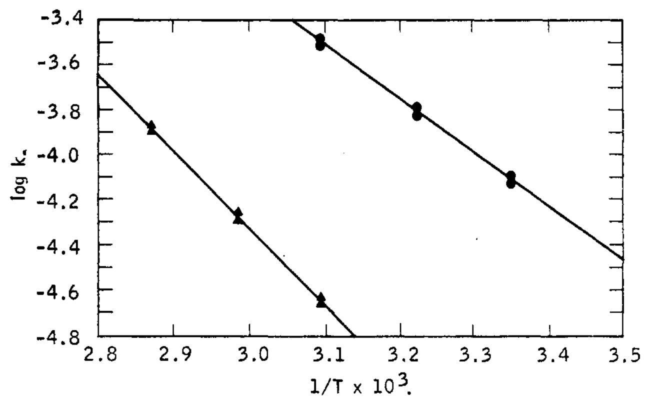

Fig. 3.—Enthalpy of activation from log *k vs.* 1/*T*: ▲, 1,3-cyclohexadiene; ●, 1,4-cyclohexadiene.

second-order reaction.[16] Quantitative analysis for amount of compound VIII (from 1,4-cyclohexadiene and I) at different temperatures was based on the ultraviolet absorption of VIII at 258 mμ (ϵ_{max} 3760). After all solvent and unchanged diene were removed from the reaction mixture the product was diluted with ethanol and the concentration of VIII determined from the ultraviolet absorption. Reproducibility of results by this method was ±0.3%. Qualitative verification for the validity of this method was based on the analysis of benzene (and therefore ethyl hydrazodicarboxylate) by v.p.c.[15] Quantitative analysis for II, V, and ethyl hydrazodicarboxylate from the reaction of 1,3-cyclohexadiene and I was done by v.p.c.[14] Molar response data[18] from known mixtures of ethyl hydrazodicarboxylate and II and ethyl hydrazodicarboxylate and V were sufficient for the quantitative analysis of all three components. Reproducibility was good to ±1%. Reaction temperatures for 1,3-cyclohexadiene and I were 25.05 ± 0.05°, 37.07 ± 0.05°, and 49.96 ± 0.05°; for 1,4-cyclohexadiene and I reaction temperatures were 49.96 ± 0.05°, 61.86 ± 0.05° and 75.22 ± 0.05°. The plot of log *k vs.* 1/*T* is shown in Fig. 3 for the reaction of ethyl azodicarboxylate and both 1,3- and 1,4-cyclohexadiene. As can be seen from Fig. 3 the plots are quite good so that over-all enthalpies of activation are good to at least ±0.5 kcal.

Acknowledgment.—The author is greatly indebted to Mr. John H. Surridge for his invaluable assistance in the experimental work. Credit is given to my colleagues, Drs. W. A. Thaler, W. C. Baird, E. I. Snyder, and J. L. Kurz, along with Professors W. E. von Doering H. C. Brown, S. J. Cristol, and P. S. Skell for their helpful discussions and suggestions. The determination of the n.m.r. spectra is credited to Dr. Boyd E. Hudson, Jr.

(18) A. E. Messner, D. M. Rosie, and P. A. Argabright, *Anal. Chem.*, **31**, 230 (1959).

Synthesis of Bicyclic Nitriles and Related Compounds. II[1,2]

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A number of polynitriles and related compounds derived from bicyclic systems have been prepared *via* the Diels–Alder reaction. Of particular interest is the reaction of chloromaleic anhydride with 1-carbomethoxycyclohexa-1,3-diene, which affords but one of the two structurally possible isomers; chlorine appears in the 2-position of the adduct. The preparation of 2,3-diacetoxycyclohexa-1,3-diene is described, but the compound failed to react satisfactorily in the Diels–Alder synthesis.

A previous publication[1] in this series described the synthesis of a number of bicyclic nitriles and related compounds whose synthesis was stimulated by the unexpected antileukemia activity of the Diels–Alder adduct of fumaronitrile and cyclohexa-1,3-diene. The present paper is, in part, an extension of this exploratory synthesis and, in part, related to the broader problem of the scope and limitations of the Diels–Alder reaction with functionally substituted cyclic dienes and the steric course of this reaction.

Following up the reaction of fumaronitrile with cyclopentadiene[6] and cyclohexa-1,3-diene, it has been found that it is in general a practicable dieneophile, good yields of adducts being obtained with furan and cyclohepta-1,3-diene.[7]

A potential intermediate[8] in the preparation of fumaronitrile, α-chloroacrylonitrile, also proved to be a practicable dieneophile, with cyclopentadiene and cyclohexa-1,3-diene. The two purified adducts, which probably are the less soluble members of two epimeric pairs, surprisingly showed complete inertness to refluxing with silver nitrate solution. Thus, one may tentatively assign an *endo* configuration to the chlorine, for in the *exo* configuration one might reasonably expect comparatively labile chlorine.

An examination of the α-chloroacrylonitrile adducts by n.m.r. affords additional support for the *endo*-chlorine configuration: the vinyl protons in *exo*- and *endo*-bicyclo[2.2.1]hept-5-ene-2-carbonitrile appear as multiplets, respectively, at 3.83 and 3.72 τ (deuteriochloroform, internal tetramethylsilane reference, 60 Mc.), whereas in the 2-chlorobicyclo[2.2.1]hept-5-ene-2-carbonitrile, the vinyl protons appear as two multiplets at 3.79 and 3.52 τ suggesting that one of them (on C-6) is in approximately the same environment as in the unchlorinated compound while the other is less shielded due to the *endo*-chlorine. In 2-chlorobicyclo[2.2.2]oct-5-ene-2-carbonitrile a multiplet for two protons falls at 3.64 τ, which suggests about the same environment as for the [2.2.1] analog.

Further evidence for the *endo*-chlorine configuration appears in the reduction of 2-chlorobicyclo[2.2.1]heptane-2-carbonitrile by lithium aluminum hydride. The product, isolated as the hydrochloride, consists of

(1) Previous paper in this series: P. Scheiner and W. R. Vaughan, *J. Org. Chem.*, **26**, 1923 (1961).

(2) Work supported in part by a research grant (CY 5406) from the National Cancer Institute to The University of Michigan.

(3) National Institutes of Health Predoctoral Fellow, 1960–1961.

(4) Abstracted in part from a portion of the Ph.D. dissertation of P. Scheiner, The University of Michigan, 1961.

(5) American Cancer Society Institutional Research Grant Fellow, Summer, 1961.

(6) A. T. Blomquist and E. C. Winslow, *J. Org. Chem.*, **10**, 149 (1945).

(7) Hi-Laboratory, Whitmore Lake, Mich.

(8) D. T. Mowry and W. H. Yanko, to Monsanto Chemical Co., U. S. Patent 2,471,767 (1949).

more than 50% *endo*-2-aminomethylbicyclo[2.2.1]heptane.[9] If one allows inversion for replacement of the chlorine, this is the expected product. The alternative involving intermediate ethyleneimine formation followed by reopening of the aziridine ring, which would lead to the product isolated from the epimer, is not particularly attractive, since other work in this laboratory[10] has shown that the aziridine system is generally stable to lithium aluminum hydride.

Similar reduction of bicyclo[2.2.2]oct-5-ene-*trans*-2,3-dicarbonitrile afforded bis-2,3-*trans*-aminomethylbicyclo[2.2.2]oct-5-ene as the dihydrochloride. The double bond in the preceding initial adduct proved to be "normal" with respect to catalytic hydrogenation, epoxidation (*cf.* acrylonitrile adduct and fumaronitrile adducts with cyclopentadiene in Experimental part), and reaction with phenyl azide [*cf.* fumaronitrile adduct with cyclopentadiene, and norbornadiene (bis adduct) with phenyl azide in Experimental part].

Further structural isomers of the desired bicyclic dinitriles might be expected *via* the reaction of acrylonitrile with cyclohexa-1,3-diene and cyclopentadiene, each carrying an appropriate acid derivative (*e.g.*, ester) in the 1-position. To this end 1-carbomethoxycyclohexa-1,3-diene and 1-carbomethoxycyclopentadiene[11] were prepared. In addition, the preparation of 1-cyanocyclohexa-1,3-diene was attempted, but it appeared to be too unstable for analysis, and did not react satisfactorily with acrylonitrile, fumaronitrile, dimethyl maleate, or dimethyl fumarate, the only identifiable product (infrared spectrum) being benzonitrile at temperatures above 150°. However, adducts were obtained with tetracyanoethylene and maleic anhydride. The ultraviolet analysis of the former adduct showed conjugated nitrile. Therefore, instead of the expected diene, 2-cyanocyclohexa-1,3-diene was either obtained initially[12] or during the reaction.

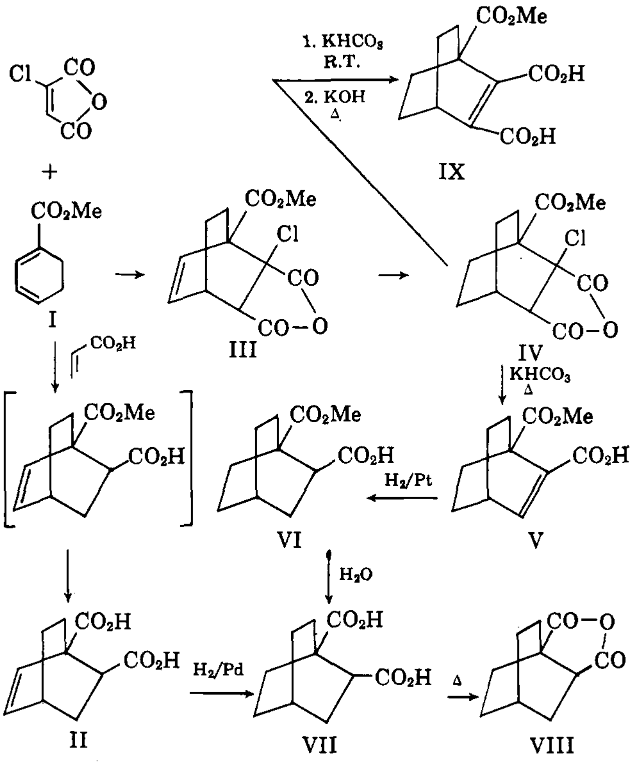
Carbomethoxycyclohexa-1,3-diene (I) also afforded a tetracyanoethylene adduct and a maleic anhydride adduct; in addition, adducts were obtained with acrylic acid and chloromaleic anhydride.

The problem of structure in the reactions of I was resolved in the following manner. I was allowed to react with both acrylic acid and with chloromaleic anhydride. In the former reaction only a dibasic acid was isolated (II), and in the latter only one characterizable product was obtained (55% yield, III). By the series of reactions, hydrogenation (IV), fragmentation (V) (dehalogenative decarboxylation), hydrogenation (VI), and hydrolysis (VII), the same product was obtained (VII) as by hydrogenation of II. The *ortho* relationship in VII was confirmed by anhydride formation, which was also achieved by heating VI. Thus the chloride in chloromaleic anhydride appears to provide a directive influence resulting in the chlorine assuming predominantly the *ortho* position in the adduct with I (*cf.* Chart I).

It is of interest to note that potassium bicarbonate at room temperature *does not* effect extensive fragmentation, but when followed with alkali produces, instead, dehydrohalogenation; thus IV → IX, and IX readily adds bromine to give a dibromide.

CHART I

EVIDENCE FOR STRUCTURE OF III



The corresponding 1-carbomethoxycyclopentadiene readily afforded a tetracyanoethylene adduct, but other derivatives were not investigated.

The problem of preparing 2,3-dicyanobicyclo[2.2.1]-hept-2-ene and the corresponding bicyclo[2.2.2]octene derivative required proceeding through the dimethyl acetylenedicarboxylate adducts with cyclopentadiene and cyclohexa-1,3-diene, respectively. Hydrogenation of the isolated double bond in each case proceeded satisfactorily, and conversion to the diamides was accomplished by methanolic ammonia catalyzed by sodium methoxide.[13] The diamides were then converted to the dinitriles by dehydration with phosphorus oxychloride.

It is appropriate to mention at this point two other bicyclic compounds available *via* a Diels–Alder reaction, of interest primarily for their potential resemblance to myleran (tetramethyleneglycolbismethanesulfonate): 2,3 - *trans* - bishydroxymethylbicyclo[2.2.1]hept - 5-ene[14] bismethanesulfonate and the corresponding saturated product obtained from it by hydrogenation.

It had been hoped to prepare a number of related functionally substituted bicyclic glycols for which 2,3-diacetoxycyclohexa-1,3-diene would be a desirable starting material, and to this end the diene was prepared from cyclohexane-1,2-dione and acetic anhydride with boron trifluoride etherate as catalyst. However, although a solid product was obtained with maleic anhydride and the new diene, it was not analytically satisfactory and proved to be too unstable to survive purification attempts.

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[9] K. Alder, K. Heimbach, and R. Reubke, *Chem. Ber.*, **91**, 1516 (1958).

[10] J. R. Wood, "Potential Anticancer Agents," Ph.D. dissertation, The University of Michigan, 1962.

[11] J. Thiele, *Ber.*, **34**, 68 (1901).

[12] V.p.c. analysis indicated a mixture, but principally one component.

[13] P. B. Russell, *J. Am. Chem. Soc.*, **72**, 1853 (1950).

[14] K. Alder and W. Roth, *Chem. Ber.* **87**, 161 (1954).

Finally, a further transformation of bicyclo[2.2.2]oct-5-ene *trans*-2,3-dicarbonitrile[6] also was carried out: lithium aluminum hydride reduction to the corresponding bisaminomethyl dihydrochloride.

Experimental[15]

7-Oxabicyclo[2.2.1]heptane-*trans*-2,3-dicarbonitrile.—A solution of 5.4 g. of 7-oxabicyclo[2.2.1]hept-5-ene-*trans*-2,3-dicarbonitrile[16] (0.37 mole) in 130 ml. of ethyl acetate was hydrogenated at 3 atm. with 0.5 g. of 5% palladium-on-carbon catalyst. A quantitative yield of product, m.p. 110–114°, was obtained after filtration and evaporation. Five crystallizations from ethyl acetate–*n*-hexane gave a product melting at 124–125°.

Anal. Calcd. for $C_8H_8N_2O$: C, 64.85; H, 5.44; N, 18.91. Found: C, 64.88; H, 5.43; N, 18.99.

Bicyclo[3.2.2]non-8-ene-*trans*-6,7-dicarbonitrile.—A solution of 7.8 g. (0.084 mole) of 1,3-cycloheptadiene[7] and 5.5 g. (0.071 mole) of fumaronitrile[17] in 27 ml. of xylene was refluxed for 48 hr. The dark reaction mixture was treated four times with Norit, then diluted with ethyl acetate and petroleum ether (b.p. 60–75°) and cooled, yielding 4.7 g. (38.5%) of a white camphor-like solid, melting above 128°. Recrystallization from petroleum ether (b.p. 90–100°) failed to change the melting point. Two vacuum sublimations at 80–90° (0.5 mm.), however, gave 3.6 g. (29%) of a white solid, m.p. 140.0–141.5°.

Anal. Calcd. for $C_{11}H_{12}N_2$: C, 76.71; H, 7.02. Found: C, 76.42; H, 6.70.

2-Chlorobicyclo[2.2.1]hept-5-ene-2-carbonitrile.—Freshly distilled cyclopentadiene (30 ml.) was added to a solution of 30 ml. of α-chloroacrylonitrile,[18] a small amount of hydroquinone, and 30 ml. of anhydrous diethyl ether. The reaction solution on standing 5 min., refluxed vigorously, and after moderation of the initial reaction, it was warmed over steam for 23 hr. After evaporation in an air stream, the resulting brown oil was sublimed at 85° (35 mm.). A fragrant white solid (41.0 g., 76%), m.p. 42–43°, was obtained. Two sublimations raised the melting point of the noncrystalline solid to 47–48° (34 g., 63%). V.p.c. analysis showed 10% of a second component. Microanalysis indicates the latter to be the epimer. N.m.r. showed vinyl protons at 3.52 and 3.79 τ.

Anal. Calcd. for C_8H_8ClN: C, 62.55; H, 5.25; N, 9.12. Found: C, 62.70; H, 5.43; N, 9.07.

Attempted Reaction of the Adduct with Silver Nitrate.—A solution of 3.6 g. (0.024 mole) of 2-chlorobicyclo[2.2.1] hept-5-ene-2-carbonitrile, 100 ml. of 5% aqueous silver nitrate, and 100 ml. of acetone was refluxed for 24 hr. The resulting solution was entirely clear with no precipitated solid. Most of the acetone was boiled off and the solution then extracted three times with 50-ml. portions of ether. After drying over sodium sulfate and removal of ether, 2.9 g. (81%) of starting material was recovered. (Poor recovery undoubtedly was due to the volatility of the starting material.)

2-Chlorobicyclo[2.2.1]heptane-2-carbonitrile.—A solution of 9.9 g. (0.065 mole) of 2-chlorobicyclo[2.2.1]hept-5-ene-2-carbonitrile in 100 ml. of ethyl acetate was hydrogenated at 3 atm. over 0.9 g. of 5% palladium on carbon. The crude product, 9.5 g. (95%), was sublimed at 53° (0.3 mm.). Two additional sublimations gave a fragrant noncrystalline white solid (7.2 g., 72%), m.p. 48.0–49.5°. Analysis by v.p.c. indicates a second component in approximately the same proportions as for the unsaturated starting material, and microanalysis implies that it is the epimer.

Anal. Calcd. for $C_8H_{10}ClN$: C, 61.73; H, 6.48; N, 9.00. Found: C, 61.97; H, 6.53; N, 8.94.

The product was reduced in ether with excess lithium aluminum hydride, and from the reaction there was isolated unreduced starting material (infrared), an uncharacterized carbonyl compound (infrared), and 50% of *endo*-2-aminomethylbicyclo[2.2.1]heptane hydrochloride,[9] identified by comparison of infrared spectrum with an authentic sample.[9]

2-Chloro-5,6-epoxybicyclo[2.2.1]heptane-2-carbonitrile.—A solution of 102 ml. of chloroform containing 9.5 g. (0.069 mole) of peroxybenzoic acid was added dropwise (0°) to 10.0 g. (0.069 mole) of 2-chlorobicyclo[2.2.1]hept-5-ene-2-carbonitrile. The clear solution was allowed to reach room temperature gradually, and the course of the reaction was followed titrimetrically. The reaction was completed in 24 hr. After washing with 55 ml. of 5% sodium hydroxide, followed by re-extraction of the aqueous layer with 50 ml. of chloroform, the combined organic layers were washed with 100 ml. of water and dried over magnesium sulfate. Evaporation in an air stream followed by sublimation of the fragrant oil over steam at 35–40 mm. produced 7.5 g. (68%) of a fragrant white, noncrystalline solid. The melting point of the compound, 90–96°, was not sharp, and did not improve on further sublimation. Analysis by v.p.c. indicated 20% of a minor component, and microanalysis implies an isomeric epoxide.

Anal. Calcd. for C_8H_8ClNO: C, 56.65; H, 4.76; N, 8.26; Cl, 20.90. Found: C, 56.91; H, 5.03; N, 7.91; Cl, 20.51.

5,6-Epoxybicyclo[2.2.1]heptane-2-carbonitrile.—A solution of 25 ml. of 40% peroxyacetic acid in acetic acid was added, in small amounts, to 11.9 g. (0.10 mole) of bicyclo[2.2.1]hept-5-ene-2-carbonitrile[19]) cooled in an ice–salt bath. The vigorous reaction which occurred caused the solution to boil for a few minutes. The cooled, colorless reaction mixture was evaporated to a thick oil in an air stream, then diluted with 50 ml. of ether, and washed cautiously with 50 ml. of 5% sodium bicarbonate solution. After drying over sodium sulfate, the organic layer was evaporated, yielding 10.0 g. (74.0%) of a viscous, sweet-smelling oil. Sublimation at 75° (0.3 mm.) produced a fragrant, noncrystalline white solid, melting from 82–83°. Five additional sublimations did not change these physical properties.

Anal. Calcd. for C_8H_9NO: C, 71.09; H, 6.71; N, 10.36. Found: C, 70.82; H, 6.63; N, 10.37.

5,6-Epoxybicyclo[2.2.1]heptane-*trans*-2,3-dicarbonitrile.—A 122-ml. chloroform solution containing 8.85 g. (0.064 mole) of peroxybenzoic acid was added to 7.2 g. (0.050 mole) of bicyclo-[2.2.1]hept-5-ene-*trans*-2,3-dicarbonitrile. The resulting solution remained at room temperature for 23 days, at which time standard thiosulfate indicated that reaction was complete. The solution was washed with 60 ml. of 5% sodium hydroxide, and the aqueous extract was extracted with 40 ml. of chloroform. The combined chloroform layers, washed with an equal volume of water, were dried over magnesium sulfate, filtered, and evaporated, yielding 7.8 g. (97.5%) of white solid, m.p. 160–165°. After four crystallizations from benzene–*n*-hexane, the compound melted at 184–185° (5.4 g., 68%).

Anal. Calcd. for $C_9H_8N_2O$: C, 67.48; H, 5.04; N, 17.49. Found: C, 67.88; H, 5.00; N, 17.39.

3a,4,5,6,7,7a-Hexahydro-5-(or 6)-chloro-1-phenyl-4,7-methano-1*H*-benzotriazole-5-(or 6)-carbonitrile.—A 70-ml. solution containing 9.7 g. (0.077 mole) of phenyl azide in carbon tetrachloride was mixed with 10.0 g. (0.065 mole) of 2-chlorobicyclo[2.2.1]hept-5-ene-2-carbonitrile, and the resulting solution was allowed to stand at room temperature for 4 days. On evaporation, 12.5 g. (70.5%) of solid, melting at about 130°, was collected in five crops. Repeated recrystallization of this material from petroleum ether (60–75°)-benzene (4:1) gave material melting at 146–147° dec. (7.1 g., 40%).

Anal. Calcd. for $C_{14}H_{13}ClN_4$: C, 61.65; H, 4.80; N, 20.54. Found: C, 61.61; H, 4.95; N, 20.46.

5,6-Epoxybicyclo[2.2.2]octane-*trans*-2,3-dicarbonitrile.—Bicyclo[2.2.2]oct-5-ene-*trans*-2,3-dicarbonitrile[1] (12.0 g., 0.076 mole) was dissolved in 185 ml. of a chloroform solution containing 12.0 g. (0.087 mole) of peroxybenzoic acid. The course of reaction, completed after 9 days at room temperature, was followed titrimetrically. The reaction solution was washed with a solution of 4.0 g. (0.10 mole) of sodium hydroxide in 75 ml. of water. The aqueous layer was re-extracted with 70 ml. of chloroform and combined with the original organic layer. After two washings with water, the chloroform solution was dried over magnesium sulfate and evaporated, yielding 14.6 g. (110%) of a viscous yellow oil. Repeated crystallization from *n*-hexane–benzene gave a sticky white solid, m.p. 188.5–189.5° (8.1 g., 61%).

Anal. Calcd. for $C_{10}H_{10}N_2O$: C, 68.94; H, 5.79; N, 16.08. Found: C, 69.06; H, 5.79; N, 15.97.

2-Chlorobicyclo[2.2.2]oct-5-ene-2-carbonitrile.—A solution of 14.6 g. (0.183 mole) of 1,3-cyclohexadiene,[20] 16.0 g. (0.183 mole)

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(15) Melting and boiling points are uncorrected. Microanalyses were by Spang Microanalytical Laboratory, Ann Arbor, Mich. N.m.r. spectra (Varian A-60) were obtained by Mr. B. E. Wenzel of this department (deuteriochloroform, internal tetramethylsilane, 60 Mc.).

(16) D. T. Mowry, *J. Am. Chem. Soc.* **69**, 573 (1947).

(17) Kindly supplied by Monsanto Chemical Co.

(18) Kindly supplied by American Cyanamid Co.

(19) H. A. Bruson, *J. Am. Chem. Soc.*, **64**, 2457 (1942).

(20) A. T. Blomquist and J. Kwiatek, *ibid.*, **73**, 2098 (1951).

of α-chloroacrylonitrile[21] (partially polymerized), a few crystals of hydroquinone, and 30 ml. of anhydrous xylene was refluxed for 24 hr. The clear solution was filtered away from the large amounts of polymer present in the original flask and evaporated to yield 2.8 g. (9.2%) of a fragrant white solid, m.p. 72.0–73.5°. Four sublimations at 110–120° (1.0–2.0 mm.) gave a noncrystalline solid melting at 84–85° (1.9 g., 6.3%). N.m.r. showed vinyl protons as multiplet at 3.64 τ.

Anal. Calcd. for $C_9H_{10}ClN$: C, 64.48; H, 6.01; N, 8.36. Found: C, 64.22; H, 6.22; N, 8.15.

Treatment with silver nitrate as for the bicycloheptene analog also afforded no observable reaction and good recovery.

3a,4,5,6,7,7a-Hexahydro-1-phenyl-4,7-methano-1*H*-benzotriazole-*trans*-5,6-dicarbonitrile.—A 44-ml. solution of 5.8 g. (0.049 mole) of phenyl azide in carbon tetrachloride was mixed with 7.0 g. (0.049 mole) of bicyclo[2.2.1]hept-5-ene-*trans*-2,3-dicarbonitrile[1] and the resulting solution allowed to stand at room temperature for 40 hr. The precipitated solid, 7.1 g. (55.0%), was filtered and recrystallized from 95% ethanol, to give a white crystalline solid, m.p. 198° dec. Four further recrystallizations raised the decomposition point to 202° (4.6 g. 36%).

Anal. Calcd. for $C_{15}H_{13}N_5$: C, 68.42; H, 4.98. Found: C, 68.27; H, 4.87.

3-(6)-Bromocyclohexene-1-carbonitrile.—In a three-necked flask fitted with a condenser and stirrer was placed 58.6 g. (0.547 mole) of cyclohexene-1-carbonitrile[22] dissolved in 300 ml. of carbon tetrachloride. The stirred solution was refluxed gently while 97.4 g. (0.547 mole) of N-bromosuccinimide was added in small portions. An additional 100 ml. of carbon tetrachloride was used to transfer the N-bromosuccinimide to the flask. The reaction mixture was then refluxed with stirring for 5 hr. After cooling and filtration the solvent was removed under reduced pressure, yielding 99.9 g. (98.0%) of a sweet-smelling yellow oil. The crude product was distilled at 103–110° (1.5–2.0 mm.) and redistilled at 85.5–90.0° (0.8–0.9 mm.). The product decomposed with loss of hydrogen bromide on standing exposed to air. It was not analyzed but was dehydrohalogenated directly.

1,3-Cyclohexadiene-2-carbonitrile.—To 52.1 g. (0.280 mole) of 3-(6)-bromocyclohexene-1-carbonitrile, stirred and chilled in ice, 73 ml. of a methanolic solution containing 15.1 g. (0.280 mole) of sodium methoxide was added dropwise over 1 hr. The reaction mixture was then diluted with 300 ml. of water and extracted twice with 100-ml. portions of ether. The combined ether extracts were dried over magnesium sulfate, and the solvent was then removed under reduced pressure, leaving 21.6 g. (89.0%) of a fragrant yellow oil. On distillation, a colorless product was obtained, b.p. 70–75° (1.0 mm.), $n^{24}D$ 1.4898. V.p.c. analysis showed two components, one in considerable excess. This material was used directly in subsequent Diels–Alder reactions.

Bicyclo[2.2.2]oct-5-ene-2,2,3,3,5-pentacarbonitrile.—A mixture of 3.3 g. (0.031 mole) of 1,3-cyclohexadiene-2-carbonitrile and 4.0 g. (0.031 mole) of tetracyanoethylene was heated in a large test tube for 1 hr. at 85° and heated an additional hour at 115°. The dark reaction mixture, after remaining at room temperature for 13 hr., was filtered and the solid material thus obtained was washed liberally with toluene and carbon tetrachloride. A yield of 5.3 g. (72.6%) of washed product was collected. Two recrystallizations from benzene gave a white crystalline solid which melted at 214–215°, but with darkening above 205° (3.1 g., 42%). Four crystallizations from *n*-hexane–benzene failed to change the melting point. N.m.r. spectrum shows one vinyl proton, 3.00 τ (multiplet).

Anal. Calcd. for $C_{13}H_7N_5$: C, 66.94; H, 3.03. Found: C, 67.03; H, 3.14.

Ultraviolet (compensated absolute ethanol) showed log ε 3.286 at 22 mμ, absorption still increasing; acrylonitrile, log ε 1.69 at 215 mμ, absorption still increasing; saturated nitriles transparent in this region.

Bicyclo[2.2.2]oct-5-ene-*cis*-2,3-dicarboxylic Acid Anhydride-5-carbonitrile.—Maleic anhydride (1.3 g., 0.013 mole) and 2.8 g. (0.027 mole) of 1,3-cyclohexadiene-2-carbonitrile were heated at 150° for 25.5 hr. After cooling and dilution with 2 ml. of *n*-hexane and 10 ml. of benzene, 1.5 g. (57%) of crude product separated, m.p. 150–160°. Four crystallizations from *n*-hexane–benzene gave pure material melting at 185–186° (0.8 g., 30%).

Anal. Calcd. for $C_{11}H_9NO_3$: C, 65.02; H, 4.47; N, 6.81. Found: C, 65.26; H, 4.67; N, 6.93.

1-Carbomethoxybicyclo[2.2.2]oct-5-ene-2,2,3,3-tetracarbonitrile.—A solution of 6.4 g. (0.050 mole) of tetracyanoethylene and 7.0 g. (0.051 mole) of 1-carbomethoxy-1,3-cyclohexadiene[23] (I) in 20 ml. of anhydrous dioxane was heated for 2 hr. at 100°. After cooling, the dark reaction mixture was filtered (13.5 g.). The adduct, recrystallized from benzene, melted at 191–193° (8.2 g., 61%). Further crystallization from the same solvent did not change the melting point.

Anal. Calcd. for $C_{14}H_{10}N_4O_2$: C, 63.15; H, 3.79; N, 21.04. Found: C, 63.16; H, 3.85; N, 21.11.

Bicyclo[2.2.2]oct-5-ene-1,2-dicarboxylic Acid (II).—A mixture of 15.6 g. (0.216 mole) of acrylic acid, 36.2 g. (0.262 mole) of I, and a few crystals of hydroquinone was heated at 150–165° for 74 hr. On dilution with *n*-pentane and ether, and cooling, 10.5 g. (24.8%) of a white solid, m.p. 195–198°, was collected. The solution yielded no other characterizable material. Three crystallizations from benzene–*n*-hexane gave 3.7 g. of material, m.p. 202–204° (II).[24] The infrared spectrum indicated a dibasic acid. This was converted directly to VII by hydrogenation with Adams' catalyst.

1-Carbomethoxy-2-chlorobicyclo[2.2.2]oct-5-ene-*cis*-2,3-dicarboxylic Acid Anhydride (III).—A mixture of 61.8 g. (0.446 mole) of I and 52.7 g. (0.420 mole) of chloromaleic anhydride was heated at 155–165° for 20 hr. The dark brown reaction mixture was placed under aspirator pressure on a steam bath for 4 hr., then cooled. The resulting brown solid crystallized from 300 ml. of benzene–*n*-hexane, affording 62.5 g. (55.0%) of crystalline solid, m.p. 120–125°. Two recrystallizations from benzene–*n*-hexane gave material, m.p. 125–126° (31.6 g., 28%).

Anal. Calcd. for $C_{12}H_{11}ClO_5$: C, 53.24; H, 4.10; Cl, 13.10. Found: C, 53.38; H, 4.20; Cl, 13.20.

1-Carbomethoxy-2-chlorobicyclo[2.2.2]octane-*cis*-2,3-dicarboxylic Acid Anhydride (IV).—A solution of 7.2 g. (0.027 mole) of 1-carbomethoxy-2-chlorobicyclo[2.2.2]oct-5-ene-*cis*-2,3-dicarboxylic acid anhydride in 150 ml. of ethyl acetate was hydrogenated with 0.2 g. of Adams' catalyst under 3-atm. pressure. After the theoretical uptake of hydrogen, the catalyst was filtered, the solvent was evaporated, and 7.3 g. (100.0%) of white crystalline product was obtained, m.p. 136.5–138.0°. Further recrystallization from *n*-hexane–ethyl acetate failed to change the melting point.

Anal. Calcd. for $C_{12}H_{13}ClO_5$: C, 52.85; H, 4.80; Cl, 13.00. Found: C, 52.92; H, 4.96; Cl, 12.99.

1-Carbomethoxybicyclo[2.2.2]oct-2-ene-2-carboxylic Acid (V).—A solution of 10.4 g. (0.104 mole) of potassium bicarbonate in 40 ml. of water was added to 14.0 g. (0.0513 mole) of 1-carbomethoxy-2-chlorobicyclo[2.2.2]octane-*cis*-2,3-dicarboxylic acid (IV) at room temperature. It was then immediately heated on the steam bath for 20 min., during which time the initial carbon dioxide evolution moderated and finally ceased. After filtration, the solution was acidified with concentrated hydrochloric acid and cooled in the refrigerator for 2 hr. The resulting white solid was filtered, washed with water, and dried at 70° (30 mm.) for 2 hr.: yield, 9.5 g. (90.9%), m.p. 140.5–142.0°. Three crystallizations from *n*-hexane–benzene (2:1) gave material melting at 144–145° (6.7 g., 64%).

Anal. Calcd. for $C_{11}H_{14}O_4$: C, 62.85; H, 6.71. Found: C, 62.75; H, 6.83.

1-Carbomethoxybicyclo[2.2.2]octane-2-carboxylic Acid. (VI).—A solution of 24.4 g. (0.116 mole) of 1-carbomethoxybicyclo-[2.2.2]oct-2-ene-2-carboxylic acid (V) in 220 ml. of ethyl acetate and 60 ml. of acetone was hydrogenated with 0.3 g. of 5% palladium-on-carbon at 3 atm. The hydrogenated solution was evaporated in an air stream to a viscous oil, 21.9 g. (89.0%). On standing, this oil solidified to a white powder, m.p. 66–67°. Two recrystallizaions from *n*-hexane gave material melting at 85–86° (10.4 g., 42%).

Anal. Calcd. for $C_{11}H_{16}O_4$: C, 62.25; H, 7.60. Found: C, 62.22; H, 7.69.

Bicyclo[2.2.2]octane-1,2-dicarboxylic Acid (VII).—A solution of 1.07 g. (5.44 moles) of bicyclo[2.2.2]oct-5-ene-1,2-dicarboxylic acid (II) in 70 ml. of ethyl acetate was hydrogenated at atmospheric pressure with 0.10 g. of platinum dioxide. Work-up in the

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[21] This compound was inert to silver nitrate in ethanolic solution at room temperature.

[22] O. H. Wheeler, and I. Lerner, *J. Am. Chem. Soc.*, **78**, 63 (1956).

[23] A. Sayigh, dissertation, Columbia University, 1952, p. 86.

[24] This compound corresponds in melting point to the same product prepared *via* a different route by J. Kazan and F. D. Greene. Results were kindly furnished prior to publication by Professor Greene.

usual manner gave 0.70 g. (65.4%) of product, m.p. 200–202°. Two recrystallizations from *n*-hexane–ethyl acetate (1:2) gave the pure acid, m.p. 200.5–201.0° (0.32 g., 33%).[24]

Anal. Calcd. for $C_{10}H_{14}O_4$: C, 60.59; H, 7.12. Found: C, 60.62; H, 7.09.

This compound was identical in melting point and infrared spectrum with the diacid resulting from either acidic or basic hydrolysis of VI. A mixture melting point determination of the two showed no depression.

Bicyclo[2.2.2]octane-1,2-dicarboxylic Acid Anhydride (VIII).—In a small round-bottom flask 0.3 g. of bicyclo[2.2.2]octane-1,2-dicarboxylic acid (VII) was heated for 2.5 hr. at 200° (±3°). The sublimed material in the neck of the flask, m.p. 125–163°, was removed, boiled with 20 ml. of *n*-hexane, and filtered. On concentration, white crystals separated, m.p. 163–164°. Two subsequent recrystallizations gave material melting at 166–167°.[24] The infrared spectrum of this compound showed the characteristic cyclic anhydride doublet (1865 and 1779 cm.$^{-1}$), but no carboxylic acid adsorption in the carbonyl region.

Anal. Calcd. for $C_{10}H_{12}O_3$: C, 66.65; H, 6.71. Found: C, 66.69; H, 6.76.

Distillation of VI at 140° (0.07 mm.) gave a mixture of anhydride and VI. Solid VIII separated from the mixture on cooling.

1-Carbomethoxybicyclo[2.2.2]oct-2-ene-2,3-dicarboxylic Acid (IX).—1-Carbomethoxy-2-chlorobicyclo[2.2.2]oct-2-ene-2,3-dicarboxylic acid anhydride (IV) (28.2 g., 0.107 mole), was treated with 21.4 g. (0.214 mole) of potassium bicarbonate in 87 ml. of water. The mixture was allowed to stand at room temperature until a clear solution was obtained, then heated 2–3 min. After acidification with concentrated hydrochloric acid and standing for 5.5 hr., a gummy white solid, 13.0 g., was obtained, m.p. 110–125°. This material was refluxed with 7.0 g. (0.125 mole) of potassium hydroxide in 40 ml. of 62% aqueous methanol for 2.5 hr. After concentration, acidification, and filtration, the resulting white solid was recrystallized from water, yielding 2.5 g. (9%) of solid, m.p. 221° dec. Two further crystallizations from 10% ethanol failed to change the melting point. The compound reacted immediately with potassium permanganate solution, and had an ester band in the infrared spectrum at 1739 cm.$^{-1}$.

Anal. Calcd. for $C_{12}H_{14}O_6$: C, 56.69; H, 5.55; neut. equiv., 258. Found: C, 56.72; H, 5.48; neut. equiv., 254.

1-Carbomethoxy-*trans*-2,3-dibromobicyclo[2.2.2]octane-2-carboxylic Acid.—Bromine (4.8 g., 0.030 mole) in 25 ml. of chloroform was added slowly to a stirred solution of 6.3 g. (0.030 mole) of 1-carbomethoxybicyclo[2.2.2]oct-2-ene-2-carboxylic acid (V) in 25 ml. of chloroform. The reaction flask was illuminated with a 100-w. bulb for 10 hr., at which time the deep bromine color of the original solution was discharged. Evaporation gave a brown oil which did not crystallize from *n*-hexane–benzene mixtures. After standing 5 days, this oil partially crystallized and was found then to be recrystallizable from *n*-hexane–benzene. Three such crystallizations gave material melting at 170.0–171.5°.

Anal. Calcd. for $C_{11}H_{14}Br_2O_4$: C, 35.70; H, 3.81; Br, 43.19. Found: C, 35.74; H, 3.89; Br, 43.32.

1-Carbomethoxybicyclo[2.2.1]hept-5-ene-2,2,3,3-tetracarbonitrile.—A solution of 2.5 g. (0.020 mole) of freshly distilled 1-carbomethoxy-1,3-cyclopentadiene[11,25] and 2.6 g. (0.020 mole) of tetracyanoethylene in 16 ml. of dioxane was heated on the steam bath for 1.5 hr. After concentration in an air steam, 2.2 g. (43%) of the crude adduct was obtained. Three crystallizations from ethyl acetate gave pure product, m.p. 229–230° dec.

Anal. Calcd. for $C_{13}H_8N_4O_2$: C, 61.90; H, 3.20; N, 22.21. Found: C, 61.74; H, 3.32; N, 22.18.

***trans*-2,3-Dihydroxymethylbicyclo[2.2.1]hept-5-enebismethanesulfonate.**—A solution of 17.2 g. (0.150 mole) of methanesulfonyl chloride in 10 ml. of anhydrous chloroform was added slowly to a cooled solution of 11.7 g. (0.073 mole) of *trans*-2,3-dihydroxymethylbicyclo[2.2.1]hept-5-ene[14] and 11.9 g. (0.150 mole) of anhydrous pyridine in 20 ml. of chloroform. During the addition the temperature rose to 60°. After standing 20 hr. at room temperature, the colorless solution was poured onto a mixture of 90 g. of ice and 150 ml. of 10% hydrochloric acid. The organic layer was separated and the aqueous solution reextracted twice with 90-ml. portions of chloroform. The combined organic layers were separated and the aqueous layer re-extracted twice with 90-ml. portions of chloroform. The combined organic layers were then dried with magnesium sulfate and evaporated to yield 19.8 g. (85.0%) of a dark oil. Crystallization readily occurred from absolute methanol, the analytically pure compound being obtained after two such crystallizations (11.7 g., 50.2%), m.p. 66–67°.

Anal. Calcd. for $C_{11}H_{18}O_6S_2$: C, 42.57; H, 5.84; S, 20.66. Found: C, 42.59; H, 5.87; S, 20.71.

***trans*-2,3-Dihydromethylbicyclo[2.2.1]heptanebismethanesulfonate.**—A solution of 5.3 g. (0.017 mole) of *trans*-2,3-dihydroxymethylbicyclo[2.2.1]hept-5-enebismethanesulfonate in 70 ml. of ethyl acetate was hydrogenated with 0.4 g. of Adams' catalyst at 3 atm. Removal of the solvent gave 5.3 g. (quantitative) of pale yellow oil which, on cooling, and addition of a small amount of absolute methanol, crystallized. Two crystallizations from absolute methanol gave a white crystalline solid, melting at 83–84° (3.5 g., 70%).

Anal. Calcd. for $C_{11}H_{20}O_6S_2$: C, 42.29; H, 6.45; S, 20.53. Found: C, 42.40; H, 6.50; S, 20.53.

Bicyclo[2.2.2]oct-2-ene-2,3-dicarbonitrile.—Dimethyl bicyclo-[2.2.2]octa-2,5-diene-2,3-dicarboxylate[26] was subjected to partial hydrogenation with a 5% palladium-on-carbon catalyst, giving dimethyl bicyclo[2.2.2]oct-2-ene-2,3-dicarboxylate (quantitatively) which was then converted into bicyclo[2.2.2]oct-2-ene-2,3-dicarboxamide by methanolic ammonia containing a catalytic amount of sodium methoxide.[13]

Anal. Calcd. for $C_{10}H_{14}N_2O_2$: C, 61.83; H, 7.27; N, 14.42. Found: C, 61.96; H, 6.71; N, 14.50.

Initial attempts to prepare the dinitrile by dehydrating the amide with thionyl chloride yielded only a cyclic amide irrespective of whether solvent was used or not. However, phosphorus oxychloride was effective. Bicyclo[2.2.2]oct-2-ene-2,3-dicarboxamide (12.47 g. 0.0655 mole) was heated on a steam bath with phosphorus oxychloride for 4.5 hr. The cooled solution was slowly poured onto crushed ice (150 g.) with constant stirring and then extracted with benzene (300 ml.).

The benzene extract was washed with water till neutral, then with ice-cold 5% sodium hydroxide (45 ml.), then again with water; it was dried over magnesium sulfate and the benzene was evaporated through a fractionating column. The residue obtained was crystallized from petroleum ether (m.p. 60–75°) giving light cream needles (6.18 g., 61%), m.p. 93°.

Anal. Calcd. for $C_{10}H_{10}N_2$: C, 75.92; H, 6.37; N, 17.71. Found: C, 76.03; H, 6.24; N, 17.61.

Bicyclo[2.2.1]hept-2-ene-2,3-dicarbonitrile.—The bicyclo-[2.2.1]hept-2-ene-2,3-dicarboxamide was prepared in an analogous manner to the bicyclo[2.2.2]oct-2-ene-2,3-dicarboxamide.

Anal. Calcd. for $C_9H_{12}N_2O_2$: C, 59.98; H, 6.71; N, 15.55. Found: C, 59.91; H, 6.71; N, 15.61.

The diamide (14 g. 0.078 mole) was heated with phosphorus oxychloride (100 ml.) on the steam bath for 4 hr. and was worked up as for the homolog, yielding a compound which was crystallized from petroleum ether (b.p. 60–75°) giving white plates (7.94 g., 70.6%), m.p. 42.5°.

Anal. Calcd. for $C_9H_8N_2$: C, 74.97; H, 5.59; N, 19.43. Found: C, 74.86; H, 5.56; N, 19.46.

***trans*-2,3-Bisaminomethylbicyclo[2.2.2]oct-5-ene Dihydrochloride.**—A solution of bicyclo[2.2.2]oct-5-ene-*trans*-2,3-dicarbonitrile (10.9 g., 0.069 mole) in anhydrous ether (200 ml.) and benzene (100 ml.) was added dropwise with stirring to a slurry of lithium aluminum hydride (3 g., 0.34 mole) in anhydrous ether (100 ml.). During the addition which required 30 min., the reaction mixture was refluxed gently and the stirring was continued a further 30 min. Then water (5.5 ml.) was slowly added, followed by 10% sodium hydroxide (5 ml.) and the stirring was continued for a further 3 hr. The solution was filtered and the filtrate dried over potassium hydroxide for 18 hr. Anhydrous hydrogen chloride was then passed through the solution for 1 hr., during which time a bulky precipitate (16.3 g., 0.0683 mole, 99%) formed. The solid was recrystallized from ethanol–acetone (3:2) giving a pure white salt, m.p. 288.5° (9.6 g., 58%).

Anal. Calcd. for $C_{10}H_{18}N_2\cdot 2HCl$: C, 50.20; H, 8.43; N, 11.71. Found: C, 50.16; H, 8.23; N, 11.58.

2,3-Diacetoxycyclohexa-1,3-diene.—Cyclohexane-1,2-dione, acetic anhydride, and boron trifluoride etherate were purified by distillation, then the dione (6.5 g. 0.058 mole) and acetic anhydride (15 ml.) were added to a dry, nitrogen purged flask and boron trifluoride etherate (1 ml.) was added to the solution

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(25) K. Alder, F. H. Flock, A. Hausweiler, and R. Reeber, *Chem. Ber.*, **87**, 1752 (1954).

(26) O. Diels and K. Alder, *Ann.*, **490**, 236 (1931).

through which nitrogen was passed. The flask containing the solution, covered by an atmosphere of nitrogen, was tightly stoppered and allowed to stand at room temperature for 2 days.

The brown liquid was then distilled under nitrogen giving a clear liquid (4.35 g., 0.022 mole, 38%), b.p. 54° (1 mm.). The distillate showed only ester absorption in the infrared.

Anal. Calcd. for $C_{10}H_{12}O_4$: C, 61.21; H, 6.17. Found: C, 61.10; H, 6.21.

Bis-2,3,5,6-(N-phenyl-*vic*-triazolino)bicyclo[2.2.1]heptane (Phenyl Azide–Norbornadiene Adduct).—A 76-ml. carbon tetrachloride solution containing 12.0 g. (0.10 mole) of phenyl azide was added to 4.6 g. (0.05 mole) of bicyclo[2.2.1]heptadiene. The pale green precipitate which first appeared after 12 hr. at room temperature was collected after 48 hr. A yield of 9.1 g. (55%), m.p. 229° dec., was obtained. This material proved insoluble in the usual solvents. Recrystallization was effected, however, in nitrobenzene (7.3 g., m.p. 229° dec.). The once recrystallized material was boiled with absolute ethanol and chloroform, to give analytically pure material (6.7 g., 41%), m.p. 229° dec.

Anal. Calcd. for $C_{19}H_{18}N_6$: C, 69.07; H, 5.49. Found: C, 69.07; H, 5.64.

This compound reacts to form a bright blue solution on treatment with glacial acetic acid.

Bicyclo[2.2.2]octane-1,2-dicarboxylic Acid[1]

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Bicyclo[2.2.2]octane-1,2-dicarboxylic acid has been synthesized *via* the reaction of dimethyl 1,3-cyclohexadiene-1,6-dicarboxylate with maleic anhydride (Chart I) and *via* the reaction of ethyl 1,3-cyclohexadiene-1-carboxylate with ethyl acrylate (Chart II). The latter reaction affords the four possible Diels–Alder adducts in the ratio of 30 (head-to-head *endo*): 8 (head-to-tail *endo*): 5 (head-to-head *exo*): 1 (head-to-tail *exo*). Stereochemical and structural assignments for the intermediates in the syntheses are described.

As part of a program for the investigation of the behavior of cyclic diacyl peroxides,[2] an aliphatic six-membered cyclic diacyl peroxide was desired. Since peroxides prepared from the cyclohexane-1,2-dicarboxylic acids have been reported to be unstable,[3] a requirement placed on the system at the outset was a structure in which bisdecarboxylation would be difficult. The system selected was bicyclo[2.2.2]octane-1,2-dicarboxylic acid (**9**). The preparation and proof of structure of compounds in this series are reported in this paper.

Bicyclo[2.2.2]octane-1,2-dicarboxylic acid (**9**) was prepared by two routes. The chemical evidence for the structural assignments is summarized in Charts I, II, and III. A higher over-all yield of **9** was obtained from the (less direct) route shown in Chart I, patterned after a synthesis reported by Grob, Ohta, Renk, and Weiss.[4] However, the Diels–Alder reaction between ethyl 1,3-cyclohexadiene-1-carboxylate and ethyl acrylate (Chart II) shows a fourfold preference for the formation of head-to-head adducts over the head-to-tail adducts; and this preference for head-to-head reaction, coupled with the ease of separation of 1,2-diacid **9** from 1,3-diacid **17** by means of the cyclic anhydride **10**, renders route II a reasonable one for compound **9**.

A few aspects of structure require amplification: (a) the structure of the product **3** of the base-catalyzed isomerization of dimethyl 1,4-cyclohexadiene-1,2-dicarboxylate (**2**); and (b) the stereochemistry of **7**, **19**, and **4**.

Isomerization of 2.—Structure **2**, expected by the method of synthesis, is supported by the ultraviolet ($\lambda_{\max}^{\text{MeOH}}$ 239, ϵ 2259)[5] and n.m.r. data. The n.m.r. spectrum exhibits three regions of absorption of area ratio 2:4:6 at 4.21 τ [one band weakly split into a triplet (vinyl H)]; 7.06 τ [one band weakly split into a doublet (methylene)]; and 6.30 τ [singlet (methyl)]. Compound **2** is readily isomerized by base. Of the six possible diene diesters, the new isomer is assigned structure **3** on the basis of the n.m.r. spectrum (five regions of absorption of area ratio 1:2:6:1:2 at 3.02 τ [broadened triplet (1 vinyl H)]; 3.96 τ [multiplet (2 vinyl H's)]; 6.27 and 6.38 τ [two sharp singlets (6 methyl H's)]; 6.5 τ [multiplet, partly obscured by the methyl peaks (1 tertiary H)]; 6.83–7.98 τ [complex multiplet (2 methylene H's)]. Further support for this assignment is found in the infrared absorption at 1710 and 1735 cm.$^{-1}$ (both conjugated and unconjugated esters) and the ultraviolet absorption at $\lambda_{\max}$ 288 (ϵ 8120) [compare with ethyl 1,3-cyclohexadiene-1-carboxylate **14**, $\lambda_{\max}$ 292 (ϵ 8260)]. That no further isomerization of **3** occurs during the Diels–Alder reaction with maleic anhydride may be concluded from an examination of Charts I and III and the spectral data cited in the Experimental section.

The base-catalyzed isomerization of **2** to **3** rather than to either of the two conjugated isomers (1,2-dicarbomethoxy-1,3-cyclohexadiene or 2,3-dicarbomethoxy-1,3-cyclohexadiene) is probably associated with the unfavorable steric situation between the adjacent ester groups in the latter two cases. The ester groups in **3** may be staggered, permitting full conjugation of one of the groups with the diene system.[6a]

Stereochemistry of 7 and 19.—Compound **7** may be isomerized by sodium methoxide in methanol, affording a mixture in which the *endo* isomer **19** predominates over the *exo* isomer **7** by a ratio of 3.5 to 1.[6b] The assignment of the *exo* structure to **7** and the *endo* to **19** is based on the inability of the former, and the ability of the latter, to afford a bromo lactone (Chart III). In addition, examination of the n.m.r. and

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[1] Supported in part by the research program of the Atomic Energy Commission under Contract No. AT(30-1)-905. Reproduction is permitted for any purpose of the U. S. Government.

[2] See F. D. Greene and W. W. Rees, *J. Am. Chem. Soc.*, **80**, 3432 (1958).

[3] W. von E. Doering, M. Farber, and A. Sayigh, *ibid.*, **74**, 4370 (1952).

[4] C. A. Grob, M. Ohta, E. Renk, and A. Weiss, *Helv. Chim. Acta*, **41**, 1191 (1958).

[5] For related cases, see A. T. Nielson, *J. Org. Chem.*, **22**, 1539 (1957).

[6] (a) The positions of equilibria in cyclohexadienes present a number of points of special interest. W. von E. Doering, Abstracts, Carbanion Symposium, 144th National Meeting of the American Chemical Society, Los Angeles, Calif., April, 1963. (b) In methyl bicyclo[2.2.1]hept-5-ene-2-carboxylate the *endo–exo* ratio is 51.5:48.5 [A. C. Cope, E. Ciganek, and N. A. LeBel, *J. Am. Chem. Soc.*, **81**, 2799 (1959)].