Nonaromatization Reactions of Bicyclo[2.2.0]hexa-2,5-diene (Dewar benzene)

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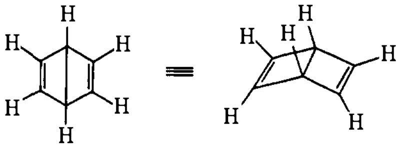
Abstract: A series of diverse, but representative, reactions of bicyclo[2.2.0]hexa-2,5-diene (Dewar benzene) (**1**) have been carried out. These reactions include the conversion of **1** to (1) dibromides **13** and **14**, as well as two tetrabromides, by appropriate amounts of molecular bromine, (2) monoepoxide **20**, by *m*-chloroperbenzoic acid, (3) tetrol **24**, by osmium tetroxide, followed by reduction of the osmate ester, (4) the $PdCl_2$ coordination compound **25**, by $PdCl_2$–$2C_6H_5CN$, (5) cyclohexane, by catalytic reduction over Pd/C, (6) 3,4-dichlorobicyclo[3.2.0]hepta-2,6-diene (**27**), by dichlorocarbene, (7) the bis adduct **33** or **34**, by 1,3-diphenylazocarbene, (8) Kekulé benzene, by ultraviolet irradiation or by treatment with sulfuric acid.

During the 5 years following the appearance of the first bicyclo[2.2.0]hexa-2,5-dienes (Dewar benzenes) (**1**),[1] few reactions of this structural type were reported, despite constitutional features which gave promise of novel chemical behavior. It was observed, however, that, without exception and as anticipated, Dewar benzenes undergo a thermal reaction which circumvents the Woodward–Hoffmann rules and provides the Kekulé benzene counterparts. Furthermore, in the case of parent Dewar benzene, proof of structure rested in part on diimide reduction to bicyclo[2.2.0]hexane. Also, undoubtedly the most significant development during this period was the recognition that the Dewar benzene system can in certain cases undergo photochemical isomerization to benzvalenes (**2**) and prismanes (**3**), structural types which are also involved in the interconversions observed with various ortho-, meta-, and para-disubstituted benzenes.[2] Because of the multiplicity of bulky, *tert*-butyl substituents on some of the first Dewar benzenes reported, chemical behavior could not in such cases be anticipated as representative or even practical; also, in such cases, as in the first parent Dewar benzene synthesis, accessibility remained a limiting factor. In our laboratory, with the development of the electrolytic method for decarboxylation of the precursor diacid,[3] the parent bicyclohexadiene became available in such measure as to permit a general survey of Dewar benzene reactivity.[3]



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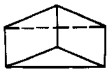

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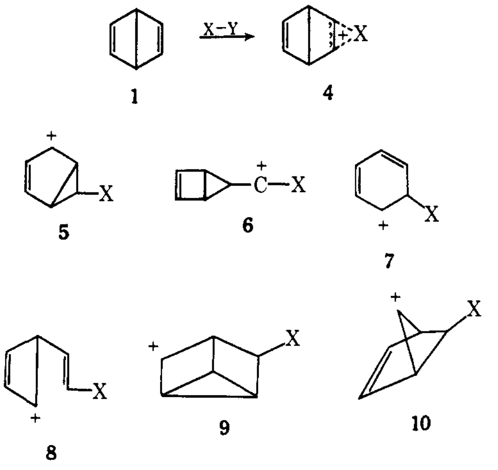
Electrophilic addition represents an obvious area of investigation with Dewar benzenes, and a good share of our efforts were devoted to this matter. Reagents selected for study along these lines included bromine, peracid, and osmium tetraoxide. The first transition metal complex was prepared by direct reaction of Dewar benzene with $PdCl_2$–$2C_6H_5CN$. Catalytic reduction was briefly investigated, and the photolytic conversion to Kekulé benzene was established. Finally, a carbene insertion was carried out, and a representative 1,3-dipolar addition reaction was executed. In choosing reactions for study, we avoided possibilities that might permit serious concurrent thermal isomerization of Dewar benzene.

Since interaction of a positively charged species, such as halonium ion, with a Dewar benzene implies the generation of a cyclobutyl carbonium ion (**4**), rearrangements of the type characteristic of that charged system emerge as possibilities in this given case. If still other reasonable courses are added to the above, a large total number of plausible intermediate species, such as **5**–**10**, come into consideration. Aromatization possibly involving cyclohexadienyl cation **7** would be a favorable outcome on thermodynamic grounds.

Chart I



Significantly, with Dewar benzene no such reaction outlets, and only simple additions, were observed in our laboratory.

The addition of 2 mol of bromine, without skeletal rearrangement, to bicyclo[2.2.0]hexa-2,5-diene can theoretically lead to ten stereochemically different tetrabromides. In the actual event, treatment of bicyclo-

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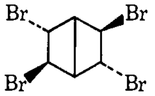
[1] (a) E. E. van Tamelen and S. P. Pappas, *J. Amer. Chem. Soc.*, **84**, 3789 (1962); (b) E. E. van Tamelen and S. P. Pappas, *ibid.*, **85**, 3297 (1963).

[2] K. E. Wilzbach and L. Kaplan, *ibid.*, **87**, 4004 (1965).

[3] E. E. van Tamelen and D. Carty, *ibid.*, **89**, 3922 (1967).

[2.2.0]hexa-2,5-diene with an excess of bromine, under conditions known to involve ionic addition, gave rise to at least two of these isomeric tetrabromides. The major product was a white crystalline solid, melting sharply at 120.0–120.5°. The nuclear magnetic resonance (nmr) spectrum was entirely consistent with a Dewar benzene tetrabromide structure in that signals appeared at τ 5.10 (4 H, multiplet) and 6.50 (2 H, broad singlet). This same substance was formed from 2,3-*trans*-dibromobicyclo[2.2.0]hex-5-ene (see below) on treatment with elemental bromine, thereby establishing stereochemistry at two asymmetric centers. Preliminary X-ray data suggested that the compound was *trans,anti,trans*-2,3,5,6-tetrabromobicyclo[2.2.0]hexane (**11**).[4] The second isomer was not obtained in a



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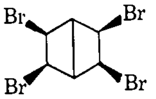
pure state, and its characterization rests only on nmr data. The most striking feature of the spectrum was the sharpness of the three signals, with integrals in the ratio of 1:1:1 and widths at half-height of 3 Hz. Broad resonance lines in Dewar benzene derivatives, primarily a result of fine splitting, are the rule rather than the exception. Therefore, the relatively narrow resonance lines observed for the second tetrabromide required a structural feature which could explain this behavior. The symmetry of an *all-cis*-tetrabromide (**12**) is consistent with the observed nmr spectrum; and



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moreover, in view of the 30:70 cis:trans ratio noted in the Dewar benzene dibromides, tetrabromide **12** becomes a probable structure for the second isomer.

A complex mixture of di- and tetrabromides was secured when equimolar amounts of Dewar benzene were allowed to interact. However, by using an excess (2:1 ratio) of bicyclo[2.2.0]hexa-2,5-diene, a 30:70 mixture (by nmr) of *cis*- and *trans*-2,3-dibromobicyclo[2.2.0]hex-5-enes (**13** and **14**), uncontaminated with tetrabromide, was obtained. The reaction mixture was examined by nmr (see Figure 1) immediately after removal of solvent. The integral of the spectrum indicated a relationship between three of the lines (equal intensity), while the remaining signals revealed a differ-

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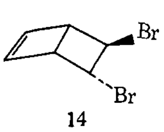

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ent ratio of small whole numbers. It was established by a combination of spectroscopic and chemical evidence that these resonance lines do indeed represent *cis*- and *trans*-2,3-dibromobicyclo[2.2.0]hex-5-enes.

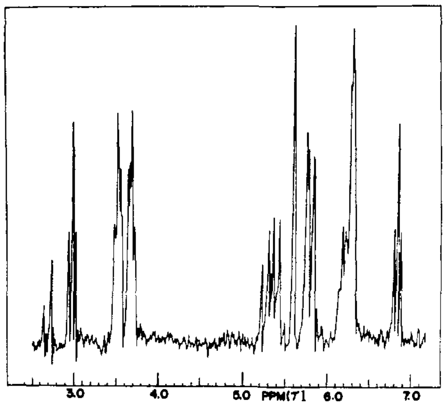

Figure 1. Nmr spectrum of mixture of *cis*- and *trans*-2,3-dibromobicyclo[2.2.0] hex-5-enes (**13–14**).

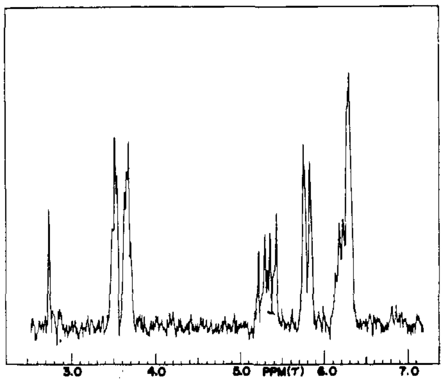

Figure 2. Nmr spectrum of *trans*-2,3-dibromobicyclo[2.2.0]hex-5-ene (**14**).

Exposed to light and air, the dibromide mixture was unstable. One isomer could be separated readily by rapid chromatography of the mixture of Florisil. This purified material appeared as one spot on thin layer chromatography (tlc), and a comparison of its nmr spectrum (see Figure 2) with that of the primary dibromide mixture (see Figure 1) disclosed the absence of three peaks: the triplet at τ 2.97, the singlet at 5.62, and the triplet at 6.85. Proof that these missing resonances represented an isomer of the dibromide obtained by chromatography was demonstrated by comparison of the mass spectra of the mixture and the single isomer. These spectra (see Figures 3 and 4) were virtually identical. Furthermore, it was evident, from the mass number of the molecular ion and the characteristic patterns of the two bromine isotopes, that both compounds possessed the elemental composition $C_6H_6Br_2$.

The nmr spectrum (see Figure 2) of the purified dibromide isomer permitted assignment of its structure. The two olefinic proton resonances, τ 3.52 (1 H) and 3.67 (1 H), arose through umsymmetrical interaction of the two olefinic hydrogens with protons at the trans-oriented bromine site. The signals for the two hydrogens on carbon-bearing bromine exhibited well-defined chemical shifts: τ 5.32 (1 H) and 5.80 (1 H), the splitting of these signals being more pronounced. Environments of the two methine hydrogens were not sufficiently different, and their resonances merged into a multiplet at 6.25 (2 H). This spectrum could not be accommodated by any $C_6H_6Br_2$ structure other than **14**.

The three-line nmr spectrum of the second $C_6H_6Br_2$ isomer was more ambiguous. Two structures could be accommodated equally well: *cis*-2,3-dibromobi-

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(4) J. Kahrle, Stanford University, personal communication.

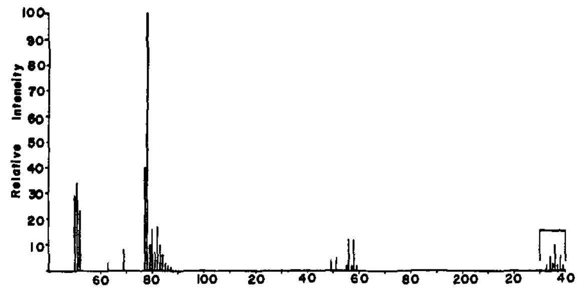


Figure 3. Mass spectrum of dibromide **13–14** mixture.

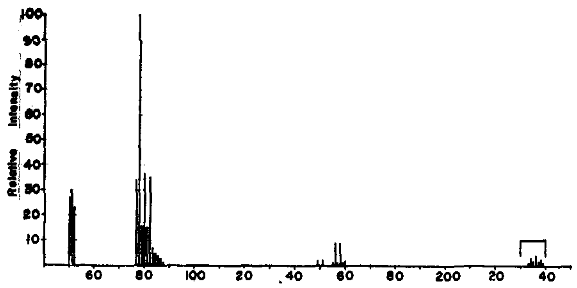
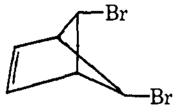


Figure 4. Mass spectrum of dibromide **14** (trans).

cyclo[2.2.0]hex-5-ene (**13**) and 2,6-dibromobicyclo[2.2.1]hex-4-ene (**15**). The high degree of symmetry in both these structures, along with the coincidental similarity of hydrogen environments, precluded distinction between the structures on the basis of nmr. Although the main spectral data described above suggested that the two dibromides were stereoisomers, we sought supporting chemical evidence. In an oxidative cleavage of the double bond, structure **13** would lead to a *cis*-1,2-cyclobutanedicarboxylic acid, whereas the oxidation of **15** would result in *cis*-1,3-cyclobutanedicarboxylic acid. Provision for removal of the bromines, conversion of the derivative acids to esters, and vpc comparison with authentic cyclobutanedicarboxylate esters[5] constituted a means whereby the correct structure could be assigned to the second $C_6H_6Br_2$ isomer.



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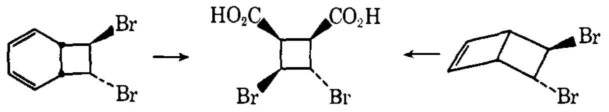
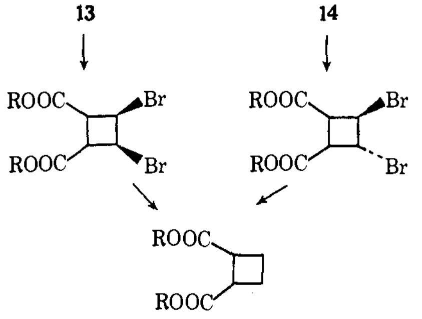
Our ozonization experiments were modeled after the oxidation of 2,3-*trans*-dibromobicyclo[4.2.0]octa-5,7-diene[6] (**16**), and control experiments were actually carried out on this substance since the product was the useful 3,4-*trans*-dibromocyclobutane-*cis*-1,2-dicarboxylic acid (**17**). Comparison of the latter material (methyl ester) with the corresponding oxidation product of 2,3-*trans*-dibromobicyclo[2.2.0]hex-5-ene (**14**) showed they were identical in all respects.

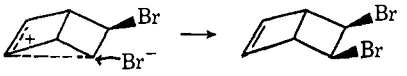


16 **17**

Since chromatography of the mixture of Dewar benzene dibromides had given only one isomer with no trace of the second and because other attempts to separate the isomers had failed, the original mixture was subjected to ozonolysis. Tlc examination of the reaction product (after conversion to dimethyl ester) revealed a spot corresponding to authentic dimethyl 3,4-*trans*-dibromocyclobutane-*cis*-1,2-dicarboxylate ester, and overlapping a faster running spot which was ascribed to the isomeric dibromide. Conditions for complete separation could not be found and further transformations were performed on the mixture. Removal of halogen from the esters was accomplished quite readily and in excellent yield by hydrogenolysis in the presence of triethylamine. Parallel ozonization–hydrogenolysis sequences were run with pure 2,3-*trans*-dibromobicyclo[2.2.0]hex-5-ene and the isomeric mixture. The yields of *cis*-cyclobutane-1,2-dicarboxylic ester from the two runs were comparable (67 and 61%, respectively), and vpc examination of the hydrogenolysis product from the mixture indicated only a trace of the cyclobutane-*cis*-1,3-dicarboxylate (or some other material with identical vpc retention time). These data provided the basis for assignment of structure to the second dibromide, namely 2,3-*cis*-dibromobicyclo-[2.2.0]hex-5-ene.



Cis-halogenation under ionic conditions is uncommon, but not rare.[7] Double bond participation could explain cis addition of bromine (**18**); however, no evidence for tricyclic dibromide (attack of bromide ion at C-6) was observed. A second compatible explanation is based on the instability of the bromonium ion brought about by ring strain—the classical carbonium ion may be relatively more stable than the bromonium ion because of this strain. The carbonium ion could form paired with a bromide ion, and rapid collapse of the ion pair **19** might lead to overall cis addition.[8]



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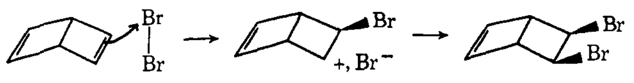

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Alternatively, bromonium ions surviving long enough to experience backside attack would give trans addition.

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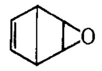
(5) N. L. Allinger, *J. Org. Chem.*, **30**, 1945 (1965).

(6) E. Vogel, *Justus Liebigs Ann. Chem.*, **615**, 14 (1958).

(7) (a) H. Kwart and J. L. Nyce, *J. Amer. Chem. Soc.*, **86**, 2601 (1964); (b) M. J. S. Dewar and R. C. Fahey, *ibid.*, **85**, 2245, 2248, 3645 (1963); (c) J. V. Smirnov-Zankov and G. A. Piskovitina, *Ukr. Khim. Zh.*, **28**, 531 (1962).

(8) R. Breslow, "Organic Reaction Mechanisms," W. A. Benjamin, New York-Amsterdam, 1965, pp 115–117.

Treatment of bicyclo[2.2.0]hexa-2,5-diene with an equimolar amount of *m*-chloroperbenzoic acid at room temperature resulted in a 75% yield of a water-white liquid which proved to be 2,3-epoxybicyclo[2.2.0]hex-5-ene (**20**). This reaction did not give phenol as a product, as shown by vpc examination of the reaction mixture. Separation of the reaction components by preparative vpc afforded a material (single peak on reinjection) which possessed spectroscopic properties expected for the monoepoxide. The mass spectrum had a molecular peak at 94 and a base peak at *m*/*e* 78, the relative intensity of which changed quite significantly with time at 100°, intimating that thermal rearrangement was occurring. This observation led to a series of thermal and photochemical experiments designed to show that oxide **20** was capable of rearranging to benzene oxide (**21**)–oxepin (**22**). Benzene oxide and oxepin have been shown, by nmr study at various temperatures,[9] to be in rapid thermal equilibrium,[10] and the system has also been well characterized by ultraviolet (uv) study.



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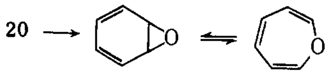
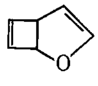


21 **22**

Dewar benzene oxide (**20**) was isomerized thermally at 115° to benzene oxide–oxepin at such a rate that half of the starting material was consumed in 18 min. The resulting products, when examined by nmr, were shown to have peaks corresponding to those reported for benzene oxide–oxepin mixtures. Contrary to the observations of Vogel and his coworkers,[9] in our experiment, phenol, which has two narrow intense uv bands at 271 and 277 mμ, was not generated as a pyrolysis product of benzene oxide–oxepin. An examination of the thermolysis product from oxide **20** showed only a broad band at 270 mμ with a shoulder at 312, data consonant with the nmr results. Analysis of the reaction mixture by vpc indicated only two products and the starting material.

Photochemical isomerization, which was followed spectrophotometrically, proceeded rapidly under the influence of a low-pressure mercury arc (major output at 2537 Å) to give a total of four products. Three of these were easily identified as phenol, benzene oxide–oxepin by their characteristic uv and vpc behavior. The fourth product had a relatively short retention time on vpc and may have been the source of a band at 240 mμ which appeared early in the photolysis and was unassigned. Vogel and Gunther[9] mentioned that photolysis of benzene oxide–oxepin gave almost quantitative conversion to 2-oxabicyclo[3.2.0]hepta-3,6-diene (**23**), and it is possible that the dihydrofuran is the fourth photolysis product of Dewar benzene oxide.[11]



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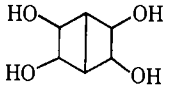
Excess osmium tetroxide in diethyl ether at room temperature converted Dewar benzene to the tetrol **24**, mp 184–186°. Strongly periodate positive, the white solid exhibited behavior in the mass spectrum compatible with the assigned structure. The nmr spectrum of the tetrol **24** consisted of three broad singlets at τ 5.25 (2 H, hydroxyl), 5.97 (2 H, hydrogen on carbon bearing hydroxyl), and 7.72 (1 H, methine). The low-field signal disappeared under deuterium exchange conditions. In this reaction system, osmium tetroxide neither detectably isomerized bicyclo[2.2.0]hexa-2,5-diene to Kekulé benzene nor converted it to phenol.



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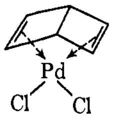
A relatively stable metal coordination complex (**25**) was prepared by interaction of bicyclo[2.2.0]hexa-2,5-diene with dichloro(bisbenzonitrile)palladium in methylene dichloride. This reaction finds close analogy in the reaction of norbornadiene with the same reagent.[13] The reaction proceeded under mild conditions and in nearly quantitative yield. Precipitating from solution, the light-brown amorphous solid, presumably dimeric,[13] was very slightly soluble in acetone and was either insoluble in or reacted with all other solvents tried. Heating in acetic acid decomposed the complex, as did its dissolution in dimethyl sulfoxide.



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The nmr behavior of the complex was interesting. A single broad signal was observed at τ 5.60. Such behavior apparently resulted from rehybridization of the olefinic centers, thereby shifting the signal of these protons to higher field, whereas the position of the methine hydrogens shifted to lower field. That both the signals had the same chemical shift is apparently coincidental; nevertheless, this same type of behavior was observed in the case of bicyclo[2.2.0]hepta-2,5-diene-(pentane-2,4-dionato-) rhodium.[14]

Chatt and coworkers[15] were able to split dimeric complexes of palladium and platinum with toluidine and pyridine, while keeping the ligands intact. The resulting compounds were generally soluble in organic solvents and possessed properties similar to those of conventional organic compounds. Conversion of complex **25** to a monomeric species offered these desirable results plus the introduction of an internal standard for nmr integration. While being observed by nmr means, pyridine-d_5 was added to a suspension of complex **25** in chloroform-d_1. The solids dissolved and reprecipitated, which phenomena were accompanied by the appearance of two resonance signals ascribed to

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(9) E. Vogel and H. Günter, *Angew. Chem., Int. Ed. Engl.*, **6**, 385 (1967).

(10) E. Vogel, W. A. Boll, and H. Günter, *Tetrahedron Lett.*, 609 (1965).

(11) Hexamethyl(Dewar benzene) also is converted by means of peracid to unrearranged epoxide.[12]

(12) W. Schäfer and H. Hellman, *Angew. Chem.*, **79**, 566 (1967); *Angew. Chem., Int. Ed. Engl.*, 6, 518 (1967).

(13) R. A. Alexander, N. C. Baenziger, C. Carpenter, and J. R. Doyle, *J. Amer. Chem. Soc.*, **82**, 535 (1960).

(14) F. Bonati and G. Wilkinson, *J. Chem. Soc.*, 3156 (1964).

(15) J. Chatt, L. M. Vaillarino, and L. M. Vernanzi, *ibid.*, 2496, 3413 (1957).

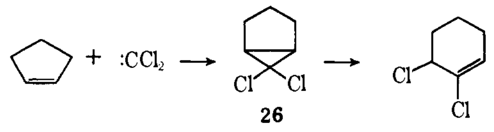
Dewar benzene. No Kekulé benzene was detected, and cleavage of the dimer was therefore accompanied by displacement of the original, hydrocarbon ligand. These data preclude the structural possibility of Kekulé benzene–$PdCl_2$, which in fact remains unknown.

A sample of bicyclo[2.2.0]hexa-2,5-dienedichloropalladium was placed under high vacuum at room temperature for several hours, while the mass spectrum was obtained under increasingly higher inlet temperatures. This procedure gave rise to m/e peaks up to and including mass number 78, but no higher. Apparently the Dewar benzene complex decomposes before sufficiently high temperatures were reached to volatilize the complex.[16]

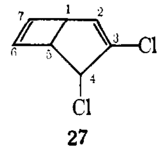
In a series of sporadic experiments, we carried out[17] a study of the photochemical isomerization of Dewar benzene, in the hope that conversion to parent prismane might occur. In a typical trial, the photolysis was run at −23° (refluxing dimethyl ether), and the reaction mixture was analyzed periodically by nmr means. Kekulé benzene was observed as the only detectable product, after one-half of the Dewar benzene had been consumed. In no experiment was there any hint of prismane formation.

Whereas diimide reduction of Dewar benzene affords a good yield of bicyclo[2.2.0]hexane,[16] catalytic reduction under 1 atm of hydrogen, using palladium/charcoal as catalyst, resulted in a quantitative yield of cyclohexane. Stirring the catalyst and substrate together for 2 hr resulted in no change. By contrast, reduction of hexamethyl(Dewar benzene) with hydrogen using normal pressure and platinum/charcoal gave rise to 1,2,3,4,5,6-hexamethylbicyclo[2.2.0]hex-2-ene in 85% yield.[12] Hydrogenation of bicyclo[2.2.0]hexane, under conditions similar to those used for reducing Dewar benzene, produced a quantitative yield of cyclohexane. This observation is surprising, since hydrogenolysis of cyclopropane and cyclobutane normally requires high temperatures (120 and 200°, respectively) and high pressure.[18]

An unusual rearrangement occurs during the addition of dihalocarbenes to strained olefins. For example, cyclopentene and dichlorocarbene form an adduct **26** which rearranges to 1,2-dichlorocyclohex-2-ene



(**26**), while cyclohexene and dichlorocarbene combine to yield 7,7-dichloronorcarane, which undergoes comparable rearrangement only under forcing conditions.[19] Similar reaction patterns are observed with norbornene and norbornadiene.[20] Generation of dichlorocarbene in the presence of an equimolar amount of Dewar benzene gave a modest yield of the expected ring expansion product. Vapor phase chromatographic examination of the reaction mixture revealed the presence of not only Dewar and Kekulé benzenes, but also material of long retention time. Isolation of this latter substance was accomplished by preparative vpc, and the oil obtained in this manner was homogeneous, as indicated by vpc reinjection. The adduct possessed only end absorption in the uv, while it gave rise to strong infrared absorption at 6.1 (unsymmetrical olefin stretch), 13.8 and 14.5 μ (carbon chlorine vibrations). The nmr spectrum exhibited six lines: a doublet at τ 3.57 (1 H, J = 1 Hz); a partially resolved doublet at 3.86 (1 H, J = 1 Hz); a partially resolved doublet at 3.97 (1 H, J = 1 cps); a partially resolved doublet at 5.43 (1 H, J = cps); a quartet at 6.18 (1 H, J = 2 cps); and a broad singlet at 6.40 (1 H). The mass spectrum possessed peaks at m/e 160 and 162, and at 125 and 127 in the intensity ratios of 3:1 as required by isotope distribution in a compound containing two chlorine atoms. These data are in agreement with the structural assignment **27**.



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The uv and nmr data, in particular, rule out other possible structures, such as **28**, **29**, and **30**, and are perfectly compatible with the 3,4-dichlorobicyclo[3.2.0]hepta-2,6-diene structure **27**. The low-field resonance at τ 3.57 was assigned to the olefinic hydrogen on C-2, a peak split into a doublet by the methine hydrogen on C-1. The resonances at τ 3.86 and 3.97 were assigned to the two remaining olefinic hydrogens at positions 6 and 7, in slightly different chemical environments because of the asymmetry of the molecule. The doublet at τ 5.43 was ascribed to the hydrogen on carbon bearing chlorine. The remaining two resonances must be assigned to the bridgehead hydrogens; the one at C-5 must generate the quartet signal, since this proton is in the more asymmetric environment and the dihedral angle between this methine hydrogen and the hydrogen at C-2 is likely to result in the observed J value.

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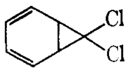

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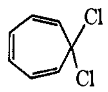

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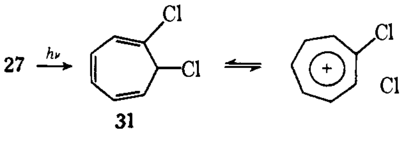
Additional chemical observations could be interpreted in terms of the structure **27**. Heating an n-octane solution of the oil at 130° for 1.5 hr resulted in no change in the uv spectrum; however, irradiation with light of 2537 Å for 5 min caused appearance of maxima at 235 and 297 mμ, and further irradiation (30 min) caused gradual diminution of the absorption. Thermal isomerization of 3,4-dichlorobicyclo[3.2.0]hepta-2,6-diene is disallowed by orbital symmetry rules, whereas photochemical (disrotative) isomerization is permitted.[21] The product of the latter would be a cycloheptatriene (**31**). The species which gave rise to the



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[16] E. O. Fischer, C. G. Kreiter, and W. Berngruber (*Angew. Chem.*, **79**, 623 (1967) have described the preparation and spectral properties of tetracarbonyl(hexamethylbicyclo[2.2.0]hexadiene)chromium.

[17] Carried out in collaboration with T. Whitesides.

[18] R. Willstätter and J. Bruce, *Chem. Ber.*, **40**, 3979 (1907).

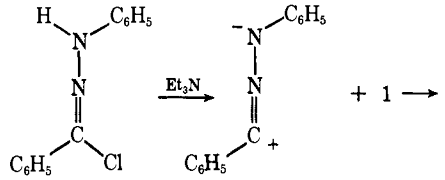
[19] E. Bergman, *J. Org. Chem.*, **28**, 2211 (1963).

[20] W. R. Moore, R. Moser, and J. E. LaPrade, *ibid.*, **28**, 2200 (1963).

[21] R. B. Woodward and R. Hoffmann, *J. Amer. Chem. Soc.*, **87**, 2045 (1965).

absorption maxima is probably the tropylium ion resulting from ionization, since fairly good correlation with compounds of similar structure was noted, *i.e.*, Dauben and coworkers reported that chlorotropylium perchlorate in concentrated sulfuric acid solution had absorption maxima at 237 and 310 mμ.[22]

Huisgen and coworkers described addition of 1,3-diphenylazocarbene (**32**) to norbornadiene to form the bis adduct in moderately good yield.[23] A similar reaction sequence utilizing bicyclo[2.2.0]hexa-2,5-diene provided a light-yellow solid, mp 260–262°, which had spectral properties completely consistent with structure **33** or **34**. The nitrogen atoms strongly influence the fragmentation processes taking place under mass spectrometric conditions, and each of the major peaks in the mass spectrum (see Figure 5) could be rationalized by removing initially an electron from one (or two) of the nitrogens atoms. The nmr spectrum featured four signals in the integral ratio of 20:2:2:2, which corresponded with the ratio required for structure **33–34**. The signal at τ 2.80 (20 H) clearly was due to the aromatic hydrogens, and there was little question that the signal at τ 6.76 belonged to the methine hydrogens. The other two signals were tentatively assigned as follows: τ 4.92, allylic hydrogens; 5.42, hydrogens on carbon bearing nitrogen. The uv spectrum was very similar to that reported for the norbornadiene adduct:[23]



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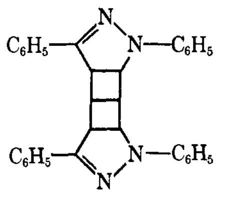
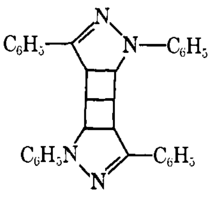


or



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Adduct	$\lambda_{\max}^{\mathrm{CHCl_3}}$, mμ	Log ε
Norbornadiene	244	4.39
	359	4.52
Dewar benzene	243	4.44
	363	4.56

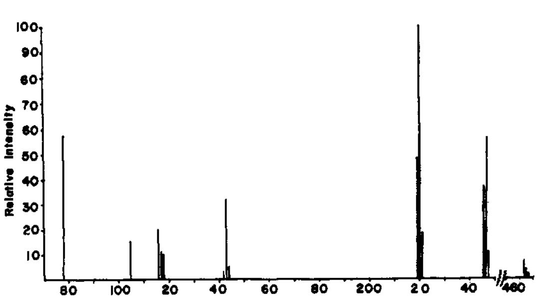
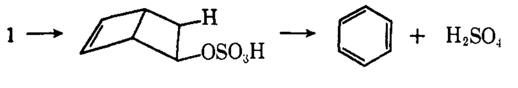


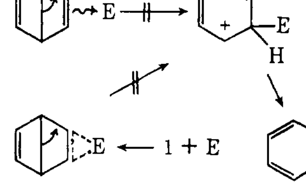
Figure 5. Mass spectrum of bis adduct of 1,3-diphenylazocarbene and Dewar benzene.

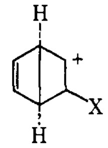
After sulfuric acid was added to a benzene-d_6 solution of bicyclo[2.2.0]hexa-2,5-diene at room temperature, a deep reddish-brown color developed on shaking the resulting two-phase mixture. Nmr analysis of the reaction mixture after 60 sec indicated the absence of Dewar benzene. Only 36% of the Dewar benzene initially present was accounted for by Kekulé benzene, which was the sole product detected. However, an increase in the amount of Kekulé benzene occurred on allowing the sample to stand at room temperature; 10 min after the addition of the sulfuric acid, the per cent conversion had increased to 55%, and after 1 hr the value was 85%. These observations can be rationalized by initial addition of sulfuric acid to a double bond



followed by slower solvolysis of the sulfate ester and concomitant aromatization.[24]

On the basis of the above examples, it seems that an olefinic bond in parent Dewar benzene is prone to interact with an electron-deficient species while retaining a cyclobutene unit, despite the availability of an aromatization pathway involving an isomerization of the well-recognized cyclobutyl-(cyclopropylcarbinyl-) homoallyl cation type. It thus appears that the orbital-symmetry factors which inhibit nonphotochemical conversion of Dewar benzene to Kekulé benzene can operate as well in the transition state of a reaction with an electrophilic external agent, or even in a cyclobutenylcarbinyl cation (**35**) produced from Dewar benzene by such a reaction. As in a simple cyclobutene, concerted disrotatory ring opening of system **36** to 1,3-dienylcarbonium ion is forbidden, and the allowed, conrotatory change is prevented in carbonium ion **35** by





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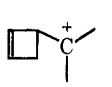

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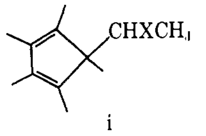
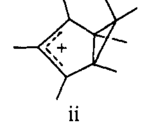
(22) H. Dauben, F. A. Gadecki, K. M. Harmon, and D. L. Pearson, *J. Amer. Chem. Soc.*, **79**, 4557 (1957).

(23) R. Huisgen, G. Wallbillich, and M. Seidel, *Tetrahedron*, **17**, 3 (1962).

(24) Schäfer and Hellman[12] reported that addition of dry hydrogen chloride to hexamethyl(Dewar benzene) produced three products: hexamethyl-5-chloro-6*H*-cyclohexa-1,3-diene, and smaller amounts of hexamethylbenzene and hexamethyl-5-chloro-6*H*-bicyclo[2.2.0]hex-3-ene. However, L. A. Paquette and G. R. Krow (*Tetrahedron Lett.*, 2139 (1968)) assigned the cyclopentadiene structure i to the single product formed in good yield with either hydrogen chloride or hydrogen bromide and adduced evidence for the intermediacy of cyclopropylcarbinyl cation ii.



i



ii

the geometry of the bicyclic framework. However, with appropriate structural modifications in the Dewar benzene starting material, annular isomerizations can occur, probably as a consequence, in part, of altered carbonium ion stability. Thus, hexamethyl(Dewar benzene), on treatment with hydrogen halide, is converted to ring isomerization product, presumably by means of intermediate carbonium ion rearrangement. The only such reaction observed with parent Dewar benzene is the sulfuric acid induced conversion to Kekulé benzene, described above, the mechanism of which has not been established.

Experimental Section

Analyses were carried out at the Stanford University Microanalytical Laboratory by E. Meier and J. Consul. Melting points were determined on a microscope hot stage and are uncorrected. Vapor-phase chromatography (vpc) was carried out using two dual column F and M Model 700's, one equipped with a thermal conductivity detector and the other with a flame ionization detector; preparative work was carried out using the instrument equipped with thermal conductivity detector, whereas the flame unit was used for qualitative analyses. When oven temperature programming was employed a power proportioning temperature programmer (available from F and M) was utilized. The column employed exclusively was an 8 ft × $^1/_4$ in. stainless steel column packed with 10% Ucon Polar LB550X on 100–120 mesh Diataport S.

Infrared (ir) spectra were determined using a Perkin-Elmer spectrometer either Model 421 or 137. Ultraviolet (uv) spectra were obtained with a Cary Model 14 spectrophotometer. Mass spectra were obtained on one of two instruments, an AEI MS-9 or a CEC Model 103-C.

Nuclear magnetic resonance (nmr) spectra were obtained using one of three instruments: a Varian Model A-60 with variable temperature probe, a Varian Model HR-100, or a Varian Model HA-100. Solvent was chloroform-d_1 with internal tetramethylsilane as reference standard unless otherwise noted. Chemical shifts are given as τ in parts per million relative to tetramethylsilane at τ 10.0.

Silica gel G and GF$_{254}$, as supplied by Merck, were used for thin-layer chromatography (tlc). Preparative tlc was done on Merck silica gel GF$_{254}$, 1.0 mm thick. Analytical tlc was accomplished on Merck silica gel H coated (as chloroform suspension) by immersion of microscope slides. Florisil (Floridin Co.) was used in column chromatography. Solvents were either redistilled or chromatographic grade.

Electrolysis of *exo*-Bicyclo[2.2.0]hex-5-ene-2,3-dicarboxylic Acid. The Electrolysis Cell. The electrolysis cell was constructed from a platinum crucible (30 × 25 mm), a no. 6 one-hole rubber stopper, a thermometer, a platinum wire (100 × 1 mm), a square of platinum foil (10 × 10 × 0.1 mm), and a sheet of tin foil. The tin foil was folded into a rectangle (25 × 300 mm) and wrapped about the upper part of the platinum crucible to extend the walls approximately 20 mm. This foil was secured to the crucible by means of electrician's tape. The platinum foil was affixed to the platinum wire which had been pushed through the center of the rubber stopper. The thermometer had previously been positioned in the rubber stopper. By seating the rubber stopper in the cylinder formed by the tin foil and adjusting the penetration of the platinum foil and the thermometer, an enclosed electrolysis cell capable of holding 10 ml of solution was obtained. The electrical leads were attached, one to the tin foil and one to the platinum wire, using alligator clips. Stirring was accomplished with the aid of a small magnetic stirring bar. The electrical source was a constant voltage (DC) power supply (Gates Electronics Co., New York, N. Y.) capable of handling 1.0 A of current.

Electrolysis. Bicyclo[2.2.0]hex-5-ene-2,3-dicarboxylic acid (75 mg, 0.5 mmol) was placed in the electrolysis cell. Nine milliliters of pyridine, 1.0 ml of water, and 125 μl of triethylamine were added. The cell was assembled and lowered into a cooling bath composed of isopropyl alcohol saturated with Dry Ice, and the electrical leads were attached. Electrolysis was then carried out at 225 V (dc), keeping the temperature below 25°. This operation required close attention since the temperature rose very rapidly, particularly in the early stages of the electrolysis. Reversal of the direction of current flow at periodic intervals kept the electrodes free of sludge. This reversal was accomplished by a double-throw knife blade switch installed in the circuit between the cell and the power supply. When the current flow had dropped to 10% of its initial value (2–3 hr) the electrolysis was stopped.

Work-up. The dark reaction mixture was diluted with an equal volume of water and extracted with hydrocarbon (MCB, Chromatoquality) solvent[25] (four 2-ml portions). The combined extracts were washed with water (three 3-ml portions), 5% aqueous hydrochloric acid (three 3-ml portions), and water (three 3-ml portions). The hydrocarbon solution was then dried over anhydrous magnesium sulfate. Vapor phase chromatographic analysis of the solution for bicyclo[2.2.0]hexa-2,5-diene content indicated a 40% yield of Dewar benzene (**1**). Small amounts of Kekulé benzene were also present.

Catalytic Hydrogenation of 1. Palladium (5% on charcoal) catalyst (50 mg) was suspended in 3.0 ml of a 0.04 *M* solution of Dewar benzene in *n*-hexadecane. The reaction vessel (50-ml flask) was stoppered with a rubber septum, flushed with nitrogen, and then stirred for 2 hr. Examination by vpc indicated no change. The flask was then filled with hydrogen and stirred at room temperature for 17 hr. Examination of the reaction mixture by vpc indicated the complete conversion to a single product. The volatile product was separated from the nonvolatile solvent by standard vacuum line techniques. Comparison of nmr, ir, and vpc data with authentic material conclusively identified the material as cyclohexane. Under these conditions, bicyclo[2.2.0]hexane was also converted quantitatively to cyclohexane.

***m*-Chloroperbenzoic Acid Oxidation of Bicyclo[2.2.0]hexa-2,5-diene (1).** *m*-Chloroperbenzoic acid (76 mg, 0.44 mmol) was weighed into a 5-ml flask and bicyclo[2.2.0]hexa-2,5-diene (0.5 mmol) was added as a solution in 1.0 ml of diethyl ether. The vessel was filled with nitrogen, stoppered, and allowed to stand for 12 hr. Examination of the reaction mixture at the end of this time revealed the presence of bicyclo[2.2.0]hexa-2,5-diene, Kekulé benzene, and a product whose vpc retention time was relatively large (63 min), in a yield of approximately 75%. Comparison of vpc behavior showed conclusively that this product was not phenol and furthermore established that phenol was not present in the reaction mixture.

The separation of the volatile components was accomplished by vacuum transfer using standard vacuum techniques. The product of the reaction was conveniently obtained in the pure state by preparative vpc. Collection was performed using 10 cm × 2 mm straight glass tubing connected to the exit port of the chromatograph (column, 60°; injector, 90°; detector, 90°). Cooling of the collection tube was accomplished with powdered Dry Ice heaped in small piles on the tube and supporting plate.

The product so obtained was a water-white liquid which exhibited three lines in its nmr spectrum: τ 3.16 (2 H, broad singlet), 5.97 (2 H, doublet, J = 3 Hz), 6.68 (2 H, broad singlet). The uv spectrum showed only end absorption. Strong bands at 7.58, 5.75, 8.10, and 11.80 μ were present in the infrared spectrum. The mass spectrum exhibited a molecular ion at 94 mass units whose relative intensity was 28% as strong as that of the peak at m/e 78 (base peak). However, the features of the spectrum changed with time and after 1 hr at approximately 100° (inlet chamber temperature) the relative intensities had changed significantly; the m/e 94 was now the base peak and the peak at m/e 78 was now 86% of the base peak.

Isomerization of 2,3-Epoxybicyclo[2.2.0]hex-5-ene (20). A. Light-Induced Isomerization. A 3.0-ml quartz uv cuvette was used as the irradiation vessel, which facilitated spectrophotometric analysis of the reaction's progress. A low-pressure mercury lamp was used as the radiation source (90% of the radiation at 2536 Å). The heat generated by the source was dissipated by passing cool air over the lamp and the sample and in this way a temperature of approximately 30° was maintained in the vicinity of the sample.

A solution (5.3 × 10^{-3} *M*) of Dewar benzene oxide (**20**) in *n*-pentane was photolyzed for 45 min. Reaction was apparent after 2 min, as evidenced by a diminution of end absorption and the appearance of a band at 240 mμ. Within 20 min an additional broad band

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(25) Several different alkanes were used with success during the course of this work. The choice was generally predicated on the basis of the procedures to which the sample would subsequently be subjected. For example, *n*-pentane was chosen for one experiment because the difference in the boiling points between solvent, starting materials, and products was such that efficient fractionation could be effected in a simple pot-pot vacuum line transfer. On the other hand, *n*-hexadecane was often used because its high boiling point offered the advantage of easy separation and/or transfer of bicyclo[2.2.0]hexa-2,5-diene to another solvent *via* standard vacuum line techniques.

extending from 250 to 330 mμ was evident. Superimposed on this broad band were two sharp maxima at 271 and 277 mμ. Further irradiation (total irradiation time, 65 min) served only to increase the intensity of this spectrum.

Vapor-phase chromatography (column, 110°; injector, 110°; detector, 270°) indicated three products in the reaction mixture, retention times, 4.8, 6.9, and 10.3 min. To this sum must be added a fourth, since phenol (not detected by vpc under the conditions used) is required by the maxima (at 271 and 277 mμ) in uv spectrum.

An authentic sample of benzene oxide–oxepin[10] had two vpc peaks, retention times, 4. 8 and 6.9 min. Furthermore, irradiation of the authentic benzene oxide–oxepin with a low-pressure mercury lamp for 5 min at room temperature gave rise to phenol as evidenced by the 271- and 277-mμ maxima in the uv spectrum.

The identity of the fourth product of the photolysis of Dewar benzene oxide and the relationship of the uv band at 240 mμ were left unassigned.

B. Thermal Isomerization. Isomerizations were run in sealed melting point capillaries using constant temperature oil bath as a heat source. A stock solution (4.3×10^{-3} *M*) of Dewar benzene oxide in *n*-dodecane was prepared and used as needed. The isomerization was observed to proceed smoothly at 115°, yielding two products as revealed by vpc analysis. Retention times of the products (4.8 and 6.9 min) were identical with those of authentic benzene oxide–oxepin mixtures.[10] The half-life of this reaction was found to be 18 min at 115°.

As further confirmation of the identity of the products obtained, the thermal rearrangement was carried out in cyclohexane-d_{12} as solvent. The nmr spectrum of the reaction mixture was compared with that reported for benzene oxide–oxepin[10] and found to be identical. No evidence for the formation of phenol was observed.

Bromination of Bicyco[2.2.0]hexa-2,5-diene (1). A. Excess Bromine. A solution of Dewar benzene (59 mg, 0.75 mmol) in 15 ml of *n*-octane was placed in a 50-ml round-bottomed flask covered with aluminum foil. The reaction vessel was cooled in an ice–water bath. A freshly prepared solution of bromine in *n*-octane was added by syringe (2.0 mmol of bromine). The mixture was allowed to stand for 10 min under a nitrogen atmosphere.

Removal of the solvent and excess bromine left 272 mg of off-white solids. Examination of the volatile material by vpc and uv revealed the absence of bromobenzene. The residue consisted of at least four components as indicated by tlc analysis, one major and three minor. The solids were washed with cold pentane (4 × 5 ml). The washings were combined and the solvent was removed to leave 106 mg of semisolid material. This was labeled fraction B. Fraction A (that portion of the reaction mixture not readily soluble in cold pentane) was taken up in a minimum amount of boiling *n*-pentane and the solution was allowed to stand at −10°. Small prisms, mp 120.0–120.5°, were obtained. The nmr spectrum of this material exhibited signals τ 5.10 (4 H, multiplet) and 6.50 (2 H, poorly resolved multiplet). *Anal.* Calcd for $C_6H_6Br_4$: C, 18.10; H, 1.51; Br, 80.40. Found: C, 18.17; H, 1.28; Br, 80.89.

An nmr spectrum of fraction B indicated a mixture of compounds as did tlc (four spots) analysis. A pentane solution of fraction B deposited 32 mg of solids, mp 120°, on standing at −10°. The mother liquor was chromatographed on Florisil (7.4 g) using *n*-hexane as eluent. Twenty-seven fractions, 2.0-ml each, were collected (72% recovery of material). A dark band at the top of the column was not eluted. Fractions 8–10 contained as a major component a compound whose nmr spectrum consisted of three lines: τ 5.57 (1 H, singlet), 5.65 (1 H, singlet), 6.85 (1 H, singlet). These lines were unusually sharp relative to the signals generally observed in this work (width at half-height, 3 Hz). The material did not crystallize on several months standing in the refrigerator and was not further characterized.

B. Excess Bicyclo[2.2.0]hexa-2,5-diene (1). Dewar benzene (0.92 mmol) in 10 ml of *n*-octane was treated with bromine (0.44 mmol) at 0° in the dark. The solution was allowed to stand under an atmosphere of nitrogen for 10 min. The water-white reaction mixture was then distilled using standard vacuum-line techniques, leaving a clear oil as a residue (58 mg, 56% yield). Later experiments revealed that dibromides distill under these conditions (0.01 Torr and 25°). Therefore, for high yields (95–100%), a better choice of solvent was the volatile *n*-pentane.

An nmr spectrum of the residue was immediately obtained which suggested the presence of two components in the ratio of 30:70. This postulate was based on the ratios of the integrals of the several signals. Rapid chromatography of the mixture (53 mg) on Florisil (35 g) using a series of solvents, going from nonpolar (*n*-hexane) to polar (methanol), gave only 12 mg of a water-white oil in one of the early fractions.

The oil, isolated from the chromatography, was one spot on tlc and on the basis of its nmr spectrum (see Figure 4) (τ 3.52 (1 H, broad singlet), 3.67 (1 H, broad singlet), 5.32 (1 H, multiplet), 5.80 (1 H, doublet, $J = 4$ Hz), 6.25 (2 H, multiplet)), it was assigned the structure of 2,3-*trans*-dibromobicyclo[2.2.0]hex-5-ene (**14**). The mass spectrum of this oil was virtually identical with that of the initially obtained mixture and indicated that both isomers possessed the elemental composition $C_6H_6Br_2$. Further bromination of this material led to a mixture of tetrabromides with one major component (estimated from nmr to be 95%), which was shown to be identical with tetrabromide **11**.

Addition of Bromine to 2,3-*trans*-Dibromobicyclo[2.2.0]hex-5-ene (14). An excess of bromine was added to a carbon tetrachloride solution of 2,3-*trans*-dibromobicyclo[2.2.0]hex-5-ene (7 mg) at 0° in the dark. Removal of the volatiles left a solid residue (10.0 mg). Examination of the residue *via* nmr indicated the presence of one major component with signals at τ 5.1 and 6.5. An integral was not obtained but the estimated ratio of the two signals was 2:1, respectively. Furthermore, the shapes and positions of the signals were identical with those observed for tetrabromide **11**. Crystallization from *n*-pentane gave prisms, mp 120.0–120.5°. The mixture melting point of this material with tetrabromide **11** was not depressed.

Ozonolysis of 2,3-*trans*-Dibromobicyclo[2.2.0]hex-5-ene (14) and the Mixture of 2,3-*trans*-Dibromobicyclo[2.2.0]hex-5-ene and Its Isomer. Parallel experiments were run on the pure isomer **14** and the mixture of $C_6H_6Br_2$ isomers to establish that preferential destruction of one of the isomers was not occurring. The procedure was essentially that used by Vogel[6] to obtain 3,4-*trans*-dibromocyclobutane-*cis*-1,2-dicarboxylic acid (**17**) from cyclooctatetraene dibromide (**16**). The acids were converted to their methyl esters for tlc purposes. Ozone was obtained using a Welzbach ozone generator.

A. Oxidation of Pure 2,3-*trans*-Dibromobicyclo[2.2.0]hex-5-ene (14). An aliquot (33 mg) of the isomeric $C_6H_6Br_2$ mixture was chromatographed on 4.0 g of Florisil, giving rise to 17.2 mg (0.07 mmol) of pure *trans*-dibromide. A solution of the *trans*-dibromide in 5 ml of ethyl acetate was placed in an ozonolysis cell and cooled to −78°, and ozone was passed through the solution until the blue color persisted. The solution was purged with oxygen for 15 min and allowed to warm to 0°. An equimolar amount of peracetic acid (40%) was added and the resulting solution stored at 0° for 12 hr. After this time had elapsed, the water-white solution was warmed to 50°, the ethyl acetate was removed on a rotary evaporator, and a fourfold excess of peracetic acid was added. This solution was heated at 50° for 48 hr, after which the excess peracetic acid was destroyed with platinum black. The mixture was filtered and the filtrate was distilled under high vacuum at room temperature.

The slightly colored residue was treated with a solution of diazomethane in ether until the yellow color of diazomethane persisted. Removal of the volatiles on a rotary evaporator gave a residue of crude dimethyl 3,4-*trans*-dibromocyclobutane-*cis*-1,2-dicarboxylate ester shown to be identical in all respects with an authentic sample[6] by comparion of nmr and ir spectra; yield, 14.5 mg (67%).

B. Oxidation of the Mixture of 2,3-*trans*-Dibromobicyclo[2.2.0]hex-5-ene (14) and Its $C_6H_6Br_2$ Isomer. The mixture was treated in an exactly parallel manner as the pure trans isomer **14**, using 67.5 mg (0.28 mmol), which gave rise to 56.5 mg of dicarboxylate ester (61% yield). Thin-layer chromatography of the reaction mixture showed the presence of two overlapping spots, of which the slower running was shown to be the 3,4-*trans*-dibromocyclobutane-*cis*-1,2-dicarboxylate ester by comparison with authentic sample. Preparative tlc did not resolve the isomers.

Hydrogenolysis of Methyl 3,4-*trans*-cyclobutane-*cis*-1,2-dicarboxylate Ester. Catalyst (5% palladium on charcoal, 25 mg) was weighed into a tared vessel. A solution of ester (4 mg, 0.013 mmol) in 3 ml of methanol was added. A fourfold excess of triethylamine was added by microsyringe. The vessel was flushed with nitrogen and then filled with hydrogen. Uptake of hydrogen was nil after 30 min.

The catalyst was removed by filtration and the filtrate was evaporated to leave a residue of 6.9 mg. Triturating the residue with carbon tetrachloride removed 2.0 mg. Examination of the triturate by means of vpc confirmed the presence of a single product. Comparison of vpc and ir data with an authentic sample of dimethyl cyclobutane-*cis*-1,2-dicarboxylate ester[5] showed the two materials were identical; yield, 97%.

The carbon tetrachloride insoluble portion of the reaction residue, white needles, was readily soluble in water, suggesting triethylamine hydrobromide as its identity.

Ozonolysis, Esterification, and Hydrogenolysis of a Mixture of 2,3-*trans*-Dibromobicyclo[2.2.0]hex-5-ene (14) and Its $C_6H_8Br_2$ Isomer. A mixture (30:70) of "unknown" and *trans*-dibromides was carried through the reaction sequence ozonolysis, esterification, and hydrogenolysis without any intervening purification steps. The procedures used were identical with those described above for the individual reactions. Analysis of the resulting product by vpc under conditions (column, 120°, injector, 130°, detector, 200°) known to separate dimethyl cyclobutane-*cis*-1,2-dicarboxylate from the isomeric dimethyl cyclobutane-*cis*-1,3-dicarboxylate ester indicated the presence of only a trace of the latter (or some other material with identical retention time). The ratio of peak areas for cis-1,2 and cis-1,3 was 140:1.

Osmium Tetroxide Reaction with Bicyclo[2.2.0]hexa-2,5-diene (1). A solution of osmium tetroxide in diethyl ether (0.5 mmol in 20.0 ml) was prepared and cooled to −5°. While maintaining the system under an atmosphere of nitrogen, Dewar benzene (0.39 mmol) was added as a solution in 4.5 ml of *n*-octane. After allowing the reaction mixture to stand for 30 min, the precipitate which had formed was separated by filtration. This greenish-brown solid (233 mg) was dissolved in 10 ml of methanol, cooled to −5°, and treated with hydrogen sulfide gas. The resulting black slush was filtered, and the off-white filtrate was evaporated down under high vacuum to leave 15.0 mg of solids. Totally insoluble in chloroform, the material was crystallized from methanol–chloroform, mp 184–186°. The material, which gave a strong periodate test for glycols, exhibited nmr signals (solvent, dimethyl-d_6 sulfoxide) at τ 5.25 (4 H, broad singlet), 5.97 (4 H, broad singlet), and 7.72 (2 H, broad singlet). The addition of deuterium oxide to the sample caused the signal at τ 5.25 to collapse. The mass spectrum of the product (see Figure 10) possessed a molecular ion peak at *m/e* 146 and had a rich fragmentation pattern which was consistent with the tetrol structure.

Reaction of Dichloro(bisbenzonitrile)palladium with Bicyclo[2.2.0]hexa-2,5-diene (1). A solution of dichloro(bisbenzonitrile)palladium (140 mg, 0.37 mmol) in 0.7 ml of dichloromethane was placed in a 5-ml flask which was then connected to a vacuum line. Using standard vacuum line techniques, bicyclo[2.2.0]hexa-2,5-diene (18 mg, 0.23 mmol) was distilled into the solution of dichloro(bisbenzonitrile)palladuim. After warming to room temperature, a light-brown precipitate formed. The precipitate was triturated with dichloromethane and dried at room temperature (yield, quantitative). The amorphous solid was very slightly soluble in acetone and insoluble in chloroform. Heating a suspension of the solid in acetic acid caused the precipitation of palladium metal. Dissolution in dimethyl sulfoxide was immediately followed by reprecipitation of solids which were not characterized.

The product was dried under high vacuum for several hours and then submitted for mass spectral analysis. The highest *m/e* peak was 78 corresponding to C_6H_6. The material did not exhibit a sharp melting point but darkened over a wide temperature range around 150°. The nmr spectrum possessed a broad resonance line at τ 56 and no other signals. The ir spectrum possessed strong bands at 7.18, 7.97, and 8.51 μ (KBr). *Anal.* Calcd for $C_6H_6PdCl_2$: C, 28.35; H, 2.35; Pd, 41.61; Cl, 27.52. Found: C, 28.82; H, 2.28; Pd, 38.57; Cl, 26.74.

When a chloroform suspension of the complex was treated with a few drops of pyridine-d_5, the solid partially dissolved and reprecipitated. Concurrently, the two resonance lines corresponding to the nmr spectrum of Dewar benzene appeared. No Kekulé benzene was detected.

Reaction of Dichlorocarbene with Bicyclo[2.2.0]hexa-2,5-diene (1). A solution of bicyclo[2.2.0]hexa-2,5-diene (31.0 mg, 0.4 mmol) in 3 ml of *n*-pentane was placed in a 15-ml flask. Sodium methoxide (21.6 mg, 0.4 mmol) was added, followed by an equimolar amount of ethyl trichloroacetate.[26] An additional 0.2 mmol of sodium methoxide was added and the mixture stirred at room temperature under a nitrogen atmosphere for 1 hr. The supernatant liquid became brownish-yellow in color. The flask was then attached to a vacuum line and the volatile materials were transferred to a receiver by means of standard vacuum line techniques.

Analysis of the distillate by vpc revealed the presence of several components: Dewar benzene, Kekulé benzene (roughly the same absolute amount as was present initially), two components which possessed carbonyl bands in their ir spectra (these materials were not further examined), and a component which possessed a much longer retention time relative to the other compounds present in the reaction mixture. This latter material had no band in the carbonyl region of its ir spectrum. The ir spectrum did, however, possess strong bands at 6.1, 13.8, and 14.5 μ plus several bands in the fingerprint region.

Isolation of the product was accomplished by preparative vpc (yield, 30% based on Dewar benzene). The retention time of the material was 62 min under the following conditions: column 100°; injector 110°; detector, 300°. Collected material was homogeneous on reinjection.

The uv spectrum exhibited only end absorption. The mass spectrum exhibited molecular ion peaks at *m/e* 160 and 162 in the ratio expected for isotopic composition of chlorine as well as strong peaks at *m/e* 125 (base peak) and 127. The nmr spectrum possessed six resonance lines at τ 3.57 (1 H, doublet, J = 1 Hz), 3.86 (1 H, doublet, J = 1 Hz), 3.97 (1 H, doublet, J = 1 Hz), 5.43 (1 H, doublet, J = 1 Hz), 6.18 (1 H, quartet, J = 2 Hz), and 6.40 (1 H, singlet).

An *n*-octane solution of diene **27** was heated at 130° for 1.5 hr. Comparison of uv spectra obtained before and after the sample was heated indicated that no change had occurred. Photolysis of the same material in a quartz vessel with a low-pressure lamp (90% radiation at 2537 Å) caused significant changes in the uv spectrum. After 5 min of irradiation the spectrum had maxima at 235 and 297 mμ. The latter was rather broad, extending from 260 to 350 mμ. Additional irradiation (30 min) caused gradual diminution of the intensity of the spectrum.

Reaction of 1,3-Diphenylazocarbene 32 with Bicyclo[2.2.0]hexa-2,5-diene (1). Benzphenylhydrazide chloride was prepared according to the procedure of Pechman and Seeberger.[27] Tan-colored plates, mp 129–130°, were obtained (lit.[27] mp 129.5–130.5°).

To a solution of Dewar benzene (0.1 mmol) in 1.0 ml of benzene were added benzphenylhydrazide chloride (23 mg, 0.1 mmol) and triethylamine (13.8 μl, 0.1 mmol). The solution was then allowed to stand at room temperature for 8 hr.

Removal of the volatile material left a solid residue (23.8 mg). Washing the solid residue with chloroform removed 17.0 mg (the remainder was shown to be triethylamine hydrochloride). Crystallization of the chloroform-soluble portion from methanol gave yellow plates, mp 260–262°, 13.0 mg, 55% yield based on benzphenylhydrazide chloride. This high-melting adduct possessed a uv spectrum with maxima at 243 (ϵ 2.75 × 10^4) and 363 mμ (ϵ 3.65 × 10^4). The nmr spectrum had resonance lines at τ 2.80 (2 H, group of lines centered at τ value given), 4.90 (2 H, multiplet), 5.42 (2 H, multiplet), and 6.76 (2 H, broad singlet). The mass spectrum possessed a molecular ion peak at *m/e* 466 plus doubly charged molecular ion peak at *m/e* 233. Base peak was *m/e* 220.

Reaction of Bicyclo[2.2.0]hexa-2,5-diene (VIII) with Acid. A. Lewis Acid. A benzene-d_6 solution of Dewar benzene was treated with approximately 0.1 equiv of anhydrous aluminum trichloride at 30°. The nmr spectrum of the sample, which was obtained immediately before and after the addition of aluminum trichloride, indicated the clean conversion of bicyclo[2.2.0]hexa-2,5-diene to Kekulé benzene.

B. Protic Acid. A solution of Dewar benzene in benzene-d_6 was placed in a standard nmr tube. A single drop of concentrated sulfuric acid was added and the two phases were mixed by vigorous shaking. The acid phase became dark brownish-red in color. The integral of the nmr spectrum was obtained prior to and after the addition of acid. The nmr spectrum of the reaction, obtained 60 sec after addition of acid, possessed only one resonance, which corresponded to Kekulé benzene. The integral of this spectrum indicated in Kekulé benzene accounting for only 36% of the Dewar benzene. On standing an increase in the Kekulé peak was evident; after 10 min, 55% of the bicyclo[2.2.0]hexa-2,5-diene was accounted for and after 1 hr this value had increased to 85%.

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