

Title	Cyclopolyolefins Derived from Acetylene
Author(s)	Kunichika, Sango
Citation	Bulletin of the Institute for Chemical Research, Kyoto University (1953), 31(5): 323-335
Issue Date	1953-09-30
URL	<a href="http://hdl.handle.net/2433/75368">http://hdl.handle.net/2433/75368</a>
Right	
Type	Departmental Bulletin Paper
Textversion	publisher

# Cyclopolyolefins Derived from Acetylene

Sango KUNICHIKA\*

(Nozu Laboratory)

Received June 20, 1953

As is well-known, Dr. Reppe achieved a series of epochmaking discoveries, often referred to as Reppe's chemistry, in the field of acetylene chemistry. One of them was a new method of preparation of cyclopolyolefins ( $C_8H_8$ ,  $C_{10}H_8$ ,  $C_{10}H_{10}$  and  $C_{12}H_{12}$ , etc.) by the catalytic polymerization of acetylene.

Since this discovery in 1940, Reppe and his co-workers have made the valuable contributions to the chemistry of 8-membered cyclic carbon compounds. Besides themselves, many other researchers have presented a number of papers on the preparations and reactivities of these compounds and their derivatives.

This paper is but a brief descriptive introduction of the methods of preparation and reactivities of these cyclopolyolefins.

## I. CYCLOÖCTATETRAENE $C_8H_8$

Cycloöctatetraene (C.O.T.) has been prepared by Willstätter<sup>1)</sup> from pseudopelletierine *via* thirteen-steps. But as is mentioned above, Reppe<sup>2)</sup> discovered a new method of preparation of this compound. Namely he carried out the polymerization of acetylene under pressure in the presence of certain nickel catalysts and obtained cyclic hydrocarbons consisting primarily of C.O.T. and higher polymerides.

Twenty grams of anhydrous nickel cyanide, made from nickel chloride and hydrocyanic acid in alcoholic solution and followed by ignition at 175°C, 50 g. of powdered calcium carbide (for the purpose of dehydration of the reaction medium) and 2 l. of tetrahydrofuran (as a solvent) were put in an autoclave of 4 to 5 l. capacity. Air was expelled by nitrogen and under 5 atm. of nitrogen pressure the autoclave was heated to 60 to 70°C with shaking, and then acetylene was introduced to a total pressure of 15 to 20 atm. The reaction was continued for 48 to 60 hours, while acetylene was pumped in from time to time until the absorption stopped. Catalyst and cuprene were filtered off from the reaction product and the filtrate was distilled under reduced pressure. 320 to 400 g. of C.O.T., 50 g. of benzene, and 30 to 50 g. of resins were obtained.

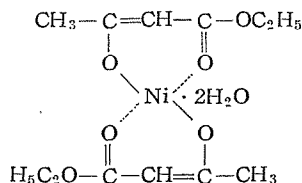
According to Barnes<sup>3)</sup>, acetylene, diluted with an inert gas under a total pressure of 10 to 25 atm., is condensed at 90 to 140°C in the presence of nickel compound catalyst and tetrahydrofuran (as a solvent) which included an antioxidant for elimination or preventing the formation of peroxide of tetrahydrofuran. As such antioxidant,

---

\*国 近 三 吾

there are proposed many compounds, such as *o*- and *p*-polyhydric phenols, oxidizable secondary arylamines, aminophenols, neutral esters of sulfuric acid, and the amounts of them to be used varied from 0.1 to 1.0 % depending on the purity of the solvent. Experiments were tried as follows : 100 cc. of purified tetrahydrofuran, 25 g. of calcium carbide, 25 g. of nickel cyanide, and 1-*tert*-butylcatechol (1 g.) were put in a 2 l. autoclave, and flushed with nitrogen, then with propane at 70 lb/in<sup>2</sup>, and heated to 90°C and acetylene was added until the total pressure attains 200 lb/in<sup>2</sup>, and then reaction was continued under this condition for 14 to 16 hours. The yield of C. O.T. was 55 to 60 g.

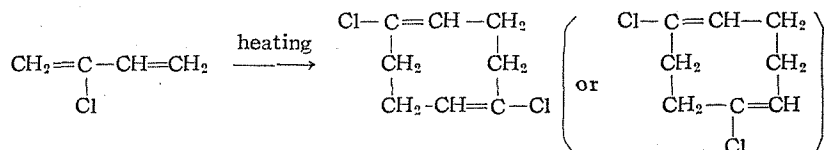
Hagihara<sup>4)</sup> reported the following experimental results : 48 g. of NiCl<sub>2</sub>·6H<sub>2</sub>O was dissolved in 250 cc. of water and to this solution 50 cc. of 28 % ammonia was added and filtered. To the filtrate 52 g. of acetoacetic ethyl ester was poured in and the precipitate was filtered, washed and dried at 100°C for 2 hours under diminished pressure. The pale blue crystals thus formed are considered to be the nickel complex salt of acetoacetic ester having the following chemical structure :



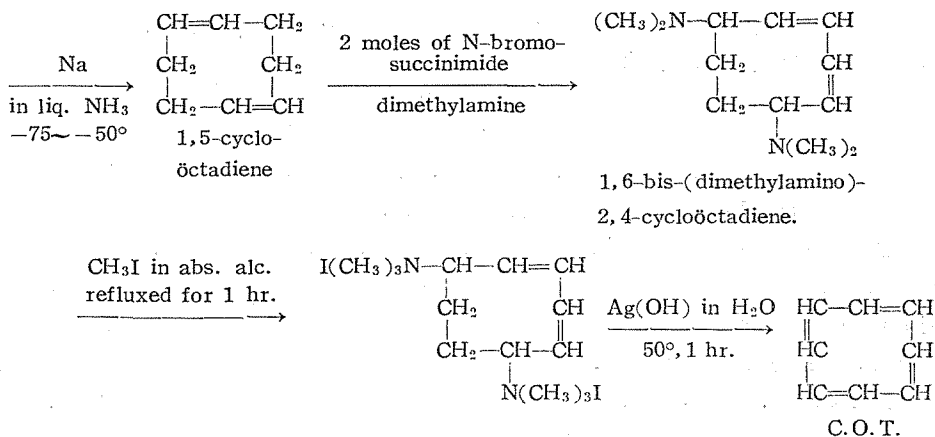
This anhydrous salt 15 g. and benzene 200 cc. were charged in 1 l. autoclave and acetylene was compressed to 16 atm. The autoclave was agitated and heated. At 70°C, the pressure rose to 30 to 32 atm., but after about 30 minutes the reaction started. The initial pressure drop was 3 to 3.5 atm./hr., and acetylene was pumped in to 30 atm. from time to time whenever the pressure dropped to 20 atm. After 30 hours, the absorption speed dropped to 0.5 atm./hr. The reaction product was distilled *in vacuo*, C.O.T. (b.p. 95 ~ 96°C/185mm.) yielded 55 g., or 55 % based on consumed acetylene. Besides this, benzene (about 10 % of C.O.T.) and 2 g. of yellow hydrocarbon C<sub>10</sub>H<sub>10</sub> (b.p. 84 ~ 85°C/20 mm.) were also obtained.

Cope and his co-workers have published those numerous reports on cyclic polyolefins, which have Part 25 up to the present.

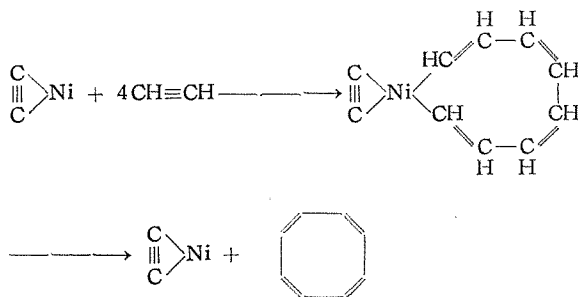
Cope and Bailey<sup>5)</sup> described a seven-steps synthesis of C.O.T. from chloroprene as the following schema : (chloroprene was prepared from acetylene by Nieuwland's method).



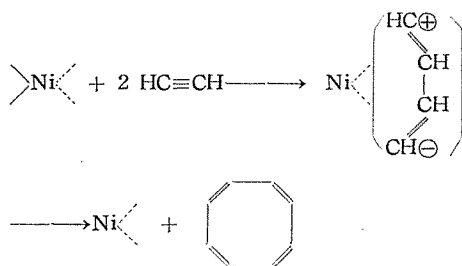
Cyclopolyolefins Derived from Acetylene



On the mechanism of C.O.T. formation, Reppe<sup>69</sup> assumed that nickel or nickel acetylide binds four molecules of acetylene and this nickel-acetylene complex decomposes, giving C.O.T. and regenerating nickel acetylide which may react in the same way again.



Bergmann<sup>70</sup> describes the dimerization of monovinylacetylene, but Hagihara<sup>80</sup> denies Bergmann's idea, on account of the decrease of C.O.T. yield and the increase of C<sub>10</sub>H<sub>10</sub> fraction when monovinylacetylene was treated with acetylene under the same conditions which he had tried in the preparation of C.O.T. He proposed consequently the dimerization theory of acetylene dimer coordinated on nickel catalyst as indicated in the following schema:



C.O.T. has the following physical constants.

Sango KUNICHIKA

B.P. 142 ~ 3°C/760 mm., 42.0 ~ 42.5°C/17 mm.

F.P. -7.0°C

$d_4^{20}$  0.9206  $n_D^{20}$  1.5290

Dielectric constant 2.74/20°C,  $1.5 \times 10^6$  Hertz

Dipole moment  $0.069 \times 10^{-18}$  e.s.u.

To determine the molecular configuration of C.O.T., there are various experiments, such as catalytic hydrogenation followed by oxidation, diene syntheses, measurement of dipole moment, calculation of energy level, Ramann spectrum, ultraviolet and infrared absorption spectra, *etc.*

But C.O.T. reacts with various reagents as if it had different structures, that is, in some reactions the 8-membered ring is left intact, but in others, benzenoid com-

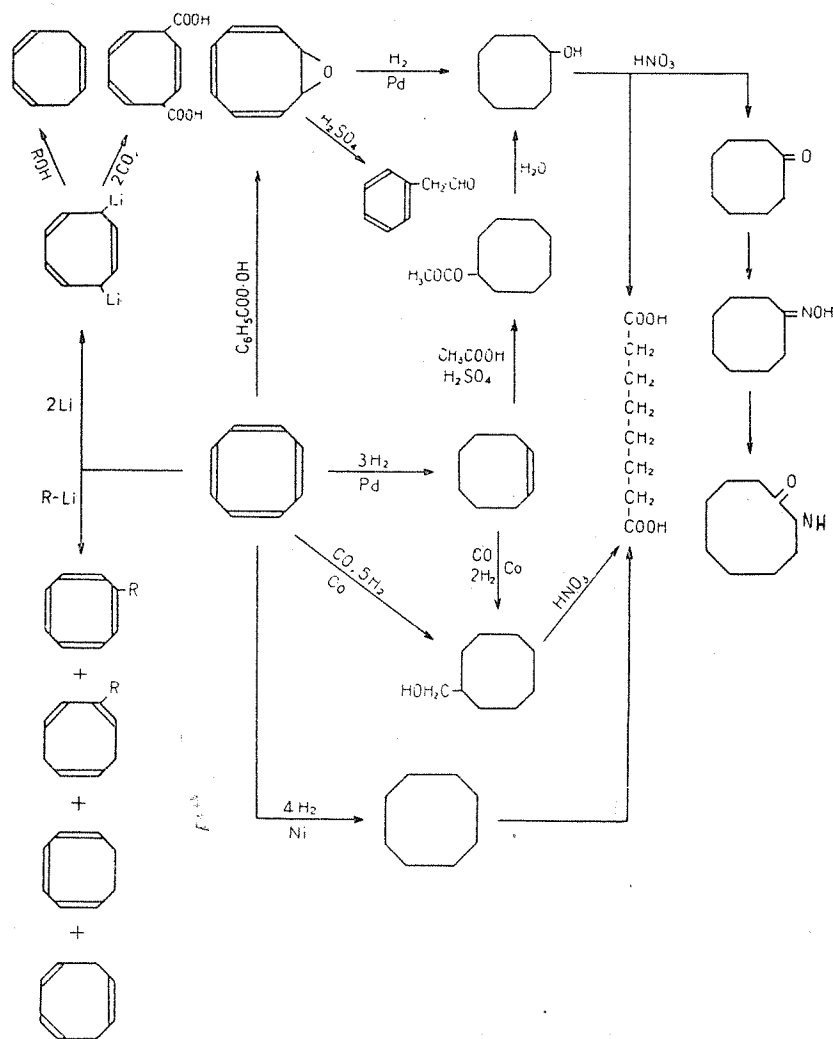
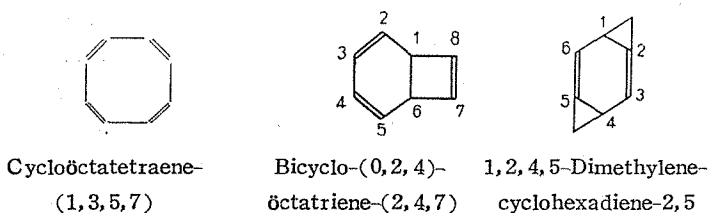


Fig. 1-1. Reactions of C.O.T.

Cyclopolyolefins Derived from Acetylene

pounds such as derivatives of ethyl benzene or *p*-xylene are obtained ; it also acts as the compound having fused ring together with 6-membered and 4-membered ring. From these points of view, the following three types of formula are postulated for C.O.T.



On each of the chemical reactions and the numerous derivatives of C.O.T., there are detailed descriptions in Reppe's voluminous paper<sup>92</sup>. Therefore, I would refrain from dwelling on them, except a few experiments carried out by other researchers and would illustrate in the following figures.

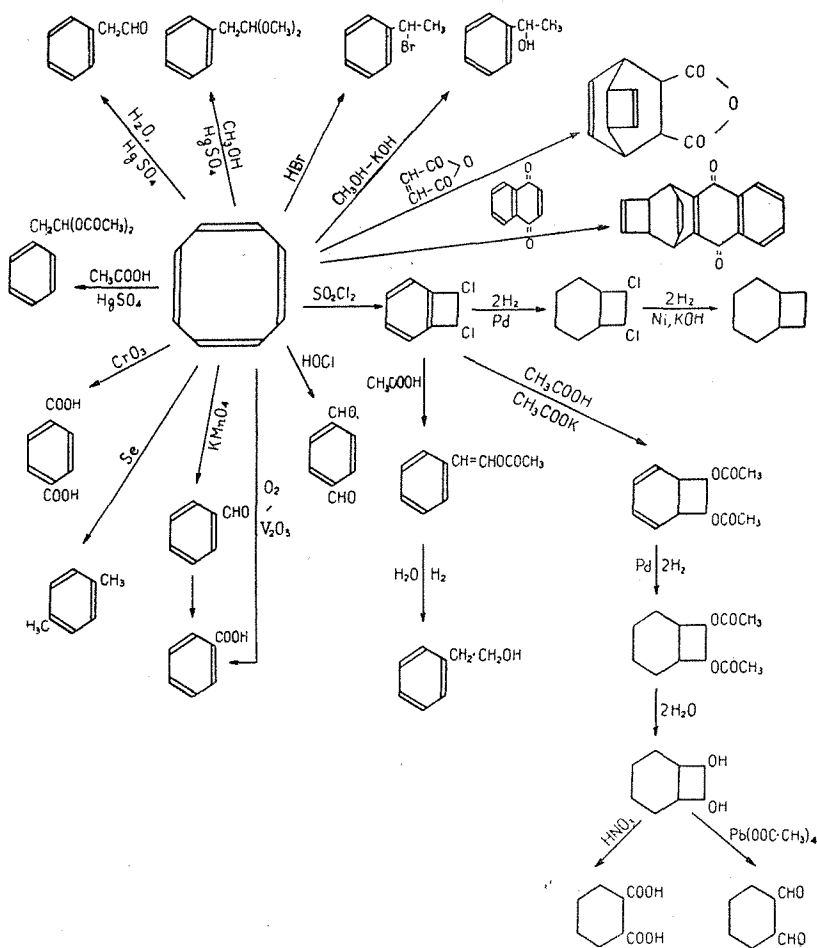


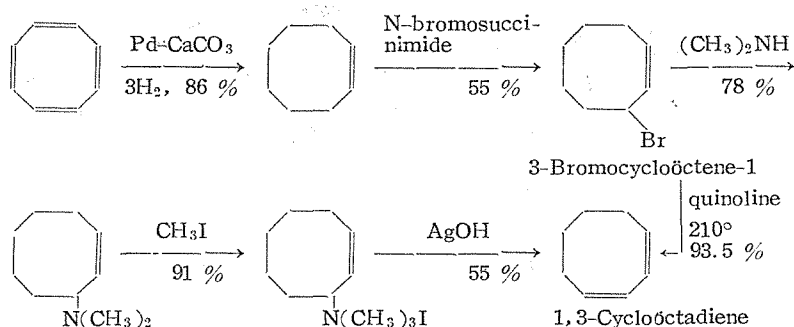
Fig.1-2. Reactions of C. O. T.

Craig and co-workers<sup>10)</sup> tried the electrolytic reduction of C.O.T. A solution of 100 g. of tetramethylammonium bromide in 1 l. of 50 % ethanol was placed in a 2 l. resin pot, the bottom of which was covered with mercury to serve as a cathode. A porous electrolysis cup containing 300 g. of 20 % sodium hydroxide as anolyte was suspended in the catholyte medium and a steel anode attached. To the catholyte was added 100 g. of C.O.T. and the resin pot was covered and fitted with a condenser and a stirrer. The pot was cooled with ice and the electrolysis carried out with a current of 6 to 8 amperes (20 volts applied) for 10 hours. The reaction products in the catholyte were extracted with petroleum ether and the extract was submitted to distillation. The product 174 g. collected at 73 ~ 75°C/80 mm. This sample absorbed 100 % of 3 molar equivalents of hydrogen in the presence of Adams catalyst to give an 84 % yield of cyclooctane (b.p. 147.5 ~ 148°C). The electrolytic reduction product was subjected to chromatography and was examined by ultraviolet absorption spectrum and it was found that the sample consisted of two materials, 75 % of 1,3,6-cyclooctatriene and 25 % of 1,3,5-cyclooctatriene. He also reduced cyclooctatetraene with sodium and *N*-ethylaniline in ether, keeping below 25°C, and examined the products by polarography and ultraviolet absorption spectrum. These data indicated that the products contained 57 % of 1,3,6-cyclooctatriene and 43 % of 1,3,5-cyclooctatriene.

According to U.S. patent, C.O.T.<sup>11)</sup> was reduced to 1,5-cyclooctadiene in 87 % yield by means of sodium and ethanol.

Treated with *N*-bromosuccinimide and *t*-butoxide in *t*-butanol, 1,5-cyclooctadiene was converted to 1,3,5-cyclooctatriene in 71 % yield<sup>12)</sup>.

1,3-cyclooctadiene was prepared from C.O.T. *via* the following steps including Hofmann exhaustive methylation procedure<sup>13)</sup>.



This material was also prepared from 3-bromocyclooctene-1 by direct dehydrobromination with quinoline, and both were confirmed to be identical by ultraviolet absorption spectra.

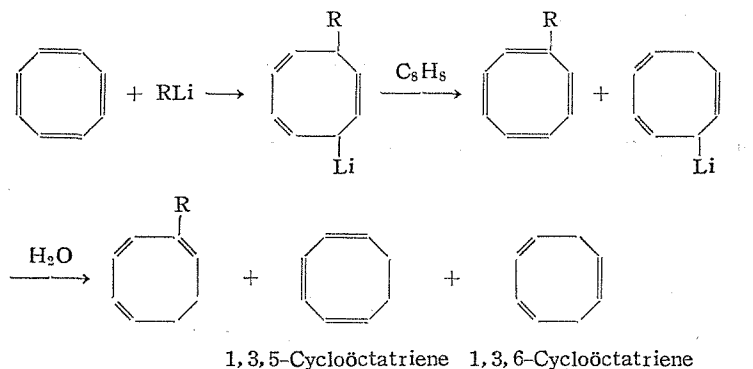
By means of copolymerization of mono- or di-substituted acetylenes with acetylene, Cope and co-workers<sup>14)</sup> found a direct method of synthesis of mono- or di-substituted C.O.T. Methyl-, *n*-propyl-, *n*-butyl-, phenyl-, and 1,2-dimethyl-C.O.T. have been

## Cyclopolyolefins Derived from Acetylene

prepared thus by this method from the corresponding acetylene derivatives and acetylene.

Cope and Smith<sup>15)</sup> prepared 1,2-diphenyl-C.O.T. by copolymerization of diphenylacetylene with acetylene in the presence of nickel acetylacetonate catalyst at 80 to 90°C. 1,2-diphenyl-C.O.T. was confirmed by hydrogenating with 10 % palladium on Norit, deriving to 1,2-diphenylcyclooctadiene, -octene, and -octane and by examining their ultraviolet and infrared absorption spectra (diene ; m.p, 113.3 ~ 113.7°C, octene ; m.p. 77.4 ~ 77.7°C, octane ; *trans*, m.p. 34.4 ~ 35°C, *cis*, m.p. 75.8 ~ 76.2°C).

Cope and co-workers<sup>16)</sup> also prepared alkyl- or aryl-cyclooctatetraenes and alkyl- or aryl-cyclooctatrienes from C.O.T. and alkyl- or aryl-lithium compounds according to the following schema :



For example, to an ether solution of *n*-butyllithium (prepared from *n*-butylbromide and lithium wire), C.O.T. was added slowly with stirring for 50 minutes at 0 to 20°C. The ether layer was extracted with 50 % aqueous silver nitrate and silver nitrate extract was treated with an excess of saturated sodium chloride solution, and the liberated hydrocarbon was fractionated and *n*-butylcyclooctatetraene was obtained (b.p. 98°C/20 mm.,  $n_D^{25}$  1.5083,  $d_4^{25}$  0.8876). Besides this, 1,3,5- and 1,3,6-cyclooctatriene and a small amount of butylcyclooctatriene were found.

These substituted C.O.T.s indicate the same chemical reactions with those of C.O.T.

## II. AZULENE C<sub>10</sub>H<sub>8</sub>

Azulene was obtained as a by-product during the preparation of C.O.T., contaminated with other higher cyclopolyolefins C<sub>10</sub>H<sub>10</sub> and C<sub>12</sub>H<sub>12</sub> as described below. The amount of these polymers depended largely upon the temperature of polymerization of acetylene and the higher the polymerization temperature, the larger were the quantities of polymers obtained, amounting to 5 to 10 % of C.O.T. But the amount of azulene was very small. In one experiment, there were obtained about 250 g. of C.O.T., 30 g. of higher cyclopolyolefins, and 0.5 g. of azulene.

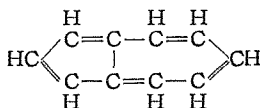
By shaking with phosphoric acid<sup>17)</sup>, this substance was separated from the petroleum



ether solution of higher boiling polymers of which C.O.T. had been distilled off. Namely, azulene reacts with phosphoric acid, while the others remain in the petroleum ether, then the acid solution is decomposed with water, then azulene separates out as crystals. These crystals were sublimed and recrystallized from methanol to give dark blue glittering tablets melting at 99 to 100°C.

Azulene was also separated out in crystalline form by means of chromatographic method, using petroleum ether as a solvent and alumina as an absorbent.

Pfau and Plattner<sup>18)</sup> proposed the following structural formula for azulene :



Azulene (Bicyclo-(0,3,5,-)decapentaene-(1,3,5,7,9))

Azulene adds with trinitrotoluene and picric acid, and the adducts melt at 167 ~ 8°C, 144 ~ 8°C, respectively.

Treibs<sup>19)</sup> has published numerous reports on azulene and its derivatives, but I do not touch them here.

### III. C<sub>10</sub>H<sub>10</sub>

In the case of the polymerization temperature of acetylene was raised to 120 to 130°C, a considerable amount of C<sub>10</sub>H<sub>10</sub> was obtained. This hydrocarbon C<sub>10</sub>H<sub>10</sub> was isolated by fractionation of the residue of which azulene had been separated by phosphoric acid. C<sub>10</sub>H<sub>10</sub> consists of orange-colored liquid and pale yellow one, and these two components have practically an identical boiling point, 47 ~ 50°C/0.2 mm., but they are different in gravity and refractive index. It is assumed, therefore, that they are stereoisomeric or mesomeric compounds.

	orange-color	yellow
b. p.	47~50°C/2 mm.	46~51°C/2 mm.
$d_4^{20}$	0.9344	0.9400
$n_D^{20}$	1.5755	1.5790

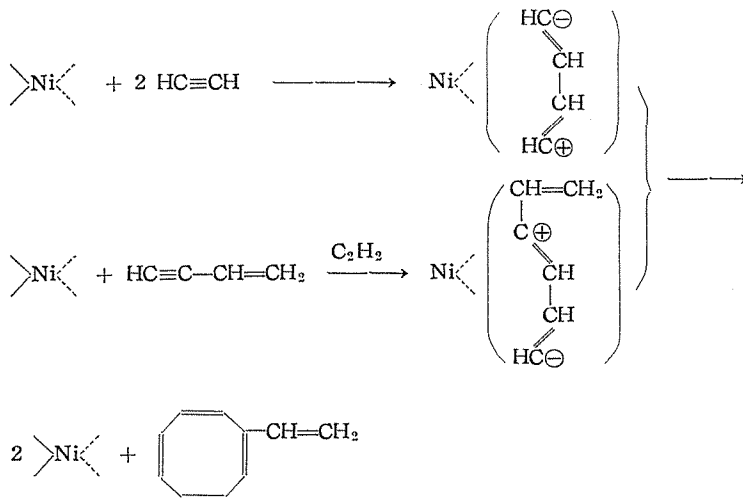
When the orange-colored hydrocarbon was hydrogenated with palladium-calcium carbonate catalyst in methanol solution, a steady absorption of hydrogen equivalent to 3.5 double bonds was observed, but the further absorption was difficult. On the other hand, the yellow hydrocarbon absorbed readily in the same conditions the hydrogen equivalent to only two double bonds, and the absorption stopped at this point. On hydrogenation, however, of these components with Raney nickel, at 20 atm. and 130 to 140°C, they both readily absorbed 5 molar equivalents of hydrogen, and was obtained a colorless hydrocarbon C<sub>10</sub>H<sub>20</sub>, boiling at 175 to 179°C.

From these experimental data, Reppe claims that C<sub>10</sub>H<sub>10</sub> will be cyclodecapentaene, but there is still some room to consider that it may be vinylcycloöctatetraene.

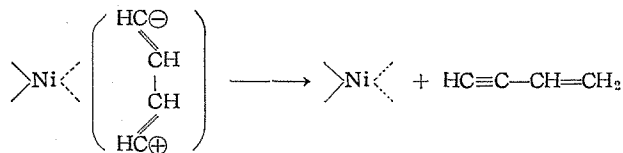
Cyclopolyolefins Derived from Acetylene



Hagihara<sup>20)</sup> proposed the following mechanism for the formation of C<sub>10</sub>H<sub>10</sub> from acetylene and monovinylacetylene.

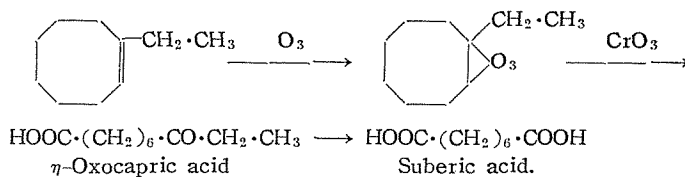


Also in the case of preparation of C.O.T. under relatively high temperature, the following mechanism for the formation of C<sub>10</sub>H<sub>10</sub> from acetylene was postulated :

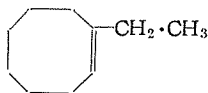


Namely, owing to the high reaction temperature, a part of acetylene dimer slips out from catalyst, followed by formation of vinylacetylene. From this vinylacetylene, C<sub>10</sub>H<sub>10</sub> was produced according to the above mechanism. He carried out the hydrogenation of C<sub>10</sub>H<sub>10</sub> in the presence of platinum oxide and obtained C<sub>10</sub>H<sub>18</sub> (b.p. 88 ~ 9°C/31 mm.) absorbing 4 molar equivalents of hydrogen. Also it was determined that this hydrocarbon C<sub>10</sub>H<sub>18</sub> contains one C-methyl and one alkyl group in the side chain. Ozonization of this substance gave ozonide, m.p. 138 ~ 9°C, and the ozonide was oxidized by chromic acid in acetic acid solution, then there were isolated suberic acid and a certain keto-acid C<sub>10</sub>H<sub>18</sub>O<sub>3</sub>. Keto-acid was confirmed by means of a mixed melting point determination to be identical with an authentic sample of  $\gamma$ -oxocapric acid prepared from C.O.T.

Sango KUNICHIKA

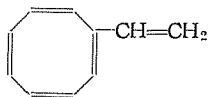


These experimental results indicate that  $\text{C}_{10}\text{H}_{18}$  is 1-ethylcyclooctene-1.

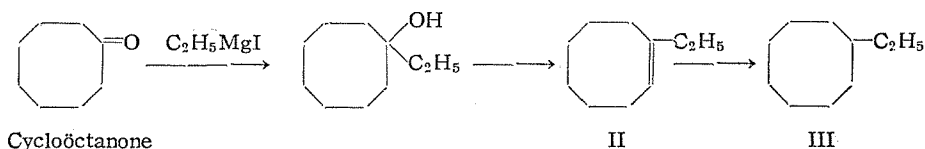


By hydrogenation with Raney nickel catalyst at 100 atm. and 150°C (4 molar equivalents of hydrogen were already absorbed at room temperature),  $\text{C}_{10}\text{H}_{20}$  (b.p., 81 ~ 82°C/28 mm.) was isolated. This substance was considered undoubtedly to be ethylcyclooctane, and was also confirmed in comparison with an authentic sample prepared from C.O.T.

In short, Hagihara claims that the structural configuration of  $\text{C}_{10}\text{H}_{10}$  is probably vinylcyclooctatetraene:



<sup>21)</sup> Craig and Larrabee examined the infrared absorption spectrum of  $\text{C}_{10}\text{H}_{10}$ , and found that the absorptions are attributable to a substituted benzene ring and to non-benzenoid conjugated double bonds. These facts indicate that  $\text{C}_{10}\text{H}_{10}$  was probably a mixture containing at least one substituted benzene and one cyclic polyolefin. They carried out the hydrogenation of  $\text{C}_{10}\text{H}_{10}$  under conditions in which the benzene ring was not hydrogenated, that is, at room temperature and at low pressure (50 lb/in<sup>2</sup>) with Adams catalyst in methanol solution. Hydrogenation product was distilled by Podbielniak's apparatus and three components were obtained: component I,  $\text{C}_{10}\text{H}_{14}$  (b.p. 182.4°C), component II,  $\text{C}_{10}\text{H}_{18}$  (b.p. 186.9°C) and component III,  $\text{C}_{10}\text{H}_{20}$  (b.p. 191.3°C). These three components were confirmed respectively, by comparison of physical constants, infrared absorption spectra (Fig. 2.), and their derivatives with those of the reported or authentic samples prepared by other methods. From the facts mentioned above, it was decided that the component I was *n*-butylbenzene, the component II ethylcyclooctene and the component III ethylcyclooctane. (II and III were prepared by the following schema).



## Cyclopolyolefins Derived from Acetylene

L. F. CRAIG AND CLIFFORD E. LARRABEE

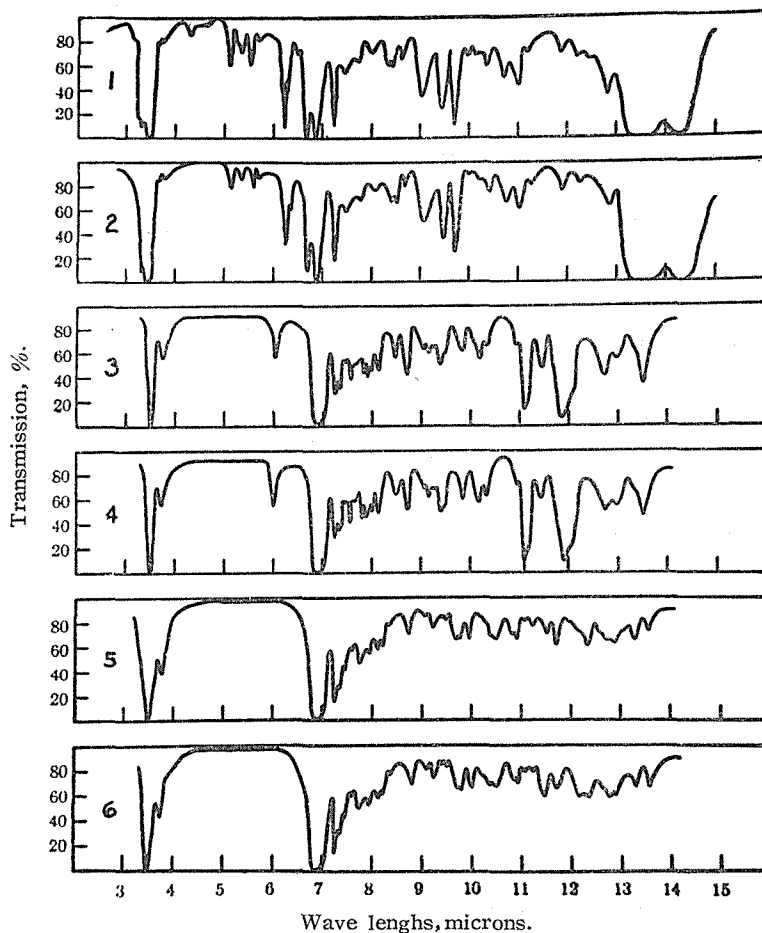


Fig. 2. -Infrared spectra: curve 1, component I; curve 2, *n*-butylbenzene; curve 3, component II; curve 4, 1-ethylcyclooctene; curve 5, component III; and curve 6, ethylcyclooctane.

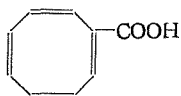
Since it can be considered that both components II and III have been generated from the same material and butylbenzene has been produced from another single material, it is most likely that the original  $C_{10}H_{10}$  was a mixture of two materials, both of empirical formula  $C_{10}H_{10}$ . In order to ascertain this consideration, they shook original  $C_{10}H_{10}$  in petroleum ether solution with 30 % aqueous silver nitrate and could separate into orange-yellow-colored aqueous solution and colorless petroleum ether solution. From aqueous solution, by treating with sodium chloride followed by steam distillation, an orange oil (b.p.  $83.3^{\circ}C/20$  mm.) was isolated. From colorless petroleum ether solution, colorless oil (b.p.  $87.7^{\circ}C/20$  mm.) was also obtained. The former was hydrogenated by Adams platinum catalyst and absorbed just 5 molar equivalents of hydrogen in the period of 45 minutes and gave ethylcyclooctane (b.p.  $188.5\sim 189^{\circ}C$ ).

The latter absorbed 2 molar equivalents of hydrogen in the same conditions and gave *n*-butylbenzene (b.p. 181 ~ 2°C). The examinations of the infrared and ultraviolet absorption spectra of these two oils (b.p. 83.3°C/20 mm. and 87.7°C/20 mm.) showed that the absorptions are attributable to vinylcyclooctatetraene and 1-phenyl-1,3-butadiene.

Consequently, Craig concluded that C<sub>10</sub>H<sub>10</sub> consists of two components, one is *cis*-1-phenyl-1,3-butadiene and the other is vinylcyclooctatetraene.

Cope and Fenton<sup>22)</sup> obtained the same results on the isolation of vinylcyclooctatetraene and *cis*-1-phenyl-1,3-butadiene from acetylene polymers.

Wither<sup>23)</sup> also found the substances described above, and obtained bromo derivatives of vinyl-C.O.T. (C<sub>10</sub>H<sub>9</sub>Br : m.p. 122 ~ 3°C), and an adduct with maleic anhydride (C<sub>10</sub>H<sub>10</sub>·2C<sub>4</sub>H<sub>2</sub>O<sub>3</sub> : m.p. 303 ~ 5°C). By oxidation of vinyl-C.O.T., C.O.T.-carboxylic acid was prepared.<sup>24)</sup> A stream of oxygen delivering 10 mg. of ozone per minute was passed into a solution of 1.30 g. of vinyl-C.O.T. in 50 ml. of pentane cooled to -70°C with a bath of dry ice and acetone for 50 minutes. The resulting mixture was stirred with 3 g. of moist, freshly prepared silver oxide for 1 hour at 0°C and 2 hours at 26°C. After being acidified with cold, dilute sulfuric acid, the mixture was extracted with three 50 ml. portions of ether. From ethereal solution C.O.T.-carboxylic acid (m.p. 69 ~ 72°C) was obtained.



#### IV. C<sub>12</sub>H<sub>12</sub>

The yellow hydrocarbon C<sub>12</sub>H<sub>12</sub> was obtained in a somewhat larger amount when polymerization temperature was raised to 140°C. On hydrogenation, it was impossible to obtain a perfect reduction product C<sub>12</sub>H<sub>24</sub>, and C<sub>12</sub>H<sub>22</sub> (b.p. 64 ~ 5°C/0.5 mm.) was obtained as the highest absorption product of hydrogen.

When the yellow C<sub>12</sub>H<sub>12</sub> was passed over palladium-carbon catalyst *in vacuo* at 250 to 260°C, a colorless liquid was obtained. This product gave picrate (yellow needles, m.p. 127 ~ 9°C) which was identical with an authentic sample of 1,2-dimethylnaphthalene picrate.

Although Reppe claims that the structure of C<sub>12</sub>H<sub>12</sub> must be cyclododecahexaene, it has not yet been decided and is a problem requiring further researches.

#### REFERENCES

- (1) R. Willstätter and E. Waser: *Ber.*, **44**, 3423 (1911).  
R. Willstätter and M. Heidelberger: *Ber.*, **46**, 517 (1913).
- (2) W. Reppe, O. Schlichting, K. Klager and T. Topel: *Ann.*, **560**, 1 (1948).
- (3) C. E. Barnes: U. S. Patent, 2,579,106 (1951), *C.A.* **46**, 6671 (1952).

Cyclopolyolefins Derived from Acetylene

- (4) N. Hagihara: *Bull. Chem. Soc., Japan*, (Pure Chemistry Section), **73**, 237 (1952).
- (5) A. C. Cope and W. J. Bailey: *J. Am. Chem. Soc.*, **70**, 2305 (1948).
- (6) W. Reppe; *loc. cit.*, "Neue Entwicklungen auf dem Gebiet der Chemie des Acetylenes und Kohlenoxyds," Springer-Verlag, S. 69. (1949).  
J. W. Copenhaver and M. Bigelow: "Acetylen and Carbon Monoxide Chemistry," Reinhold Publishing Corp., p.188 (1949).  
Kammermeyer: "Polymerization of Acetylene to Cyclooctatetraene" P. B. Reports 62, 593 (Oct. 1936) [FIAT. 967]
- (7) Bergmann: "The Chemistry of Acetylenes and Related Compounds," Interscience Publishers, p. 93. (1948)
- (8) N. Hagihara: *Bull. Chem. Soc., Japan*, (Pure Chemistry Section), **73**, 323 (1952).
- (9) W. Reppe; *loc. cit.*  
W. Reppe: "Chemie und Technik der Acetylene-Druck-Reaktionen," Verlag Chemie, S. 55 (1952).
- (10) L. E. Craig, R. M. Eloffson and I. J. Ressa: *J. Am. Chem. Soc.*, **75**, 480 (1953).
- (11) U. S. Patent: 2,594,889 (1952); *C. A.* **47**, 608 (1953).
- (12) A. C. Cope, C. L. Stevens and F. A. Hochstein: *J. Am. Chem. Soc.*, **72**, 2510 (1950).
- (13) A. C. Cope and L. L. Esters, Jr.: *J. Am. Chem. Soc.*, **72**, 1128 (1950).
- (14) A. C. Cope and Campbell: *J. Am. Chem. Soc.*, **74**, 179 (1952).
- (15) A. C. Cope and Smith: *J. Am. Chem. Soc.*, **74**, 5136 (1952).
- (16) A. C. Cope and M. R. Kinter: *J. Am. Chem. Soc.*, **73**, 3424 (1951).  
A. C. Cope and Orden: *J. Am. Chem. Soc.*, **74**, 175 (1952).
- (17) A. E. Sherndal: *J. Am. Chem. Soc.*, **37**, 167, 1537 (1915).  
R. E. Kremers: *J. Am. Chem. Soc.*, **45**, 717 (1923).  
L. Ruzicka and E. A. Rudolph: *Helv. Chim. Acta*, **9**, 118 (1926).
- (18) A. St. Pfau and Pl. Plattner: *Helv. Chim. Acta*, **19**, 858 (1936).
- (19) W. Treibs: *Ann.*, **577**, 207 (1952);  
W. von E. Doering, J. R. Mayer and C. H. DePuy: *J. Am. Chem. Soc.*, **75**, 2386 (1953).
- (20) N. Hagihara: *Bull. Chem. Soc., Japan*, (Pure Chemistry Section), **73**, 323, 373 (1952).
- (21) L. E. Craig and C. E. Larrabee: *J. Am. Chem. Soc.*, **73**, 1191, 5471 (1951).
- (22) A. C. Cope and S. W. Fenton: *J. Am. Chem. Soc.*, **73**, 1195 (1951).
- (23) D. S. Withey: *J. Chem. Soc.*, 1930 (1952).
- (24) A. C. Cope, M. Burg and S. W. Fenton: *J. Am. Chem. Soc.*, **74**, 173 (1952).