a stream of dry, prepurified nitrogen. Floruine was introduced into the nitrogen stream, and the fluorine–nitrogen mixture was passed into the reaction vessel. The volatile, entrained products in the effluent stream were passed through an iron tube containing granular sodium fluoride to remove hydrogen fluoride (present in the fluorine supply and also formed in the reaction) and then into a 100-ml. glass trap immersed in liquid air. A stream of 3% (by volume) fluorine in nitrogen was passed through the reactor at a flow rate of approximately 0.016 ft.^{3}/hr. for 3 hr. (a total of 0.10 mole of fluorine). The fluorine flow was discontinued, and the cooling bath was removed. The reactor was thereafter purged with nitrogen for 1 hr. The desired product was formed rapidly during the initial period of fluorine delivery and was produced more slowly during the later stages of fluorination. (If the solid residues were then removed from the reactor, ground into a fine powder, and returned to the reactor, additional quantities of the desired products were obtained by repeating the fluorination procedure.)

The contents of the liquid-air trap were maintained at liquid-air temperature until the purification step. The noncondensable gases were removed from the trap at liquid-air temperature under reduced pressure, and the condensate was then fractionated at 0.1-mm. pressure (while the trap was allowed to warm slowly to room temperature) through traps designated A and B. Trap A was cooled by a bath of solid carbon dioxide–trichloroethylene (−78°) and trap B was cooled by a bath of liquid nitrogen (−196°). Trap A contained 0.38 mmole of crude *cis*- and *trans*-perfluoro-3,5-dimethyl-1,2-dioxolane, which was further purified by preparative gas chromatography on the silicone gum rubber column at room temperature. The yield was 5% of the theoretical amount based on hexafluoroacetylacetone employed as the chelate. No attempts have been made to improve the yield.

Anal. Calcd. for $C_5F_{10}O_2$: C, 21.4; F, 67.4; mol. wt., 282. Found: C, 21.4; F, 66.8; mol. wt., 275 (by gas density method).

An analytical sample released 6.8 mequiv. of iodine/g. of sample from aqueous potassium iodide (calcd. for two-electron change, 7.1 mequiv.). The mass-cracking pattern of an analytical sample has peaks at m/e 69 (assigned to CF_3), 47 (assigned to CFO), 97 (assigned to CF_3CO), and 263 (assigned to the parent molecule minus one fluorine atom) in addition to many other peaks consistent with the structure. The infrared and n.m.r. data are given in Table I. Both isomers of perfluoro-3,5-dimethyl-1,2-dioxolane are immiscible with water for periods up to 1 hr. with no evidence for hydrolysis. Both isomers are recovered unchanged after exposure to mercury for 30 min. Both isomers have been stored routinely at liquid nitrogen temperature for periods up to 2 years. A mixture of the isomers has a vapor pressure of 320 ± 10 mm. at 25°; the boiling point is estimated at 45° (760 mm.).

Trap B contained approximately 0.37 mmole of a mixture of cleavage products plus a small amount of perfluoro-3,5-dimethyl-1,2-dioxolane. Isolation of the components was accomplished by gas chromatography on the perfluorotributylamine column operated at −30°. The products were identified by comparison of their infrared spectra and gas chromatographic retention times with the spectra and retention times of authentic samples. This fraction consisted of one-carbon fragments and small amounts of perfluoroacetyl fluoride, fluoroxyperfluoroethane, and 2-fluoroxyperfluoropropane.[6] The same procedure was used for fluorination of the nickel chelate of hexafluoroacetylacetone. The yield was the same for either starting material.

The results of the thermal decomposition reactions of perfluoro-3,5-dimethyl-1,2-dioxolane were determined by the infrared and n.m.r. spectra of the samples at convenient time intervals and comparison of these spectra with the spectra of authentic samples of the products.

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Bridgehead-Substituted Bicyclo[2.2.2]octanes. I. Addition of Ethylene to Cyclohexa-1,3-diene-1,4-dicarboxylic Acid Derivatives

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Addition of ethylene and other dienophiles to cyclohexa-1,3-diene-1,4-dicarboxylic acid derivatives yields disubstituted bicyclo[2.2.2]oct-2-enes with functional substituents at both bridgehead positions. These compounds were converted to a variety of 1,4-disubstituted bicyclo[2.2.2]octanes. Contrary to a recent report, the structure dimethyl cyclohexa-1,4-diene-1,4-dicarboxylate originally assigned by Baeyer to the dihydroterephthalate isomer melting at 130° is correct.

Functionally substituted bridgehead structures have been of considerable interest in the study of organic reaction mechanisms. Although many syntheses of the bicyclo[2 2.2]octane ring system have been reported, most are not suitable for the preparation of bridgehead-substituted derivatives. In particular, few 1,4-disubstituted bicyclo[2.2.2]octanes have been described, and these were obtained by rather difficult, multistep syntheses.[1,2]

In general, three approaches have been used for the preparation of bridgehead-substituted bicyclo[2.2.2]octanes and bicyclo[2.2.1]heptanes: (1) free-radical attack at the bridgehead hydrogen atom of a bicyclic hydrocarbon,[3] (2) Wagner–Meerwein rearrangement of an appropriately substituted bicyclic structure,[4] and (3) introduction of a bridge into a substituted cyclohexane derivative.[1,2,5]

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(1) P. C. Guha, *Ber.*, **72**, 1359 (1939); P. C. Guha and C. Krishnamurthy, *ibid.*, **72**, 1374 (1939).

(2) J. D. Roberts, W. T. Moreland, Jr., and W. Frazer, *J. Am. Chem. Soc.*, **75**, 637 (1953).

(3) (a) A. F. Bickel, J. Knotnerus, E. C. Kooyman, and G. C. Vegter, *Tetrahedron*, **9**, 230 (1960); (b) R. T. Blickenstaff and H. B. Haas, *J. Am. Chem. Soc.*, **68**, 1431 (1946).

(4) (a) W. von E. Doering and E. F. Schoenewaldt, *ibid.*, **73**, 2333 (1951); (b) W. R. Boehme, *ibid.*, **81**, 2762 (1959); (c) H. Kwart and G. Null, *ibid.*, **81**, 2765 (1959).

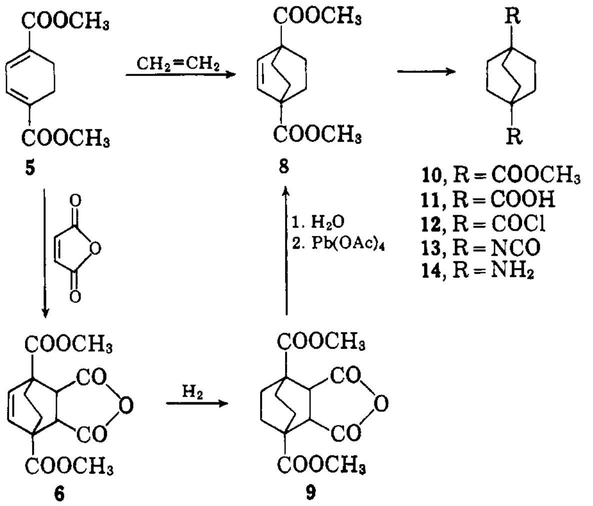
(5) See, for instance, (a) S. Hünig and H. Kahanek, *Ber.*, **90**, 238 (1957); (b) C. A. Grob, M. Ohta, E. Renk, and A. Weiss, *Helv. Chim. Acta*, **41**, 1191 (1958); (c) J. Colonge and R. Vuillemet, *Bull. soc. chim. France*, 2235 (1961).

The introduction of a two-carbon bridge *via* the Diels–Alder reaction of a 1,4-disubstituted 1,3-cyclohexadiene appeared to offer a convenient route to 1,4-disubstituted bicyclo[2.2.2]octanes. Most of the Diels–Alder reactions that have been reported involve addition of an electron-deficient dienophile to an electron-rich diene. The reverse situation, *i.e.*, the reaction of electron-rich dienophiles with electron-deficient dienes, has recently been studied by Sauer and Wiest.[6]

The reaction of unactivated dienophiles with electron-deficient dienes has been little studied, but it was hoped that with the use of ethylene under high pressure the desired Diels–Alder adduct would be obtained. Such an approach had succeeded in the synthesis of 9,10-disubstituted dihydroethanoanthracenes.[7] In this and succeeding papers, the synthesis of various bridgehead-substituted bicyclo[2.2.2]octanes using this procedure will be described.

Addition of Ethylene and Other Dienophiles to Cyclohexa-1,3-diene-1,4-dicarboxylic Acid Derivatives (Scheme I.)—Dimethyl cyclohexa-1,3-diene-1,4-dicarboxylate (5), reported originally by Baeyer,[8b] was conveniently prepared by a modification of the procedure of Guha and Hazra.[9] Since this latter procedure leads to erratic results,[10] we have reported our modification in detail. The ultraviolet and n.m.r. spectra of this diene fully confirm its assigned structure (see Table I).

SCHEME I



Ethylene at 1000-atm. pressure reacted rapidly at 165° with 5 to form dimethyl bicyclo[2.2.2]oct-2-ene-1,4-dicarboxylate (8) in high yield.[11a-c] The reaction was found to be moderately pressure sensitive. Thus, at 1000 atm., it could be carried out satisfactorily overnight at 165°. At 300 atm., however, the reaction was slow, and about one-third of the diene 5 was recovered unchanged after 18 hr. When higher temperatures were employed, isomerization and aromatization of the diene led to greatly lowered yields. On the other hand, the conversion was nearly quantitative in 18 hr. at 3000-atm. pressure at 135°. The ester 8 was hydrogenated, and the resulting saturated ester 10 was hydrolyzed to bicyclo[2.2.2]octane-1,4-dicarboxylic acid (11), identical with a sample prepared by the method of Guha[1] and Roberts, *et al.*[2]

When high-pressure ethylene is available, this procedure appears to be the method of choice for the synthesis of bicyclo[2.2.2]octane-1,4-dicarboxylic acid and its derivatives.

As an independent check on the structure of 8, the adduct of maleic anhydride with 5 was prepared by the procedure recently reported.[10,11b] This adduct 6 was hydrogenated, and the anhydride ring of the hydrogenation product 9 was opened. The resulting diester diacid when subjected to the oxidative bisdecarboxylation procedure of Grob[5b] gave the desired dimethyl bicyclo[2.2.2]oct-2-ene-1,4-dicarboxylate (8) in 45% yield, identical (infrared spectrum) with that isolated from the addition of ethylene to 5. Other workers had reported the failure of the decarboxylation.[10,11d]

Ethylene also underwent reaction with cyclohexa-1,3-diene-1,4-dicarboxylic acid (2), its diacid chloride (3), and its bis(benzylamide) to form the corresponding 1,4-disubstituted bicyclo[2.2.2]oct-2-enes. The reaction with the methyl ester, however, was the most convenient to carry out.

Dimethyl cyclohexa-1,3-diene-1,4-dicarboxylate reacts slowly with tetracyanoethylene in refluxing chlorobenzene to form Diels–Alder adduct 7. Other laboratories have reported the formation of a stable yellow π-complex between the reactants at somewhat lower temperatures.[10,11d]

Although bicyclo[2.2.2]octane-1,4-dicarboxylic acid (11) did not undergo the Schmidt reaction (probably because of its insolubility), it was converted in high yield to the diisocyanate 13 and the diamine 14 *via* the Curtius reaction. The single sharp CH_2–CH_2 peak in the n.m.r. spectra of these compounds is consistent with the structural assignments, since all of the ring hydrogen atoms in these derivatives are chemically equivalent.

Dimethyl Cyclohexa-1,4-diene-1,4-dicarboxylate (15). Structure and Reactivity.—This unconjugated diene system has been made conveniently available by the cathodic reduction of potassium terephthalate.[12] We examined the reaction of the dimethyl ester 15 with dienophiles in the hope that isomerization to the conjugated diene 5 followed by conversion to a Diels–Alder adduct would offer an alternate preparation of 6 and 8. We found no evidence for such a reaction. These results are not in agreement, however, with those reported in a recent paper.[10]

The compound, m.p. 130°, originally assigned the structure dimethyl cyclohexa-1,4-diene-1,4-dicarbox-

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[6] J. Sauer and H. Wiest, *Angew. Chem., Intern. Ed. Engl.*, **1**, 269 (1962).

[7] (a) T. W. Campbell, V. E. McCoy, J. C. Kauer, and V. S. Foldi, *J. Org. Chem.*, **26**, 1422 (1961); (b) J. S. Meek, W. B. Evans, V. Godefroi, W. R. Benson, M. F. Wilcox, W. G. Clark, and T. Tiedeman, *ibid.*, **26**, 4281 (1961).

[8] (a) A. von Baeyer, *Ann.*, **251**, 257 (1889); (b) *ibid.*, **251**, 304 (1889); (c) *ibid.*, **251**, 272 (1889); (d) *ibid.*, **251**, 303 (1889).

[9] P. C. Guha and G. D. Hazra, *J. Indian Inst. Sci.*, **22A**, 263 (1939); *Chem. Abstr.*, **34**, 2822 (1940).

[10] G. Smith, C. L. Warren, and W. R. Vaughan, *J. Org. Chem.*, **28**, 3323 (1963).

[11] (a) J. C. Kauer, U. S. Patent 3,081,334 (March 12, 1963); *Chem. Abstr.*, **59**, 6276 (1963). (b) J. C. Kauer, U. S. Patent 3,071,597 (January 1, 1963); *Chem. Abstr.*, **59**, 1504 (1963). (c) NOTE ADDED IN PROOF.—The failure of this reaction under other conditions has been recently reported.[11d] (d) L. G. Humber, G. Meyers, L. Hawkins, and M. Boulerice, *Can. J. Chem.*, **42**, 2852 (1964).

[12] Unpublished work carried out by Dr. M. L. Peterson and Dr. T. E. Young of this laboratory; details are given in the Experimental section.

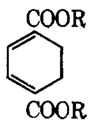
Table I

Physical Properties of Dimethyl Terephthalate Derivatives

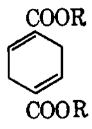
Compd.	M.p., °C.[a]	Ultraviolet spectra[b] λ_{max}, mμ (log ε)	Proton n.m.r., τ[c] Vinyl	Methoxyl	Methylene
5	83.1–84.6	309 (4.132)	2.93 [2] fs	6.23 [6] s	7.43 [4] fs[d]
15	128–129.2	203 (4.371), 240 sh (3.15)	2.94 [2] fs	6.21 [6] s	6.87 [4] fs
17	140.4–141.1	240 (4.293), 285 (3.225), 294[e] (3.147)	1.73 [4] s	5.97 [6] s	

[a] Melting point with rate of heating = 0.2°/min. [b] Ultraviolet spectra were determined in ethanol solution with ethanol in the reference beam. [c] Number of protons is given in brackets; s = singlet, fs = fine structure. [d] Ref. 10 reports τ 7.83 [4], slight fine structure. [e] Ref. 10 reports λ_{max} 398.5 mμ.

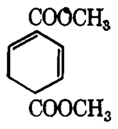
ylate (**15**) by von Baeyer[13a] was recently re-examined by Smith, Warren, and Vaughan.[10] These workers concluded that von Baeyer's assignment was incorrect. They reassigned the structure **16** to their "diene IV." They report that this material isomerizes reversibly to **5** and that like **5** it reacts with maleic anhydride to form adduct **6**.



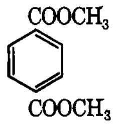
2, R = H
5, R = CH_3



15, R = CH_3
15a, R = H



16



17

We have repeated several times the preparative procedure[14] employed by Smith, Warren, and Vaughan[10] and isolated in each case a mixture of the starting material **5** with varying amounts of **15** and dimethyl terephthalate (**17**). After recrystallization from ethyl acetate[10] most of the diene **5** was removed, and large, well-formed crystals of a mixture of **15** and **17** were obtained. A synthetic 1:1 mixture of **15** and **17** was prepared by mixing equimolar portions of the pure compounds. The mixture remained essentially unchanged in composition after five successive recrystallizations from ethyl acetate and exhibited the melting point and n.m.r. and ultraviolet spectra reported by Smith, Warren, and Vaughan for the "diene IV" which they presumed to be identical with the diene (m.p. 130°) reported by Baeyer.[8a,13a]

It is interesting to note that the inseparable nature of this mixed crystal system was known to von Baeyer,[13b] and a crystallographic study of this interesting system was subsequently carried out by his colleague Muthmann.[15]

We prepared the pure diene **15** (m.p. *ca.* 130°) by an alternative procedure[12] and found that its n.m.r., infrared, and ultraviolet spectra (see Table I) are in complete agreement with the structure assigned by von Baeyer.[8c] Its melting point and crystal lattice elements[16] are in substantial agreement with the values[13b,15] reported by von Baeyer and Muthmann for the substance which they isolated. The pure diene does not rearrange to **5** on standing,[17a] nor does it undergo a Diels–Alder reaction under the conditions reported by Smith, Warren, and Vaughan.[10]

The properties of compounds **5**, **15**, and **17** are summarized in Table I. The properties of the mixtures involved are summarized in the Experimental section.

Experimental

All melting points are corrected. N.m.r. spectra were obtained with a Varian A60 spectrometer. Saturated deuteriochloroform solutions with tetramethylsilane as an internal standard were used unless otherwise noted. Peak center positions are reported as $\tau = 10 - \delta_H$ p.p.m.; number of protons (by integration) is given in brackets. Band widths were measured at half-height. Infrared spectra were determined in potassium bromide wafers with a Perkin-Elmer 21 spectrophotometer unless otherwise noted. Spectra in Nujol mulls were obtained on a Perkin-Elmer Infracord. Prominent peaks are noted. Ultraviolet spectra were determined in ethanol.

Dimethyl Cyclohexa-1,3-diene-1,4-dicarboxylate (5).—The following modification of the procedure of Guha and Hazra[9] has been employed successfully on six occasions for the preparation of the ester **5**. If care is taken, the product is nearly free of the isomeric dimethyl cyclohexa-1,4-diene-1,4-dicarboxylate.

A. **Dimethyl 1,4-Dibromocyclohexane-1,4-dicarboxylate (1).**—A mixture of 509 g. of redistilled (b.p. 122–127° at 6–7 mm.) dimethyl cyclohexane-1,4-dicarboxylate (Eastman 7570),[18] 450 g. of carbon tetrachloride, 20 g. of phosphorus tribromide, and 500 ml. of bromine was placed in a 2-l. flask equipped with an efficient reflux condenser. The solution was heated at reflux on a steam bath[19] for 7 days. Most of the unreacted bromine was removed by distillation on the steam bath.[19] Residual bromide was removed by codistillation with two 450-g. portions of carbon tetrachloride. The last traces of solvent were removed with a water pump. The product was cooled in ice, and 750 ml. of methanol was added to convert any acid bromide to the methyl ester. The flask was swirled until most of the solid had dissolved. The suspension was then heated to reflux on a steam bath overnight. The product was filtered hot (a pressure funnel is desirable) to yield 170 g. of *trans*-**1** after washing with cold methanol. The filtrate deposited 127 g. of a mixture of *cis*- and *trans*-**1** on standing overnight. The mixture was filtered, and the filtrate was evaporated with a rotary film evaporator at a bath temperature of 10° under aspirator vacuum. The resulting almost solid slurry was stirred into 800 ml. of ice-cold 75% methanol. Filtration at 5° yielded 259 g. of *cis*-**1** after washing with 800 ml. of ice-cold 75% methanol.[18] The total yield of *cis*- and *trans*-**1** was 61%.

B. **Dehydrobromination of 1.**—Potassium hydroxide (950 g.) was added cautiously while stirring to 1200 ml. of hot methanol. After heating a hot plate to dissolve the last of the alkali, the solution was poured into a 325-mm. (or larger) evaporating dish and was stirred occasionally while cooling. The evaporating

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(13) (a) A. von Baeyer, *Ann.*, **245**, 103 (1888) (Note that the structure of **15**, incorrectly given on pp. 142–145 of this reference, is corrected in ref. 8c.); (b) *ibid.*, **245**, 144, 145 (1888).

(14) These preparative conditions are much more vigorous than those employed by von Baeyer.[8d] Baeyer employed hot 20% sodium hydroxide for 3 hr. on the acid **2**. Vaughan, *et al.*,[10] employed refluxing 50% potassium hydroxide for 3.5 days on the ester **5**.

(15) W. Muthmann, *Z. Krist.*, **17**, 460 (1890); **19**, 356 (1891).

(16) The crystal lattice elements of the ester recrystallized from ethyl acetate were determined by Dr. John F. Whitney of this laboratory.

(17) (a) Our results and those of earlier workers[8a,13a,17b] suggest that the unconjugated diene **15a** is the most stable of the dihydroterephthalic acids. A recent explanation[17c] of the stability of cyclohexa-1,4-dienes based on the interaction of π-electrons across the ring may here apply. (b) F. Stohmann and C. Cleber, *J. prakt. Chem.*, [2] **43**, 1 (1891). (c) R. B. Bates, R. G. Carnighan, and C. E. Staples, *J. Am. Chem. Soc.*, **85**, 3030 (1963).

(18) The use of impure dimethyl cyclohexane-1,4-dicarboxylate may yield a product from which *cis* **1** will not crystallize. In this case the crude *cis* ester can be vacuum distilled, and the fraction boiling at 125–140° (0.7 mm.) can be collected and used in the next step.

(19) The use of an electric mantle leads to some aromatization of the product.

dish was ice cooled, and about 100 ml. of methanol was added to thin the slurry so that it would flow slowly. A mixture of 450 g. of finely divided *cis*- and *trans*-1 was added slowly to the alkali while stirring so that the temperature did not exceed 35°. Stirring was continued for 20 min. The slurry was allowed to stand at room temperature for 3 days with occasional stirring. It was then ice cooled, 500 g. of ice was added, and 1500 ml. of ice-cold concentrated hydrochloric acid was added cautiously with stirring. The resulting crude 2,3-dihydroterephthalic acid was separated by filtration and was washed twice with 2 l. of ice-water. It was air dried and vacuum dried at 60° to constant weight. The crude acid was powdered and then heated on a steam bath[19] for 2 days with *ca.* 1000 g. of thionyl chloride to which 3 drops of dimethylformamide was added. The solution was filtered hot, and solvent and excess thionyl chloride were removed by distillation under water-pump vacuum on a steam bath.[19] The residue in the distillation flask was cooled in ice until it solidified. The crude cyclohexa-1,3-diene-1,4-bis(carbonyl chloride) (**3**) was transferred to a sintered-glass funnel and washed with a small amount of cold hexane. (The conversion of this acid chloride to other derivatives of cyclohexa-1,3-diene-1,4-dicarboxylic acid is described below.) The crystals were dried in a stream of nitrogen and were added cautiously in small portions to 1 l. of cold methanol in a 3-l. flask. After the vigorous evolution of hydrogen chloride had ceased, the solution was heated at reflux for 2 hr. "Darco" (5 g.) was added, and the solution was filtered hot through a pressure funnel. When the solution had cooled, 152 g. of dimethyl cyclohexa-1,3-diene-1,4-dicarboxylate (**5**) was separated by filtration. An additional crop was obtained by evaporation of the filtrate to a volume of 100 ml. Both crops were combined and dissolved in 600 ml. of boiling methanol, and 1 g. of activated charcoal was added. The solution was filtered hot, and 100 ml. of hot water was added. The solution was allowed to cool slowly, and 133.3 g. of white crystals of **5** (m.p. 83.1–84.6°, lit.[8] m.p. 85°) was obtained. An additional 30–50 g. could be obtained by concentration and recrystallization of the residues: ν_{max} 3020, 2950, 2890, 2830, 1705 (C=O), 1645 and 1582 (C=C), 1430, 1383, 1257, 1188, 1092, 955, 920, 883, 805, 768, and 720 cm.$^{-1}$; λ_{max} 309 mμ (ϵ 12,000), lit.[10] λ_{max} 309 mμ (log ϵ 4.051). After 4 years of storage the melting point and ultraviolet and infrared spectra were unchanged.

Dimethyl Bicyclo[2.2.2]oct-2-ene-1,4-dicarboxylate (8) A. By Addition of Ethylene to Dimethyl Cyclohexa-1,3-diene-1,4-dicarboxylate.—A 400-ml., silver-lined steel autoclave equipped for shaking was charged with 156.5 g. of **5**. The vessel was then evacuated and filled with ethylene gas. The autoclave was heated at 165°, and ethylene was injected at a pressure of 1000 atm. until no further pressure drop occurred. The autoclave was cooled, and ethylene was carefully vented. The solid product (157 g.) was recrystallized from 300 ml. of boiling hexane to yield 144 g. (80%) of white crystals of dimethyl bicyclo[2.2.2]oct-2-ene-1,4-dicarboxylate (m.p. 75–76°) in two crops: ν_{max} 2970, 1735, 1628 (weak), 1450, 1343, 1268, 1145, 1091, 857, 742 cm.$^{-1}$; no λ_{max} >210 mμ; n.m.r. τ 8.25 [8] (CH_2–CH_2) symmetrical multiplet, 6.14 [6] (OCH_3) sharp, 3.33 [2] (CH=CH).

Anal. Calcd. for $C_{12}H_{16}O_4$: C, 64.27; H, 7.19; mol. wt., 224. Found: C, 64.53; H, 7.32; mol. wt., 227.

The ethylene addition could be carried out at 135° under 3000-atm. pressure. An attempt to carry out the reaction at 165° with lower ethylene pressure (*ca.* 300 atm.) yielded a mixture of **5** and **8** in a *ca.* 30:70 ratio.

B. By Oxidative Bisdecarboxylation of 1,4-Bis(methoxycarbonyl)bicyclo[2.2.2]octane-2,3-dicarboxylic acid.—The adduct of **5** with maleic anhydride (**6**, m.p. 188.0–188.6°) was prepared as described previously.[10,11b] It was catalytically hydrogenated to **9**,[10] treated successively with potassium bicarbonate solution and hydrochloric acid to yield the corresponding dicarboxylic acid which after recrystallization from water melted at 210° with loss of water. On remelting, the sample melted at 174° (lit. m.p. 177–178°,[10] 190–192°[11d]).

To a solution of 8.50 g. of the dicarboxylic acid in 50 ml. of dry benzene was added 3.5 ml. of dry pyridine. Lead tetraacetate (14.3 g.) was added, and the solution was warmed gently until gas evolution ceased. The mixture was then heated to reflux and stirred for 3 hr. It was filtered, and the precipitated lead salts were washed with benzene. The combined filtrates were stirred with water and refiltered, and the benzene layer was washed successively with 5% aqueous sodium carbonate, 5% hydrochloric acid, and water. After drying over magnesium sulfate, solvent was removed under reduced pressure. The white solid residue weighed 1.25 g. after trituration with two 50-ml. portions of pentane. This residue was identified as the anhydride **9** (16%) by its infrared spectrum. The pentane washes were concentrated under reduced pressure to yield 2.72 g. (45%) of dimethyl bicyclo[2.2.2]oct-2-ene-1,4-dicarboxylate (m.p. 71–73° after recrystallization from hexane). Identity with the product from ethylene and **5** was verified by mixture melting point and by infrared spectroscopy.

1,4-Bis(methoxycarbonyl)-2,2,3,3-tetracyanobicyclo[2.2.2]oct-5-ene (7).—A solution of 3.0 g. of **5** and 2.0 g. of tetracyanoethylene in 15 ml. of chlorobenzene was heated at reflux for 16 hr. The solution was cooled, and 3.57 g. of dark crystals of **7** were deposited. After recrystallization from benzene, the white crystalline product melted at 197–198°: ν_{max} 2970, 2250 (weak), 1750, 1440, 1315, 1290, 1273, 1110, 953, 795 cm.$^{-1}$; no λ_{max} >200 mμ; n.m.r. (acetone-d_6) τ 3.02 [2], 6.02 [6], 6.67 [4], band width 17 c.p.s.

Anal. Calcd. for $C_{16}H_{12}N_4O_4$: C, 59.26; H, 3.73; N, 17.28; mol. wt., 324. Found: C, 59.26; H, 3.87; N, 17.09, 17.50; mol. wt., 340.

Cyclohexa-1,3-diene-1,4-dicarboxylic Acid (2) and Bis(benzylamide).—A 36-g. portion of the crude cyclohexa-1,3-diene-1,4-bis(carbonyl chloride) (**3**) described above was recrystallized from 80 ml. of hexane to yield 30 g. of purified acid chloride, m.p. 60–61° (unstable on long storage). A solution of 1 g. of purified **3** in 15 ml. of tetrahydrofuran and 5 ml. of water was warmed for 1 hr. The solution was cooled, and the precipitated acid was collected and recrystallized from boiling water to give cyclohexa-1,3-diene-1,4-dicarboxylic acid (**2**): m.p. 350° dec.; ν_{max} 2620, 2540, 1690, 1660, 1420, 1275, 1105, 995, 940, 890, 785, 740, 730 cm.$^{-1}$.

Anal. Calcd. for $C_8H_8O_4$: C, 57.14; H, 4.80; neut. equiv., 84. Found: C, 57.20; H, 5.14; neut. equiv., 83.

The bis(benzylamide) prepared by treatment of **3** with benzylamine in ether crystallized as white needles from methanol: m.p. 216–216.4°; ν_{max} 3280, 1635, 1590, 1535, 1500, 1460, 1370, 1318, 1080, 1062, 1030, 972, 865, 790, 734, 690 cm.$^{-1}$.

Anal. Calcd. for $C_{22}H_{22}N_2O_2$: C, 76.27; H, 6.40; N, 8.09. Found: C, 76.20; H, 6.69; N, 8.16.

N,N′-Dibenzylbicyclo[2.2.2]oct-2-ene-1,4-dicarboxamide.—A mixture of 4 g. of the bis(benzylamide) of **2** in 25 ml. of benzene was heated in an autoclave at 180° for 14 hr. under an ethylene pressure of 2500 atm. The reaction product was recrystallized from methanol to yield white crystals of N,N′-dibenzylbicyclo-[2.2.2]oct-2-ene-1,4-dicarboxamide: m.p. 202–204°; ν_{max} (Nujol) 3400, 1650, 1560 (weak), 1530, 1320, 1300, 1140, 1080, 1070, 1035, 990, 972, 858, 735, 725, 698 cm.$^{-1}$.

Anal. Calcd. for $C_{24}H_{26}N_2O_2$: C, 76.97; H, 7.00; N, 7.48. Found: C, 77.10; H, 7.38; N, 7.41.

Bicyclo[2.2.2]oct-2-ene-1,4-dicarboxylic Acid.—A mixture of 20 g. of cyclohexa-1,3-diene-1,4-dicarboxylic acid and 40 ml. of acetic acid was heated at 200° for 14 hr. in an autoclave under an ethylene pressure of 3000 atm. The solid product was separated by filtration and washed with cyclohexane and with 95% alcohol. The solid was stirred with 200 ml. of 5% sodium carbonate solution to which 50 ml. of methanol was added. The solution was filtered and, when acidified, deposited 8.1 g. of bicyclo[2.2.2]-oct-2-ene-1,4-dicarboxylic acid. Recrystallization from acetic acid yielded white crystals: m.p. 365° dec.; ν_{max} 2970, 2870, 2650, 2530, 1700, 1625 (weak), 1455, 1420, 1307, 1270, 1105, 955, 852, 753, 703 cm.$^{-1}$.

Anal. Calcd. for $C_{10}H_{12}O_4$: C, 61.21; H, 6.17; neut. equiv., 98. Found: C, 60.94; H, 6.60; neut. equiv., 95.

The acid (2.8 g.) was warmed on a steam bath with 7.5 g. of phosphorus pentachloride, and pentane (60 ml.) was added. A 20-ml. portion of this solution was treated with methanol and yielded 0.5 g. of crystalline dimethyl bicyclo[2.2.2]oct-2-ene-1,4-dicarboxylate whose infrared spectrum was identical with that of **8**. A second 20-ml. portion of the acid chloride solution was treated with a solution of benzylamine in benzene. The product after recrystallization from aqueous methanol melted at 203–205° and was identical (infrared, mixture melting point) with the previously described N,N′-dibenzylbicyclo[2.2.2]oct-2-ene-1,4-dicarboxamide.

Reaction of Cyclohexa-1,3-diene-1,4-bis(carbonyl chloride) with Ethylene.—Ten grams of **3** was heated at 150° for 14 hr. with ethylene under a pressure of 1000 atm. Half of the resulting crude solid acid chloride (9.0 g.) was treated with methanol to produce 5.8 g. (54%) of dimethyl bicyclo[2.2.2]oct-2-ene-1,4-dicarboxylate, whose infrared spectrum was identical with that of **8**.

Dimethyl Bicyclo[2.2.2]octane-1,4-dicarboxylate (10).—A solution of 54.8 g. of **8** in 150 ml. of tetrahydrofuran was hydrodrogenated at 40 p.s.i. using 0.2 g. of platinum oxide catalyst. The mixture was filtered, and solvent was removed under vacuum. The residue was recrystallized from 80% methanol to yield 50.8 g. (92%) of dimethyl bicyclo[2.2.2]octane-1,4-dicarboxylate (m.p. 100–101°) in two crops. Two interconvertible crystalline forms were obtained. The first has peaks at ν_{max} 1725, 1255, 1190, 1075, 992, 943, 856, 828, 790, and 743 cm.$^{-1}$.

Anal. Calcd. for $C_{12}H_{18}O_4$: C, 63.70; H, 8.02. Found: C, 64.07; H, 8.06.

The second crystalline modification has peaks at 982, 943, 908, 851, 825, 789, 783, 760, and 752 cm.$^{-1}$; n.m.r. τ 8.14 [12] (CH_2) sharp, 6.25 [6] (OCH_3) sharp.

Saponification of the ester with potassium hydroxide in aqueous methanol followed by acidification yielded bicyclo[2.2.2]octane-1,4-dicarboxylic acid (**11**), in quantitative yield, m.p. 422° dec. after recrystallization from acetic acid (lit.[1] m.p. 385°). Two interconvertible crystalline forms could be obtained. The infrared spectrum of one of these forms was identical with that of a sample prepared by the method of Guha.[1]

Bicyclo[2.2.2]octane-1,4-bis(carbonyl chloride) (12).—A suspension of 79 g. of **11** (oven dried to constant weight) in 500 ml. of thionyl chloride containing 1 drop of N,N′-dimethylformamide was heated at reflux overnight. Excess thionyl chloride was removed by distillation, and the residue was fractionally distilled through a Vigreux column. The fraction boiling at 127–128° (1.7 mm.) weighed 83.4 g. and solidified to white crystals, m.p. 93–97°. This was recrystallized from hexane to yield 81.3 g. (82%) of colorless needles of bicyclo[2.2.2]octane-1,4-bis(carbonyl chloride), m.p. 97.5–98.5°, in two crops: ν_{max} (Nujol) 1790, 1290, 1250, 1170, 1135, 1090, 1015, 995, 860, 785 cm.$^{-1}$.

Anal. Calcd. for $C_{10}H_{12}Cl_2O_2$: Cl, 30.17. Found: Cl, 30.05, 30.10.

A portion of this acid chloride was treated with ethanol to yield diethyl bicyclo[2.2.2]octane-1,4-dicarboxylate, m.p. 24–25°, whose infrared spectrum was identical with that of a sample prepared by the method of Roberts, Moreland, and Frazer.[2]

Bicyclo[2.2.2]octane-1,4-diisocyanate (13).—A solution of 80 g. of **12** in 350 ml. of acetone was added slowly to a solution of 100 g. of sodium azide in 250 ml. of water at 10–15°. The reaction mixture was stirred at 5° for 1.5 hr., and after warming slowly (0.5 hr.) to 20°, 1.5 l. of an ice–water mixture was added, and the mixture was stirred for 5 min. The crystalline azide (infrared absorption 1705 and 2140 cm.$^{-1}$ in carbon tetrachloride solution) which separated was dissolved in 250 ml. of benzene. The benzene layer was separated, washed with water, and dried over magnesium sulfate. The benzene solution was then added dropwise while stirring to 500 ml. of dry refluxing benzene. Vigorous nitrogen evolution occurred. The solution was allowed to reflux for 3 hr. Solvent was removed under vacuum, and the residue was distilled to yield 61.5 g. of colorless liquid (b.p. 133–135° at 8.5 mm.) which solidified on standing. The crude bicyclo[2.2.2]octane-1,4-diisocyanate was recrystallized from 200 ml. of hexane to yield 51.2 g. (78%) of colorless plates: m.p. 111.0–112.5°; ν_{max} 2950, 2880, 2260, 1460, 1350, 1045, 968, and 845 cm.$^{-1}$; n.m.r. τ 8.03 (CH_2) sharp.

Anal. Calcd. for $C_{10}H_{12}N_2O_2$: C, 62.48; H, 6.29; N, 14.58. Found: C, 62.88; H, 6.30; N, 14.81, 15.04.

A second crop weighing 10 g. (15%) was recovered by evaporation of the filtrate.

1,4-Diaminobicyclo[2.2.2]octane (14).—A mixture of 46 g. of **13** and 350 ml. of concentrated hydrochloric acid in a 1-l. flask was swirled occasionally until gas evolution ceased. The mixture was then heated at reflux for 2 hr. after all the solid had dissolved. The solution was allowed to cool to 10° while being saturated with hydrogen chloride gas. The white crystalline 1,4-diaminobicyclo[2.2.2]octane hydrochloride was separated by filtration and was washed with concentrated hydrochloric acid. It was dried with a stream of nitrogen to yield 43.4 g. of white needles. An additional 14.3 g. was obtained by evaporation of the filtrate under vacuum.

Since 1,4-diaminobicyclo[2.2.2]octane reacts rapidly with atmospheric carbon dioxide, all succeeding operations were carried out under nitrogen. The first crop of amine hydrochloride was placed in a 200-ml. continuous liquid–liquid extraction apparatus, and 110 g. of crushed ice was added followed by 55 g. of sodium hydroxide pellets. The soution was continuously extracted with ether for 3 days. The resulting ether extract was evaporated under reduced pressure, and the residue was recrystallized from 1700 ml. of moist ether to yield 24.3 g. (64%) of 1,4-diaminobicyclo[2.2.2]octane monohydrate, m.p. 88.9–90.8°. A second crop of 9.1 g. (24%) was obtained from the filtrate: n.m.r. (CCl_4) 8.48 [12] (CH_2), band width 0.7 c.p.s.; 9.25 [4] (NH_2), band width 16 c.p.s.; ν_{max} (CCl_4) 3370, 3300, 2930, 2860, 1590, 1455, 1350, 1250, 1153, 1047 cm.$^{-1}$.

Anal. Calcd. for $C_8H_{18}N_2O$: C, 60.72; H, 11.47; N, 17.70. Found: C, 60.56; H, 10.94; N, 17.82.

The anhydrous amine was prepared by stirring an ethereal solution of the amine hydrate with a large excess of sodium hydroxide pellets for 3 days under nitrogen. The ether was distilled under reduced pressure, and the residue was sublimed (60° at 2 mm.). The sublimate (m.p. 67.5–68.5°) was recrystallized from dry ether to yield white crystals of anhydrous 1,4-diaminobicyclo[2.2.2]octane: n.m.r. (CCl_4) 8.47 [12] (CH_2), band width 0.9 c.p.s.; 9.25 [4] (NH_2), band width 7 c.p.s.

Anal. Calcd. for $C_8H_{16}N_2$: C, 68.52; H, 11.50; N, 19.98; neut. equiv., 70.1. Found: C, 68.32; H, 11.22; N, 20.53; neut. equiv., 69, 71.

Both the amine **14** and its hydrate are fairly volatile and are best stored in a sealed glass ampoule, since they will slowly sublime *through* a polyethylene stopper.

Dimethyl Cyclohexa-1,4-diene-1,4-dicarboxylate (15).[12]—A solution of 83 g. of terephthalic acid and 100 g. of 85% potassium hydroxide in 750 ml. of water was placed in an electrolysis cell equipped with a stirred mercury cathode and a porous cup filled with a 30% potassium hydroxide solution and containing a platinum anode. An electric current of about 5 amp. was passed through the cell until the evolution of a large quantity of bubbles of hydrogen from the cathode signaled the completion of the reduction. The catholyte was filtered and acidified with hydrochloric acid. The precipitated acid was washed several times with water, air dried, and finally vacuum dried. A 65-g. portion of the dried acid was suspended in 200 ml. of benzene and treated with a total of 260 g. of phosphorus pentachloride added in portions. The mixture was heated at reflux for 4 hr. Solvent was then removed on a steam bath at 20-mm. pressure. The residue was cooled, and the crude acid chloride was filtered and washed with pentane. It was cautiously added in small portions with vigorous stirring to 500 ml. of methanol. On refrigeration, crude dimethyl cyclohexa-1,4-diene-1,4-dicarboxylate (**15**) crystallized and was separated by filtration. It was stirred with 10% aqueous potassium bicarbonate, washed with water, and after recrystallization from methanol melted at 129.4–131° (lit.[13b] m.p. 130°): λ_{max} 203 mμ (ϵ 23,500) (ethanol), 240 mμ sh (ϵ 1400); ν_{max} 3030, 2960, 2900, 1710 (C=O), 1645 (C=C), 1452, 1435, 1415, 1383, 1313, 1270, 1188, 1080, 1005, 967, 927, 803, 697 cm.$^{-1}$.

Anal. Calcd. for $C_{10}H_{12}O_4$: C, 61.21; H, 6.17. Found: C, 60.96; H, 6.05.

After 7 years of storage the melting point and infrared and ultraviolet spectra were unchanged.

A solution of 11.5 g. of **15** and 5.77 g. of maleic anhydride in 30 ml. of benzene was heated at reflux (steam bath) for 140 hr. Solvent was evaporated, and 40 ml. of ether was added. The solid product (9.72 g. 84%) was pure unreacted **15**. The filtrate was found to contain only maleic anhydride and a mixture of dimethyl terephthalate with **15**.

Baeyer and Muthmann[13b] determined by goniometry the crystal lattice elements of a sample of **15** recrystallized from ethyl acetate, m.p. 130°.[13b]

$$a:b:c = 1.52:1:2.79;\ \beta = 74°$$

These elements were determined[16] by X-ray diffraction for our material similarly recrystallized.

$$a = 4.59\ \text{Å}.;\ b = 6.25\ \text{Å}.;\ c = 17.58\ \text{Å}.$$

$$a:b:c = 0.735\ (1.47/2):1:2.814;\ \beta \equiv 72°\ 40'$$

The System Dimethyl Terephthalate–Dimethyl Cyclohexa-1,4-diene-1,4-dicarboxylate.—Dimethyl terephthalate was recrystallized successively from methanol and from benzene and was vacuum dried. Dimethyl cyclohexa-1,4-diene-1,4-dicarboxylate was recrystallized successively from methanol and ethyl acetate and was vacuum dried. Samples of each were weighed into stoppered sample vials and were rapidly melted together by immersion in an oil bath maintained at 175°. The vials were rapidly cooled in ice water, and the contents were ground to a fine powder. The melting points were determined in capillary tubes in an oil bath whose temperature was raised at 0.2–0.3°/min. (Table II). A calibrated precision thermometer was employed.

TABLE II

Mole fraction of dimethyl terephthalate	M.p., °C.
0.000	128–129.2
0.111	124.1–125.6
0.159	124.6–125.5
0.301	125.8–127.6
0.500	129.4–131.1
0.739	134.0–135.3
0.876	136.5–137.8
1.000	140.4–141.1

The first temperature corresponds to the first visible appearance of liquid, and the second corresponds to the disappearance of the last solid. The results indicate that these components form a simple eutectic system at their melting point.

Properties of a 1 : 1 Mixture of 17 and 15.—A mixture of 0.2047 g. (0.001055 mole) of dimethyl terephthalate and 0.2070 g. (0.001055 mole) of dimethyl cyclohexa-1,4-diene-1,4-dicarboxylate was melted rapidly, quenched, and ground to a fine powder with a spatula.

Anal. Calcd. for $C_{20}H_{22}O_8$: C, 61.53; H, 5.68. Found: C, 61.55, 61.75; H, 5.84, 5.76.

The ultraviolet, infrared, and n.m.r. spectra were essentially linear combinations of those of the constituents: ν_{max} 698, 728, 806, 815, 874, 932, 955, 1008, 1020, 1087, 1103, 1118, 1198, 1273, 1320, 1387, 1410, 1443, 1509, 1650, 1715, 1730, 2840, 2890, 2950, 3010 cm.$^{-1}$; ultraviolet spectrum, λ_{max} mμ (log ϵ), 240 (4.024), 285 (2.928), 294 (2.848) [these agree fairly well with the values reported by Smith, Warren, and Vaughan[10] for their "diene IV": λ_{max} mμ (log ϵ), 240 (4.069), 286 (3.107), 294 (3.090). Closer agreement was obtained by a mixture containing 5% of **5** (see below)]; n.m.r. (*cf.* Table I) τ 1.73 [2.0] s, 2.86 [1.0] fs, 5.97 [3.1] s, 6.17 [3.1] s, 6.81 [2.1] fs. The corresponding values reported for "diene IV"[10] are τ 1.72 [2] s, 2.83 [1] fs, 5.97 [3] s, 6.16 [3] s, 6.80 [2] fs, and 6.13 "buried."

Properties of a Mixture of 5, 15, and 17.—A mixture of 0.0191 g. of **5**, 0.1926 g. of **15**, and 0.1976 g. of **17** was prepared as described: m.p. 126.0–130.4°; λ_{max} mμ (log ϵ based on av. mol. wt. = 195), 240 (4.012), 286 (3.071), 294 (3.070); n.m.r. τ 1.70 [2.0] s, 2.80 [1.0] fs, 5.94 [3.0] s, 6.15 [3.2] s, 6.80 [1.9] fs, 7.39 [0.2] fs. To check the analytical procedure used to analyze mixtures of **5**, **15**, and **17** (see below), the above mixture gave the following values (mole %) by integration of the n.m.r. peaks at τ 5.94, 6.15, 6.80, and 7.39: calcd. for **5**, 4.7%; **15**, 46.9%; **17**, 48.5%; found for **5**, 5.1%; **15**, 46.1%; **17**, 48.8%.

Reaction of 5 and 15 with Aqueous Potassium Hydroxide.—These experiments were carried out several times in the presence or absence of air and with variations in agitation and method of heating (oil bath or electric heating mantle). In all cases **5** yielded mixtures of **5**, **15**, and **17**, while **15** yielded **15** and **18** with at most only traces of **5**. The relative proportions of products could be estimated by integration of the n.m.r. peaks at τ 5.95 for **17** (OCH_3), at τ 6.8 for **15** (CH_2), at τ 7.38 for **5** (CH_2), and at τ 6.1–6.2 for **5** and **15** (OCH_3). In a typical experiment 1.0 g. of **5** was heated at reflux (oil bath, magnetic stirrer, air) in a solution of 1.1 g. of 85% potassium hydroxide in 1.0 ml. of water for 3.5 days. The mixture was cooled and acidified with hydrochloric acid. The resulting product was filtered, washed with water, and vacuum dried. The product (1.02 g.) was gently warmed with 5 g. of phosphorus pentachloride for 30 min. It was cooled in ice, and 10 ml. of methanol was added dropwise. The solution was refrigerated and yielded 0.54 g. of a mixture of 13% **17**, 43% **15**, and 44% **5**. After one recrystallization from ethyl acetate these values were 14, 68, and 18%, respectively. After a second recrystallization the values were 36, 62, and 2%.

When **15** was treated similarly (electric heating mantle, magnetic stirrer, air), the product after one recrystallization from ethyl acetate consisted of **15** (51%), **17** (47%), and **5** (2% max.)

Free-Radical Additions to Vinylcyclopropane and Butadiene Monoxide[1]

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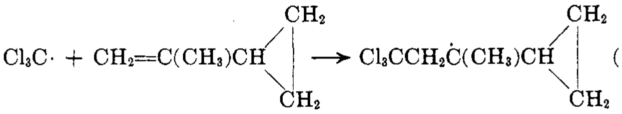
The light-induced addition of bromotrichloromethane to vinylcyclopropane gave a mixture of *cis*- and *trans*-1,1,1-trichloro-6-bromohex-3-ene. The additions of cyclopentane, cyclohexane, and cyclooctane to butadiene monoxide in di-*t*-butyl peroxide induced reactions yielded the corresponding *trans*-4-cycloalkylbut-2-en-1-ols. Isopropyl alcohol was added to butadiene monoxide in a similarly induced reaction yielding *trans*-5-methylhex-2-en-1-ol. The formation of these addition products is proposed to proceed by a β-elimination reaction involving the opening of the three-membered ring. The stereochemistry of the β-elimination reaction is discussed in terms of the conformational factors encountered in the transition states of the reactions.

In an earlier report,[3] the free-radical additions of polyhalomethanes and mercaptans to 2-cyclopropylpropene (I) were shown to yield unsaturated products that required the opening of the cyclopropyl ring. The ring opening in these reactions was a β-elimination reaction that involved the adduct radical A· yielding a rearranged radical B· which reacted with the adding reagent to produce the addition product. These steps are illustrated in the following chain sequence (eq. 1–3) for the addition of bromotrichloromethane to I. This system did not lend itself readily to a study of the stereochemistry of the β-elimination reaction. For this reason we undertook the investigation of free-radical addition reactions to vinylcyclopropane (II) and butadiene monoxide (III). These two unsaturated compounds undergo similar β-elimination reactions in free-radical additions yielding 1,2-disubstituted ethylenes as addition products, making the configura-

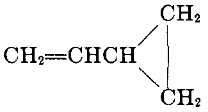


I A·

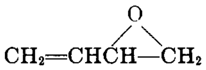
(1)

$$A\cdot \longrightarrow \underset{B\cdot}{Cl_3CCH_2C(CH_3){=}CHCH_2\dot{C}H_2} \qquad (2)$$

$$B\cdot + BrCCl_3 \longrightarrow Cl_3CCH_2C(CH_3){=}CHCH_2CH_2Br + Cl_3C\cdot \qquad (3)$$



II



III

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[2] Taken from the thesis submitted by L. R. M. in partial fulfillment of the requirements for the M.S. degree from the University of Kansas, 1964.

[3] E. S. Huyser and J. D. Taliaferro, *J. Org. Chem.*, **28**, 3442 (1963).