Competitive Acetylation Reactions.—All experiments were carried out under similar conditions. The acetyl chloride–aluminum chloride complex, dissolved in dry methylene chloride, was added dropwise to a stirred methylene chloride solution of the competing compounds. All reactions were carried out at 0° in a nitrogen atmosphere. In those reactions in which acetylferrocene was a competitor, an equivalent of aluminum chloride was added to the reaction mixture prior to the addition of the acetylating reagent. The molar equivalent of acetylating reagent never exceeded, and was generally equivalent to, that of the competitor present in lesser amount. The reactions were terminated by addition of ice-water, and the solutions worked up as previously described. Reaction products were separated chromatographically on 350–650 g. of Merck, acid-washed alumina (2% water added).

Reaction of p-Methoxyphenylferrocene with Diazotized p-Nitroaniline.—An ice-cold aqueous solution of diazotized p-nitroaniline, prepared from 6.9 g. (0.05 mole) of the amine, was added with stirring to an aqueous solution of p-methoxyphenylferricenium chloride (4.0 g., 0.014 mole). Reaction was then allowed to proceed at 0° for 20 hours. An aqueous solution of sodium bisulfite was then added and the solution was extracted repeatedly with ether. The combined ether extract was washed to neutrality, dried over magnesium sulfate and filtered. A solution of ferric chloride (2.3 g., 0.016 mole) in ether was then added and the resulting ferricenium salts were extracted into water. The combined aqueous extract was treated with bisulfite, extracted with ether and the ether extracts combined, washed to neutrality and dried over magnesium sulfate. After removal of solvent, the residue was chromatographed on 1 kg. of Merck acid-washed alumina employing low boiling petroleum ether as eluent. Several bands developed.

The first gave 37 mg. of 4-methoxy-2(4'-nitrophenyl)-phenylferrocene as red crystals, m.p. 158–159°. The compound exhibits a second crystalline form, m.p. 178–180°.

Anal. Calcd. for $C_{23}H_{19}NO_3Fe$: C, 66.83; H, 4.60; N, 3.38. Found: C, 66.78; H, 4.64; N, 3.27.

A second band gave 177 mg. of a purple oil which crystallized after 9 months. Fractional crystallization of this material, using petroleum ether gave 150 mg. of 1-p-methoxyphenyl-2-p-nitrophenylferrocene as purple crystals, m.p. 146–148°.

Anal. Calcd. for $C_{23}H_{19}NO_3Fe$: C, 66.83; H, 4.60; H, 3.38. Found: C, 67.0; H, 4.9; N, 3.5.

In addition, 2 mg. of 4-methoxy-3(4'-nitrophenyl)-phenylferrocene, m.p. 210–212°, was obtained. Additional material was obtained in a second experiment.

Anal. Calcd. for $C_{23}H_{19}NO_3Fe$: C, 66.83; H, 4.60; N, 3.38. Found: C, 67.03; H, 4.62; N, 3.57.

A third band gave 217 mg. of 1-p-methoxyphenyl-1'-p-nitrophenylferrocene as purple plates, m.p. 214–216° (from ether).

Anal. Calcd. for $C_{23}H_{19}NO_3Fe$: C, 66.82; H, 4.60; N, 3.38. Found: C, 66.82; H, 4.54; N, 3.62.

The fourth band gave 12 mg. of 1-p-methoxyphenyl-1'x-bis-p-nitrophenylferrocene, m.p. 165.5–167.5°.

Anal. Calcd. for $C_{29}H_{22}N_2O_5Fe$: C, 65.19; H, 4.12; N, 5.19; Found: C, 65.09; H, 4.12; N, 5.23.

In a second experiment employing p-methoxyphenylferrocene rather than its ferricenium salt, the remaining isomer, 9 mg. of 1-p-methoxyphenyl-3-p-nitrophenylferrocene, m.p. 193–195°, was isolated from a small band following the 1,1'-isomer.

*Anal.* Calcd. for $C_{23}H_{19}NO_3Fe$: C, 66.83; H, 4.60. Found: C, 66.43; H, 4.91.

Hydroboration of Allenes

BY DEVADAS DEVAPRABHAKARA[1] AND PETE D. GARDNER
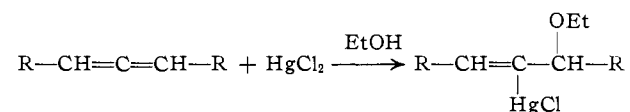
The hydroboration of 1,2-cyclononadiene followed by oxidation of the intermediate organoborane afforded cyclononanone and smaller amounts of cyclononanol and cyclononene. 1,2-Cyclodecadiene and 1,2,6-cyclononatriene behaved similarly. From the former was obtained principally cyclodecanone; the latter gave mainly cyclononene-6-one. It is concluded that the attack of diborane on the allene linkage occurs primarily at the central carbon atom.

Factors which determine the course of addition of unsymmetrical addenda to allenes are not at all understood. Hydrogen chloride, for example, adds to most allenes with placement of the chlorine atom at the central atom of the three-atom unsaturation, e.g.[2,3]

$$CH_2=C=CH-CH_3 + HCl \longrightarrow CH_3-CCl=CH-CH_3$$
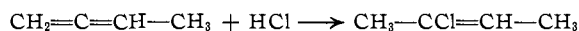
Mercuric chloride, on the other hand, adds with mercury bonding to the central atom of the three.[4] This reaction probably proceeds through a carbonium ion intermediate. The present report is concerned with

$$R-CH=C=CH-R + HgCl_2 \xrightarrow[\text{EtOH}]{} R-CH=\overset{\overset{\displaystyle OEt}{|}}{C}-\underset{\underset{\displaystyle HgCl}{|}}{CH}-R$$

the addition of diborane, a reagent well known as an electrophile[5] which adds through a four-center transition state.

The reaction of 1,2-cyclononadiene with diborane (generated in situ[6]) followed by an oxidative work-up employing hydrogen peroxide and sodium hydroxide

afforded mainly cyclononanone. A smaller amount of cyclononanol and cis-cyclononene was also obtained. These results suggest that the principal organoborane, tris-1-cyclononenylborane, is that formed from attack of boron at the central carbon atom of the allene linkage. It is the organoborane which would be formed by hydroboration of cyclononyne.[7] The formation of cyclononene is best interpreted as evidence for the competitive formation of tris-3-cyclononenylborane. This, by analogy with the facile hydrolysis of triallylborane,[8] would be expected to give rise to cyclononene under the experimental conditions employed. There exists ample evidence that other types of organoboranes are not hydrolyzed rapidly at room temperature.[9] The formation of cyclononanol is expected once it is recognized that the principal organoborane in the mixture is tris-1-cyclononenylborane. The dihydroboration of acetylenes affords (via an organoborane analogous to the nonenylborane involved here) the corresponding alcohol.[7] Cyclononanol would therefore appear to be the result of over-hydroboration. The mechanism suggested[7] for this interesting reduction seems quite reasonable.

Data presented thus far are summarized as

(1) American Oil Company Fellow, 1961–1962.

(2) G. F. Hennion and J. C. Sheehan, *J. Am. Chem. Soc.*, **71**, 1964 (1949).

(3) T. L. Jacobs and R. N. Johnson, *ibid.*, **82**, 6397 (1960).

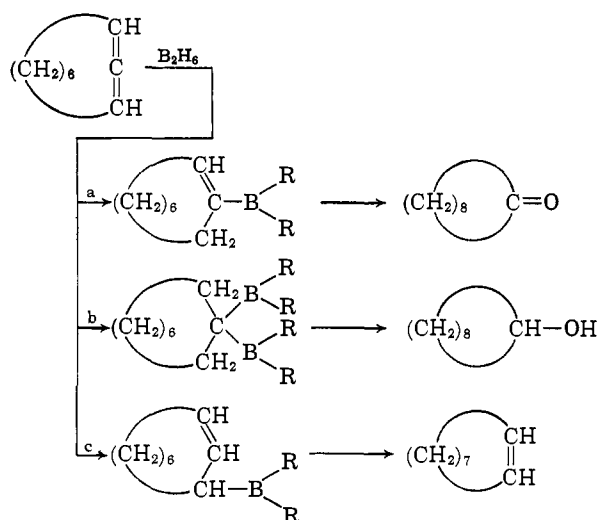(4) R. K. Sharma, B. A. Shoulders and P. D. Gardner, unpublished.

(5) H. C. Brown, "Hydroboration," W. A. Benjamin, Inc., New York, N. Y., 1962.

(6) H. C. Brown and B. C. Subba Rao, *J. Am. Chem. Soc.*, **81**, 6428 (1959).

(7) H. C. Brown and G. Zweifel, *ibid.*, **83**, 3834 (1961).

(8) B. M. Mikhailov and F. B. Tutorskaya, *Doklady Akad. Nauk SSSR*, **123**, 479 (1958); *Chem. Abstr.*, **53**, 6990 (1959).

(9) *Cf.*, H. C. Brown and K. J. Murray, *J. Am. Chem. Soc.*, **81**, 4108 (1959).

Partial confirmation of these conclusions (path b) was obtained by the treatment of 1,2-cyclononadiene with an excess of diborane. The major product was cyclononanol, while cyclononene and cyclononanone were formed in smaller amounts.

Similar results were obtained with 1,2-cyclodecadiene. The same procedure converted this allene to cyclodecanone and smaller amounts of cyclodecanol and *cis*-cyclodecene.

The high degree of reactivity of the allene linkage relative to that of an isolated double bond is illustrated with the behavior of 1,2,6-cyclononatriene. The hydroboration–oxidation sequence afforded mainly cyclononene-6-one along with a small amount of an unidentified alcohol.
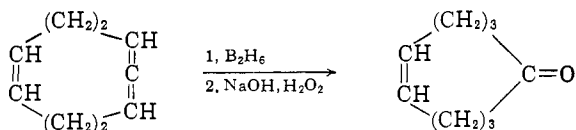
2,3-Nonadiene was examined to determine if the mode of hydroboration observed with the cyclic compounds is entirely general. Although its conversion was not quite as clean, the principal product obtained was the expected 3-nonanone.

Of the organoboranes prepared as intermediates in this study, only one was submitted to protonolysis conditions. Tris-1-cyclononenylborane underwent complete protonolysis (acetic acid) at room temperature to give *cis*-cyclononene. The facility of this reaction is consistent with that observed[7] with the substituted vinylboranes derived from acetylenes.

The observed orientation of addition in these reactions could be dictated solely by differences in steric requirement about the two carbon atoms (or three in the case of unsymmetrical allenes) in question. Alternatively, it could be due in part to the greater susceptibility of the central atom to electrophilic attack. Although a clear choice cannot be made on the basis of hydroboration experiments alone, these results suggest that the latter is an important factor even though a four-center transition state is involved.

Experimental[10]

Monohydroboration of 1,2-Cyclononadiene.—The hydroboration apparatus consisted of a 250-ml. three-necked flask outfitted with a mechanical stirrer, a pressure-equilibrated dropping funnel and an inlet and outlet (top of the condenser) for nitrogen. In the flask were placed 18.4 g. (0.15 mole) of 1,2-cyclononadiene[11–14] in 25 ml. of diglyme and a solution of 1.8 g. (0.045

mole) of sodium borohydride in 45 ml. of diglyme. A solution of 8.5 g. (0.060 mole) of freshly distilled boron trifluoride ether complex in 12.5 ml. of diglyme was poured into the dropping funnel and the entire system was purged with nitrogen. The reactor was cooled in ice and, while stirring, the boron trifluoride solution was added (1 hour). The mixture was allowed to stand at 0° for 0.5 hour and then at 30° for 2 hours. It was then cautiously treated with 10 ml. of water followed by 20 ml. of 3 N sodium hydroxide. A total of 20 ml. of 30% hydrogen peroxide was added in several portions at such a rate that gentle reflux was maintained. After being stirred for an additional hour, the mixture was extracted with several portions of ether. The extract was washed repeatedly with ice-water and then processed in the usual manner. Fractionation of the reaction mixture afforded 2.5 g. of *cis*-cyclononene, b.p. 56–58° (14 mm.), and 13.5 g. of material boiling between 95 and 100° (14 mm.).

The *cis*-cyclononene was chromatographically pure and had a retention time on a silver nitrate column identical with that of an authentic sample.[12] Its infrared spectrum was identical with that of authentic material.

The second fraction (95–100°) exhibited strong carbonyl absorption and only very weak hydroxyl absorption in the infrared. Vapor–liquid chromatography on a polyethylene glycol column showed the alcohol to be a 3.7% contaminant in the ketone. The semicarbazone derivative, m.p. 184–185°, did not depress the melting point of authentic cyclononanone semicarbazone. Regeneration[15] of the ketone from the semicarbazone afforded pure cyclononanone, b.p. 94° (12 mm.), n^{20}D 1.4724 (lit.[16] b.p. 94–95° at 13 mm., n^{20}D 1.4729). The identity of the alcohol contaminant as cyclononanol was surmised by a comparison of its chromatographic retention time with that of an authentic sample and from the experiment which follows.

Dihydroboration of 1,2-Cyclononadiene.—Following the procedure described for monohydroboration, 18.3 g. (0.15 mole) of 1,2-cyclononadiene,[11–14] 3.6 g. (0.090 mole) of sodium borohydride and 17 g. (0.12 mole) of boron trifluoride ether complex were allowed to react. The crude product obtained from the usual isolation procedure was fractionally distilled to give 2.0 g. of *cis*-cyclononene and 10.5 g. of a mixture of cyclononanone (12%) and cyclononanol (88%). The former was identified both by a comparison of its retention time with that of an authentic sample and by recognition of several of its infrared absorption bands in a spectrum of the mixture. The identity of the latter was established through its *p*-nitrobenzoate derivative, m.p. and mixture m.p. 82–83° (lit.[17] 83°).

Monohydroboration of 1,2-Cyclononadiene Followed by Protonolysis.—The organoborane was prepared as previously described from 12.2 g. (0.10 mole) of 1,2-cyclononadiene, 1.2 g. (0.030 mole) of sodium borohydride and 5.6 g. (0.040 mole) of boron trifluoride ether complex. The mixture was allowed to stand at room temperature for 2 hours following the addition of boron trifluoride solution and then treated with a small amount of ethylene glycol. Acetic acid (30 ml.) was added and the mixture was allowed to stand for 10 hours before being poured into ice-water. The crude product was isolated by extraction with ether and the usual processing of the extract. Distillation afforded 9.2 g. of colorless liquid, b.p. 56–58° (12 mm.). Vapor–liquid chromatography showed it to be a mixture of *cis*-cyclononene (95%) and cyclononane (5%). Chromatographic retention times of authentic samples on a silver nitrate column corresponded precisely with those of components of the mixture. Infrared bands exhibited by the mixture were those expected for the two substances and no non-assignable peaks were observed.

Monohydroboration of 1,2-Cyclodecadiene.—1,2-Cyclodecadiene was prepared from 10,10-dibromobicyclo[7.1.0]decane[14] by the method used for the synthesis of 1,2-cyclononadiene,[11,12] in 95% yield. Its properties corresponded well with those reported.[14]

The procedure described for 1,2-cyclononadiene was followed without change. From 13.8 g. (0.10 mole) of 1,2-cyclodecadiene, 1.2 g. (0.030 mole) of sodium borohydride and 5.6 g. (0.040 mole) of boron trifluoride ether complex, there was obtained 1.1 g. of *cis*-cyclodecene, b.p. 72–74° (12 mm.), and 7.5 g. of a mixture of cyclodecanone (87%) and cyclodecanol (13%), b.p. 100–110° (12 mm.). The olefin was identified by a comparison of its chromatographic retention time and infrared spectrum with those of an authentic sample. The ketone–alcohol mixture was analyzed both qualitatively and quantitatively by vapor–liquid chromatography using authentic samples for comparison. The

(10) Melting points are corrected, but boiling points are not.

(11) W. R. Moore and H. R. Ward, *J. Org. Chem.*, **25**, 2073 (1960).

(12) P. D. Gardner and M. Narayana, *ibid.*, **26**, 3518 (1961).

(13) L. Skattebøl, *Tetrahedron Letters*, **5**, 167 (1961).

(14) W. J. Ball and S. R. Landor, *Proc. Chem. Soc.*, 143 (1961).

(15) E. B. Hershberg, *J. Org. Chem.*, **13**, 542 (1948).

(16) L. Ruzicka, P. A. Plattner and H. Wild, *Helv. Chim. Acta*, **26**, 1631 (1943).

(17) L. Ruzicka, V. Prelog, K. Kobelt and P. Barman, *ibid.*, **32**, 256 (1949).

semicarbazone derivative of the ketone melted at 200–201° alone and when mixed with authentic material.

Monohydroboration of 1,2,6-Cyclononatriene.—Following the procedure described previously, 18.0 g. (0.15 mole) of 1,2,6-cyclononatriene[13] was allowed to react with diborane produced from 1.8 g. (0.045 mole) of sodium borohydride and 8.5 g. (0.060 mole) of boron trifluoride ether complex. The crude product, isolated in the usual way, was fractionated to give 4.5 g. of un-reacted starting material, b.p. 62–63° (14 mm.,) and 8.0 g. of a mixture, b.p. 95–100° (14 mm.). The infrared spectrum possessed weak hydroxyl absorption and strong carbonyl absorption. Vapor–liquid chromatography showed only two components in the ratio 95/5 and on the basis of the infrared data this was interpreted as a ketone/alcohol ratio. A semicarbazone derivative was prepared in the usual way and purified by three crystallizations from 50% ethanol; m.p. 170–171°.

Anal. Calcd. for $C_{10}H_{17}ON_3$: C, 61.50; H, 8.77; N, 21.52. Found: C, 61.47; H, 8.57; N, 21.39.

Regeneration[15] of the ketone from its semicarbazone afforded a pure sample, b.p. 96° (14 mm.), $n^{25}D$ 1.4931. A solution of 1.0 g. (7.2 mmoles) was ozonized at −30° with a *ca.* 4% ozone–oxygen mixture until the appearance of iodine in an adjoining potassium iodide trap. The mixture was then poured into a solution prepared by mixing 25 ml. of 10% sodium hydroxide with 25 ml. of 30% hydrogen peroxide. The flask was fitted with a reflux condenser and cautiously warmed until the onset of a vigorous reaction. When this subsided, the mixture was heated under reflux for 6 hours after which time it gave a negative test with sodium iodide. The usual work-up procedure by ether extraction afforded 0.85 g. of δ-ketoazelaic acid which melted at 110° after two recrystallizations from water (lit.[18] 110.5°). The semi-

(18) K. Sorm, *Collection Czech. Chem. Commun.*, **12**, 150 (1947).

carbazone derivative had m.p. 180–181° after crystallization from aqueous ethanol (lit.[18] 181°).

Monohydroboration of 2,3-Nonadiene.—2,3-Nonadiene was prepared from 2-octene[19] by the method used for the synthesis of all allenes required for this study.[11–13] Its preparation was un-complicated and will therefore not be described here.[20] It had properties identical with those of a sample prepared by another method.[21]

Following the procedure described for 1,2-cyclononadiene, 12.4 g. (0.10 mole) of 2,3-nonadiene was allowed to react with 1.2 g. (0.030 mole) of sodium borohydride and 5.6 g. (0.040 mole) of boron trifluoride-ether complex. Fractional distillation of the processed reaction mixture afforded 2.5 g. (fraction 1), b.p. 49–52° (20 mm.), and 6.8 g. (fraction 2), b.p. 85–90° (20 mm.). Vapor–liquid chromatography of fraction 1 showed it to be 56% starting material and 44% of a single olefin. No effort was made to identify this substance. Fraction 2 was shown by vapor-liquid chromatography to be 85% of 3-nonanone accompanied by 15% of an alcohol. The semicarbazone derivative melted at 110–112° after two crystallizations from 50% ethanol (lit.[22] 111–112°).

(19) Phillips Petroleum Company.

(20) D. Devaprabhakara, Ph.D. Dissertation, The University of Texas, 1962.

(21) A. A. Petrov and V. A. Kormer, *Doklady Akad. Nauk SSSR*, **125**, 1041 (1959).

(22) R. H. Pickard and J. Kenyon, *J. Chem. Soc.*, 1936 (1913).

The Reaction of Epoxides with Cobalt Hydrocarbonyl and Cobalt Tetracarbonyl Anion

BY RICHARD F. HECK

Cobalt hydrocarbonyl, carbon monoxide and epoxides react at 0° to give high yields of β-hydroxyacylcobalt tetracarbonyls. Complexes from ethylene oxide, propylene oxide and cyclohexene oxide have been isolated as their mono-(triphenylphosphine) derivatives. The cyclohexene oxide product was cleaved with iodine and methanol and shown to be the *trans* isomer. Isobutylene oxide gave mainly the isomer in which cobalt was attached to the primary carbon atom. Cobalt carbonyl anion in hydroxylic solvents will also react with epoxides at higher temperatures to give esters of β-hydroxyacids. Trimethylene oxide reacts readily with cobalt hydrocarbonyl and carbon monoxide to form 4-hydroxybutyrylcobalt tetracarbonyl which has been isolated as the triphenylphosphine derivative. The 4-hydroxybutyrylcobalt tetracarbonyl reacts with dicyclohexylethyl-amine to produce cobalt carbonyl anion and γ-butyrolactone. The mechanism of the cobalt hydrocarbonyl-epoxide reaction is discussed and explanations for the known reactions of epoxides with carbon monoxide are presented.
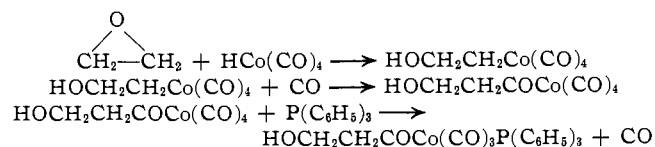
Introduction

The literature records several examples of the reaction of epoxides with carbon monoxide and water or alcohols using a cobalt salt or cobalt carbonyl as catalyst.[1–5] Generally, hydroxyacids, their derivatives or rearranged carbonyl products or both are formed. Employing the methods used in our study of the hydro-formylation reaction,[6] it has been possible to isolate organocobalt complexes which appear to be intermediates in the epoxide carboxylation reaction. The structures of the intermediates provide considerable evidence about the mechanism of the reaction.

Results

Epoxides.—Ethylene oxide in ether solution reacts rapidly with cobalt hydrocarbonyl at 0°. Under one atmosphere of carbon monoxide, 0.96 mole of gas was absorbed in less than an hour and the absorption ceased. The infrared spectrum of the reaction mixture had a strong carbonyl band at 5.89 μ as well as co-

(1) M. Séon and J. Leleu, U. S. Patent 2,782,226 (1957).

(2) H. Nienburg and G. Elschnig, German Patent 1,066,572 (1959).

(3) J. L. Eisenmann, R. L. Yamartino and J. F. Howard, Jr., *J. Org. Chem.*, **26**, 2102 (1961).

(4) W. A. McRae and J. L. Eisenmann, U. S. Patent 3,024,275 (1962).

(5) J. L. Eisenmann, *J. Org. Chem.*, **27**, 2706 (1962).

(6) R. F. Heck and D. S. Breslow, *J. Am. Chem. Soc.*, **83**, 4023 (1961).

ordinated carbonyl bands at 4.76 and 4.95 μ suggesting that 3-hydroxypropionylcobalt tetracarbonyl had been formed. This structure was confirmed by isolating the complex as the triphenylphosphine derivative. Addition of excess triphenylphosphine to the ethylene oxide–cobalt hydrocarbonyl reaction mixture led to the evolution of 0.97 mole of gas. Evaporation of the solvent and several recrystallizations from ether–pentane gave pale yellow crystals of 3-hydroxypropionyl-cobalt tricarbonyl triphenylphosphine, m.p. 95–100° dec.

$$CH_2\overset{O}{\underset{\diagdown\diagup}{-}}CH_2 + HCo(CO)_4 \longrightarrow HOCH_2CH_2Co(CO)_4$$
$$HOCH_2CH_2Co(CO)_4 + CO \longrightarrow HOCH_2CH_2COCo(CO)_4$$
$$HOCH_2CH_2COCo(CO)_4 + P(C_6H_5)_3 \longrightarrow$$
$$HOCH_2CH_2COCo(CO)_3P(C_6H_5)_3 + CO$$

A similar reaction took place between propylene oxide, carbon monoxide and cobalt hydrocarbonyl. The complex was also isolated as the triphenylphosphine derivative, m.p. ~90° dec. Two isomeric products are possible in this reaction. At 130° Eisenmann[3] reports that propylene oxide in the carboxylation reaction yields a product which is at least 95% the 3-hy-droxybutyrate derivative. It is probable that at 0°