g., 0.66 m.), water (12 g., 0.66 m.), 95% ethanol (38 g., 0.83 m.), and hydroquinone (trace) were placed in Dry Ice and then placed in a stainless steel autoclave of 300 ml. capacity. Nickel carbonyl (26 g., 0.15 m.), was frozen in a test tube and the open tube carefully placed in the autoclave. The autoclave was sealed and rocked for 1 hr., during which time no heat evolution was observed. The contents were extracted with ether, the ether solution dried (magnesium sulfate), stripped, and the residue distilled under reduced pressure (nitrogen bleeder) through a 6-in. Vigreux column. There was obtained 21 g. of a mixture which was 88% ethyl 2,3-butadienoate (II) and 12% ethyl 3-chloro-3-butenoate (III). A portion of the product was distilled through a Todd column (900 × 12 mm.) at reduced pressure and compounds II and III were obtained.

II boiled at 92–94° (140 mm.); n_{D}^{24} 1.4578. It exhibited infrared absorptions at 5.06 and 5.13 microns characteristic of the terminal allenic group, and at 5.82, 7.95, and 8.5 microns characteristic of an alpha,beta-unsaturated ester.

Anal. Calcd. for $C_6H_8O_2$: Cl, 0.0; Hydrogen No., 2.0; Sapon. Equiv., 112. Found: Cl, 0.3; Hydrogen No., 1.9; Sapon. Equiv., 121.

Saponification of II for 10 min. on a steam bath with 1*N* sodium hydroxide, followed by acidification to *p*H 4.5 with dilute sulfuric acid and extraction with ether yielded 2,3-butadienoic acid, m.p. 63–65° (4).

III boiled at 67° (75 mm.); n_{D}^{24} 1.4389. It exhibited infrared absorptions at 5.76 and 8.40 microns characteristic of an ester group. Absorptions at 6.12 and 11.16 microns indicated the presence of a branched terminal vinyl group. No allenic group absorption could be detected in this sample.

Anal. Calcd. for $C_6H_9O_2Cl$: Cl, 23.6; Hydrogen No., 2.0; Sapon. Equiv., 74.0. Found: Cl, 23.5; Hydrogen No. 2.1; Sapon. Equiv., 75.6.

Reaction of ethyl 2,3-butadienoate (II) *with concentrated hydrochloric acid.* II (3.1 g., 0.03 m.) and 12*N* hydrochloric acid (3.5 ml., 0.03 m.) were mixed with 95% ethanol (10 ml.) at room temperature with stirring. After being allowed to sit overnight, the solution was warmed on a steam bath for 15 min. and allowed to sit 1 hr. while cooling. Water was added, the layers were separated, and the organic layer was washed again with water. The water layers were combined and found by titration to contain 0.016 m. hydrochloric acid, *i.e.*, about half had reacted. The organic layer (2.3 g.) was dissolved in ether, extracted with 5% sodium bicarbonate, dried over magnesium sulfate, filtered, and concentrated. An ester residue (0.7 g.) was obtained which infrared analysis indicated was a mixture of II and III.

Proof of structure of ethyl 3-chloro-3-butenoate (III). (a) *Carbon skeleton.* A sample of compound III was hydrogenated and saponified in a manner similar to that done to ethyl 3-bromo-3-butenoate (see above). The *p*-bromophenacyl ester made from the sodium salt of the acid melted at 63–64°. The melting point of a mixture of it and authentic *p*-bromophenacyl-*n*-butyrate showed no depression.

(b) *Location of the chlorine atom.* A portion of the ethyl 3-chloro-3-butenoate was saponified, acidified, and then treated with 2,4-dinitrophenylhydrazine as was done was to ethyl 3-bromo-3-butenoate (see above). There was obtained a 2,4-dinitrophenylhydrazone melting at 122–125°. The melting point of a mixture of it and authentic acetone 2,4-dinitrophenylhydrazone showed no depression.

Catalytic carboxylation of propargyl chloride with nickel carbonyl. A series of carboxylations was run and the following is a description of a typical experment. Propargyl chloride (50 g., 0.66 m.), acetic acid (30 g., 0.66 m.), water (12 g., 0.66 m.), 95% ethanol (48 g., 1.04 m.), and hydroquinone (trace) were placed in Dry Ice and then placed in a stainless steel autoclave of 300 ml. capacity. Nickel carbonyl (2.6 g., 0.02 m.), was frozen in a test tube and the open tube placed in the autoclave and the autoclave sealed. The system was charged with 2000 p.s.i.g. carbon monoxide and the system was heated and rocked at 90° for 2 hr. The cold absorption was 1400 p.s.i. The contents (26 g.) were extracted with ether, the ether solution dried (magnesium sulfate), and the ether removed under reduced pressure (nitrogen bleeder). The residue was distilled under reduced pressure through a 6-in. Vigreux column and yielded 13 g. (12%) of material boiling at 75–80° (30 mm.), n_{D}^{23} 1.4330. The product by analysis was 73% ethyl 3-chloro-3-butenoate.

Attempted carboxylation of propargyl chloride with cobalt carbonyl. Cobalt carbonyl solution in benzene (0.1 g./ml.) was made from cobalt carbonate and $CO:H_2$ (1:1) according to the directions of Wender, Greenfield, and Orchin.[8] Proppargyl chloride was treated with cobalt carbonyl in reactions analogous to those done with nickel carbonyl and in neither the stoichiometric nor the catalytic reaction was an insoluble carboxylation product obtained.

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VERONA, PA.

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[8] I. Wender, H. Greenfield, and M. Orchin, *J. Am. Chem. Soc.*, **73**, 2656 (1957).