mixture with nmr techniques. The hydrocarbons III, V, and VI were isolated as in the methanol irradiation experiments. Table II records the results.

The quenching experiment with naphthalene was identical with run 6 (Table II) except that the irradiation medium was 0.01 *M* in naphthalene. Naphthalene (0.900 g) appeared in the isolation procedure during elution of the silica gel column with pentane, and came off just ahead of unreacted III.

The quenching experiment with oxygen was identical with run 7 (Table II) except that the system was left open to the air. After 2 days reaction time, 95% of III had undergone reaction, and yet no V or VI could be detected among the products by vpc or tlc analytical techniques.

Irradiation in Acetone. The irradiation experiment was conducted in two quartz test tubes suspended around the immersion well. No filter was used. Each test tube contained 0.075 g of III and 100 ml of acetone. The reaction was run for 5 days, the solution was filtered, and the solvent was evaporated. The residue was extracted with ether, and the extract was evaporated. The residue was submitted to preparative vpc, and 0.035 g (23%) of hydrocarbon V was isolated, as well as 30% of the starting material. Hydrocarbon V was identified by vpc, tlc, and nmr comparisons with authentic material.

Effect of Solvent on Yield of *p*-Ethylbibenzyl (V). Irradiations of III (0.700 g) in methanol, ethanol, 2-propanol, and cyclohexane were carried out under identical conditions (Corex for 3 days) for comparative purposes. The hydrocarbon products were separated on preparative vpc, and Table III records the results. The solubilities of III in the four solvents were determined by saturating the solvent with III, and analyzing an aliquot of the saturated solution by vpc.

Irradiation with Low-Pressure Lamp. The apparatus used was the same as in the other experiments except that a Nester Faust Model NFUV-300 low-pressure mercury lamp was used as light source. This lamp has an emission, 90% of which is at 2537 A. The experiment was conducted with 0.700 g of III in 700 ml of ethanol in quartz for 2 days. The only products detected (vpc, good for detection of less than 0.5% of V, VI, X, and XI) were 55% yield of unreacted III, and a 15% yield of ether IX, isolated by silica gel column chromatography.

Macro Rings. XXXIII. A 1,6 to 1,6 Cycloaddition Reaction, a Diels–Alder Insertion Reaction, and Bent Benzene Rings[1,2]

Donald J. Cram, Carroll S. Montgomery, and Graham R. Knox

Contribution No. 1834 from the Department of Chemistry of the University of California at Los Angeles, Los Angeles, California. Received August 9, 1965

Abstract: The two tetraenes, *p*-xylylene (I) and its furan analog (II), when generated in the presence of one another, underwent 1,6 to 1,6 cycloaddition reactions to give the monofuran analog (III) of [2.2]paracyclophane as the major product, and [2.2]paracyclophane (IV) and its difuran analog (V) as minor products. The monofuran analog (III), when allowed to stand in hexane in the sunlight in contact with air, slowly produced [2.2.2]paracyclophane (VI). The difuran analog (V) underwent a multiple Diels–Alder reaction with dimethyl acetylenedicarboxylate to give the very highly condensed polycyclic compound (VII) which when heated reverted to the starting materials. Treatment of III with zinc and hydrochloric acid gave [8]paracyclophane (X), whose spectral and chemical properties indicated the benzene ring to be seriously deformed from a planar configuration. Hydrolysis of III produced 3,6-diketo[8]paracyclophane (XI), which through formation of its monothioketal (XIII) and treatment of this substance with Raney nickel, gave 3-keto[8]paracyclophane (XIV), 3-hydroxy[8]paracyclophane (XV), and 3-keto-4-[8]paracyclophene (XVI). The ultraviolet spectrum of the last substance indicated that the two chromaphores were somewhat coupled with one another. The tosylate of alcohol XV when acetolyzed gave 4-[8]paracyclophene (XIX) as the major product, and bridge-aromatic ring alkylated material (XX) as the minor product. The rate of this reaction was 52 times faster than that of cyclohexyl tosylate. Oxidative hydrolysis of monofuran analog III gave *cis*-3,6-diketo-4-[8]paracyclophene (XXIII), which when heated gave the *trans* isomer (XXII). Each of these isomers when treated with butadiene gave the corresponding isomeric adducts (XXVI and XXVII), which resisted attempts at aromatization. The *trans*-enedione (XXII) when treated with *l*-menthyl N-aminocarbamate formed the bis-hydrazone (XXIX) in high yield, and the substance appeared to be a single chemical entity (not a mixture of diastereomers). The ultraviolet, infrared, and nuclear magnetic resonance (nmr) spectra of many of these compounds were taken, and the last were particularly useful in making structural assignments.

In previous papers of this series,[3] the spectral, π-base strength, and chemical properties of the [*m*]- and [*m.n*]paracyclophanes were compared both with one another and with open-chain model compounds These comparisons allowed an identification of transannular electronic effects and of benzene ring deformation effects in the [*m.n*]paracyclophanes, particularly since the lower homologs of the [*m*]paracyclophanes contain nonplanar benzene rings without being pressed face to face with a second aromatic nucleus. Since conventional methods of synthesis of the [*m*]paracyclophanes failed when $m = 9$, and the next lower homolog ($m = 8$) was desired, an indirect approach to this substance was developed, inspired by the 1,6 to 1,6 cycloaddition reactions of Winberg, *et al.*[4] The synthetic

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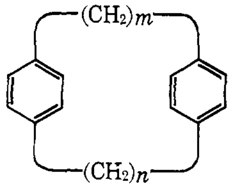
(1) This investigation was supported in part by grants from the National Science Foundation and the U. S. Army Research Office (Durham). The authors wish to thank these agencies for their interest.

(2) Parts of this paper were reported in communication form: D. J. Cram and G. R. Knox, *J. Am. Chem. Soc.*, **83**, 2204 (1961).

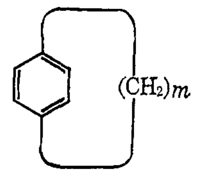
(3) (a) D. J. Cram and H. U. Daeniker, *ibid.*, **76**, 2743 (1954); (b) D. J. Cram, N. L. Allinger, and H. Steinberg, *ibid.*, **76**, 6132 (1954); (c) D. J. Cram and M. Cordon, *ibid.*, **77**, 4090 (1955); (d) D. J. Cram and M. F. Antar, *ibid.*, **80**, 3109 (1958); (e) D. J. Cram and R. H. Bauer, *ibid.*, **81**, 5971 (1959); (f) D. J. Cram, R. H. Bauer, N. L. Allinger, R. A. Reeves, W. J. Wechter, and E. Heilbronner, *ibid.*, **81**, 5977 (1959); (g) D. J. Cram and D. I. Wilkinson, *ibid.*, **82**, 5721 (1960); (h) D. J. Cram and M. Goldstein, *ibid.*, **85**, 1063 (1963).

(4) H. E. Winberg, F. S. Fawcett, W. E. Mochel, and C. W. Theobald, *ibid.*, **82**, 1428 (1960).

approach developed also provided compounds useful for an extension of the studies of carbonium ions generated in the face of benzene rings,[3h] and for an examination of the course and stereochemistry of a unique multiple Diels–Alder reaction.

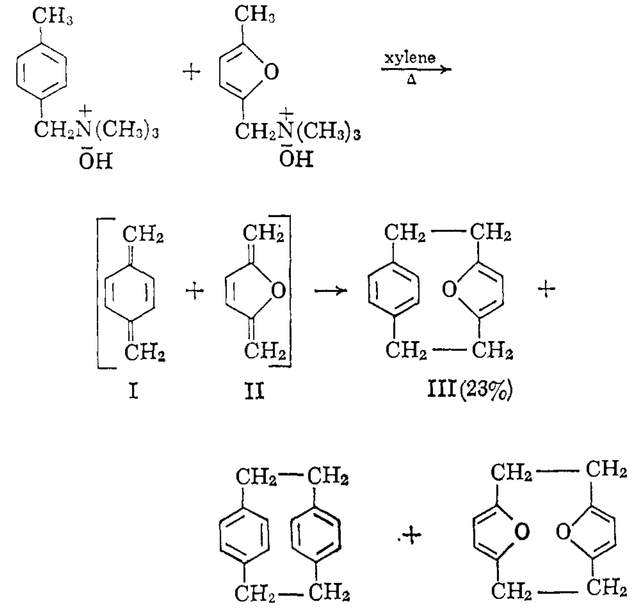


[*m.n*]paracyclophane



[*m*]paracyclophane

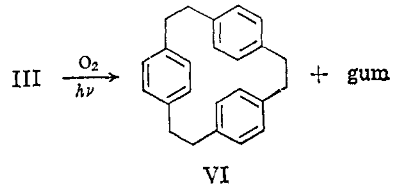
Crossbreeding 1,6 to 1,6 Cycloaddition Reaction. Reflux of an equimolar mixture of 5-methylfurfuryltrimethylammonium hydroxide[4] and *p*-xylyltrimethylammonium hydroxide[4] in toluene produced a mixture of the monofuran analog (III), the difuran analog (V), and [2.2]paracyclophane (IV) itself. These compounds must have been derived from the two tetraenes, *p*-xylylene (I) and 2,5-dimethylene-2,5-dihydrofuran (II) by 1,6 to 1,6 cycloaddition reactions. The yield pattern of the three adducts was not far from statistical, a fact that suggests that the rates of generation and consumption of I and II were close to one another, and that the activation energies for the three cycloaddition reactions were also close together.



I II III(23%)

IV (12%) V (9%)

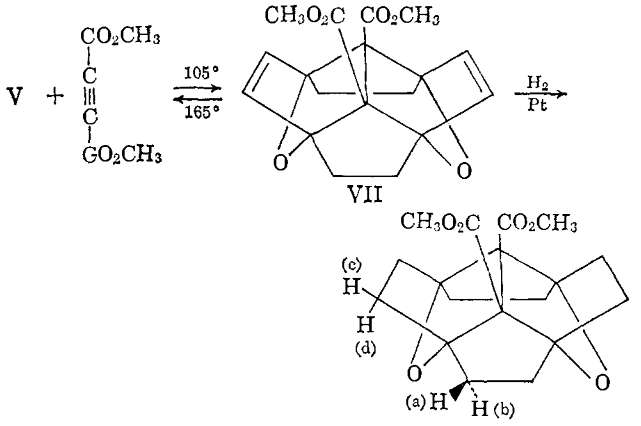
Compound III was stable when protected from oxygen and light. When allowed to stand for several weeks in the sunlight in cyclohexane, III generated [2.2.2]paracyclophane (VI),[5] presumably by a dissociative and recyclization mechanism. The fate of the furan portion of III was not determined. It was established that VI was not a contaminant of the starting material for this reaction.



VI

A Multiple Diels–Alder Reaction. Difuran compound V when heated at 105° with dimethyl acetylenedicarboxylate gave a one-to-one adduct whose spectral and chemical properties are uniquely compatible with structure VII. When heated to 165°, the substance reverted to starting materials, a fact that indicates that only cycloaddition–decycloelimination processes were involved in the forward and reverse reactions. Compound VII, when reduced with hydrogen over platinum, absorbed 2 moles of hydrogen to give VIII, which when heated to 235° failed to undergo any decyclization reaction.

The ultraviolet spectrum of VII exhibited only end absorption above 210 mμ, and the infrared spectrum indicated a strong nonconjugated carbomethoxyl band (in chloroform) at 5.8 μ. These data coupled with the



VII

VIII

hydrogenation result indicate that the conjugated double bonds of both furan rings and the acetylenic esters were consumed in the production of VII. The stereochemical structure of VII was demonstrated from the nmr spectrum of VII and VIII in deuteriochloroform.[6] The two methyl groups occurred as a sharp singlet at τ 6.28 in the spectrum of VIII, which moved upfield to τ 6.43 (sharp singlet) in VII, probably due to the proximity effect of the ring current in the flanking double bonds in VII. The four vinyl hydrogens of VII are observed as a sharp singlet at τ 3.32, and probably occur at this low field because of the strained ring system and not because of the ring current effects of the carbonyl groups. The spectrum of VII also exhibits an A_2B_2 pattern (quartet) of eight hydrogens centered at τ 7.51. The 16 methylene hydrogens of VIII absorb in a complex of bands that range from τ 7.68 to 8.47. These bands fall roughly into two groups, the first eight collecting at about τ 7.77, and the second occurring as a multiplet probably composed of two A_2B_2 systems at higher field than the first, but not completely separated from the first. The first group is probably the eight hydrogens (a) and (b), and these hydrogens are far enough removed from the ether oxygen on one side and the carbomethoxy group on the other to be nearly equivalent in environment. The second group of eight hydrogens are probably of the (c) and (d) variety,

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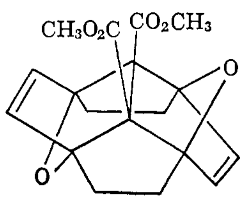
(5) W. Baker, J. F. W. McOmie, and J. M. Normon, *J. Chem. Soc.*, 1114 (1951).

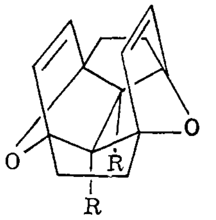
(6) The authors wish to thank Dr. George Slomp for our initial spectra.

four of which are close to the carbomethoxyl and the other four to the ether oxygen.

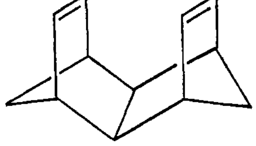
The fact that VII exhibits only one kind of methoxyl and only one kind of vinyl hydrogen indicates that the substance must contain two perpendicular planes of symmetry, as does structure VII. Of the reasonable alternate structures, VIIa does not fulfill this condition, whereas VIIb does possess two planes of symmetry. However, structure VIIb is inconsistent with the following facts. A comparison of molecular models of VIIb and IX indicates that the two double bonds in each compound are similarly located with respect to one another. Compound IX exhibits an ultraviolet absorption spectrum with λ_{max} 242 mμ,[7] whereas VII has only end absorption above 210 mμ. Although not unequivocal, the data strongly support structure VII for the multiple Diels–Alder product.



VIIa

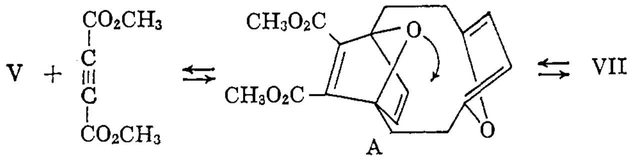


VIIb, R = CO_2CH_3

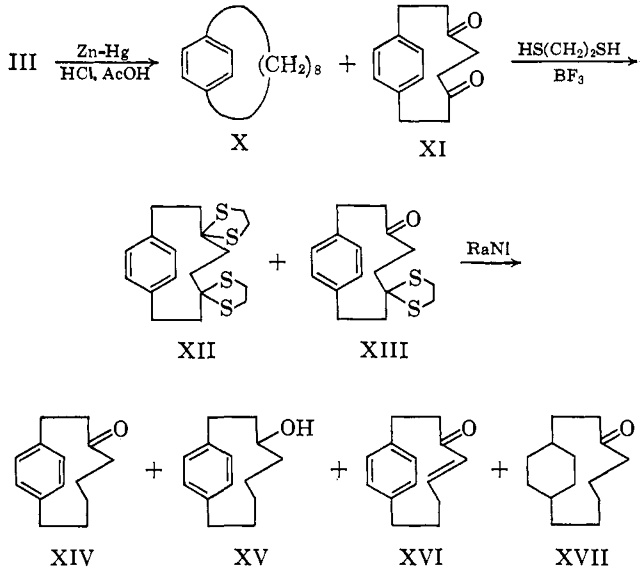


IX

Since compound V has been assigned the *trans* configuration,[4] production of VII must occur by a two-state mechanism. In the first stage, intermediate A is probably produced, and VII arises by the oxygen of the modified furan ring passing across the face of the trans-annular furan ring. In the production of starting materials from VII at higher temperatures, the reverse of these stages is envisioned. The first stage of the forward reaction probably has an equilibrium constant unfavorable to the highly strained adduct. Attempts to form such adducts from V and succinic anhydride or tetracyanoethylene failed to give products. Attempts to induce reaction between [2.2]paracyclophane and dimethyl acetylenedicarboxylate gave back starting material.



Reactions in the Side Chain of [8]Paracyclophane. When crossbred adduct III was subjected to Clemmensen reduction conditions, [8]paracyclophane (X) was produced in 55% yield, with 3,6-diketo[8]paracyclophane (XI) as a by-product (15%). Diketone XI was probably an intermediate in the production of hydrocarbon X since III gave XI (82%) when heated with glacial acetic acid–sulfuric acid. In the nmr spectrum of diketone XI, the four aromatic protons occurred as a singlet at τ 2.90, the four protons between the two keto groups of the side chain as a singlet at τ 8.22, and the other eight protons of the side chain as an A_2B_2 pattern centered at τ 7.28. The four protons between the two carbonyl groups are moved upfield by about one τ unit from τ 7.30 observed for the corresponding protons in 2,5-hexanedione. This shielding effect is probably due to the aromatic ring current similar to that observed previously in [10]paracyclophane.[8]



Diketone XI when treated with 1 mole of ethanedithiol in acetic acid–boron trifluoride etherate gave a mixture of bisethanedithioketal XII (9%) and the mono derivative XIII (66%). The monothioketal XIII gave an nmr spectrum in which the four aromatic protons appeared as a broad quartet centered at τ 2.85 (A_2B_2 pattern). Apparently the lack of symmetry of the side chain in this substance makes the four aromatic protons nonequivalent. These protons occur as a singlet at τ 2.77 in the spectrum of the bisthioketal XII. The methylene groups of the five-membered ring give sharp singlets at τ 6.78 in XIII and at 6.92 in XII. The other protons of XIII give a complex of bands that range from τ 6.9 to 9.2. These are much more clearly defined in the spectrum of the bisthioketal. The protons between the two thioketal groups occur as a singlet at τ 9.0 whereas the other eight protons occur as two triplets centered at τ 7.10 and 8.00. The four protons centered above the benzene ring clearly are moved upfield by the ring current of the aromatic system.[8]

An extensive investigation of the desulfurization of the monodithioketal (XIII) with Raney nickel led to 3-keto[8]paracyclophane (XIV) in 80% yield. Other experimental conditions produced 3-hydroxy[8]paracyclophane (XV), *trans*-3-keto-4-[8]paracyclophene (XVI), and 3-ketohexahydro[8]paracyclophane (XVII). The structure of XVI was assigned on the basis of its infrared spectrum, which gave a carbonyl absorption at 1687 cm^{-1} (α,β-unsaturated ketone), a strong band at 1620 cm^{-1} (double bond conjugated with carbonyl

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(7) S. Winstein, *Accad. Nazl.* (Lincei) (1964); R. Orloski, Thesis, University of California at Los Angeles, 1963.

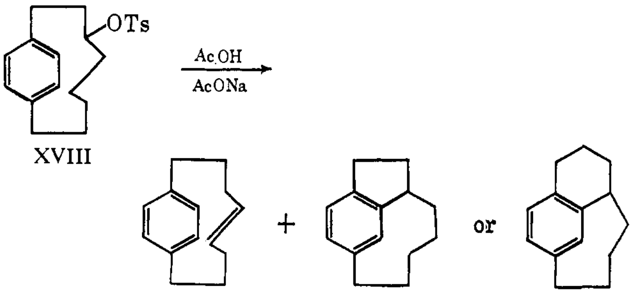
(8) J. S. Waugh and R. W. Fessenden, *J. Am. Chem. Soc.*, **79**, 846 (1957).

group), and a strong band at 965 cm^{-1} (*trans* olefin).[9] The production of XVI represents a dehydrogenation, not dissimilar to some observed previously.[10]

The nmr spectrum of the α,β-unsaturated ketone, XVI, was compatible with the assigned structure. The four aromatic protons gave a singlet at τ 2.95, whereas the two vinyl protons gave an unsymmetrical singlet at about τ 5.0, which is upfield of the position normally observed for protons of α,β-unsaturated ketones (τ 3.8–4.2),[11] and is attributable to a ring current effect. The other protons absorb in a complex series of peaks that range from about τ 7 to 8.3. In the nmr spectrum of ketone XIV, the four aromatic protons absorbed as a singlet at τ 2.88, and the other protons exhibited a complex series of peaks that ranged from about τ 7.0 to 9.5. In the nmr spectrum of alcohol XV, the aromatic protons occurred as a multiplet centered at τ 2.88, and the other protons as a complex series of peaks that ranged from about τ 6.6 to 9.5. The fact that the aromatic protons are different from one another is possibly associated with hydrogen bonding of the hydroxyl group of the bridge with the 2 position of the aromatic ring.

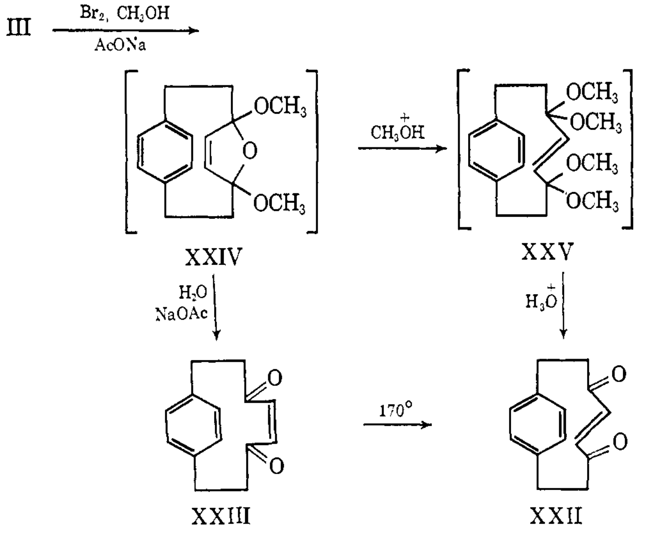
Alcohol XV was also prepared by reduction of ketone XIV with lithium aluminum hydride.

The tosylate (XVIII) of alcohol XV was prepared and acetolyzed to give a mixture of three hydrocarbons (no acetate), the major component (60%) of which was 4-[8]paracyclophene (XIX). This material was identified by its elemental analysis, and particularly by its nmr spectrum. The singlet at τ 6.00 integrated for two protons, and is presumed to be due to absorption of the olefinic protons which lie directly over the face of the benzene ring. The four aromatic protons provided a sharp singlet at τ 2.90, the four benzyl protons a broad singlet at 7.38 and the remaining eight methylene protons a broad singlet at 8.35. The symmetry properties of this spectrum (*e.g.*, only one kind of vinyl proton) point to structure XIX for the olefin, since molecular models of the much less symmetrical 3-[8]-paracyclophene indicated that the two vinyl hydrogens occupy positions with respect to the benzene ring quite different from one another. Of the other two hydrocarbons produced (39 and 1%) only the major component was isolated in a pure state. Elemental analysis and nmr spectrum indicate that the substance possesses either structure XXa or XXb. The three aromatic protons occur as a pentet centered at about τ 2.9, whereas the single methine proton occurs as a broad doublet centered at about τ 6.5. The remaining 14 aliphatic protons absorb to give a complex of bands that range from about τ 6.8 to 9.0. The ultraviolet spectrum (see next section) also supports this structural assignment. The same ratio of hydrocarbon products was obtained when the acetolysis was carried out in the presence of enough sodium acetate to neutralize the *p*-toluenesulfonic acid generated. The kinetics and mechanism of acetolysis are discussed in a later section.



In an attempt to prepare 4-hydroxy[8]paracyclophane (XXI), olefin XIX was treated with first excess diborane and then hydrogen peroxide.[12] A mixture of alcohols was obtained which could not be separated into pure components. Treatment of the mixture with tosyl chloride and pyridine at 0° gave a 33% yield of XVIII and a 62% yield of a hydrocarbon mixture, 94% of which was 4-[8]paracyclophene. It seems probable that some isomerization occurred during the hydroboration reaction.[12b] The alcohols produced appeared to be a mixture of 3- and 4-hydroxy[8]paracyclophane, the latter of which formed a tosylate unstable to the reaction conditions for its formation.

In a second series of reactions,[13] the crossbred adduct III was treated with bromine in methanol at −30° (heterogeneous), and the mixture was added to 5% sulfuric acid to give *trans*-enedione (XXII). When the bromine addition was conducted at 0° (homogeneous) and the reaction mixture was poured into water, the product was *cis*-enedione (XXIII). A mixture of the two isomers was obtained when the reaction was conducted at −30° (heterogeneous) and the product was poured into water. Although enough sodium acetate was present in the three runs to neutralize the hydrogen bromide generated, at −30° this base was insoluble, and apparently the hydrogen bromide generated caused the *trans* isomer to form. The possibility that the *cis* was isomerized to the *trans* in the reaction mixture by the acid generated was ruled out by the fact that *cis*



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(9) K. Nakanishi, "Infrared Absorption Spectroscopy," Nankodo Company Ltd., Tokyo, Japan, 1962, pp 24, 42.

(10) (a) J. Fishman, M. Torigae, and H. Gusik, *J. Org. Chem.*, **28**, 1443 (1963); (b) G. R. Pettit and E. E. Van Tamelen, *Org. Reactions*, 12, 409 (1962).

(11) L. M. Jackman, "Nuclear Magnetic Resonance Spectroscopy," Pergamon Press Ltd., New York, N. Y., 1962, p 61.

(12) (a) H. C. Brown and B. C. Subba Rao, *J. Am. Chem. Soc.*, **81**, 6428 (1959); (b) H. C. Brown, "Hydroboration," W. A. Benjamin, Inc., New York, N. Y., 1962, p 137.

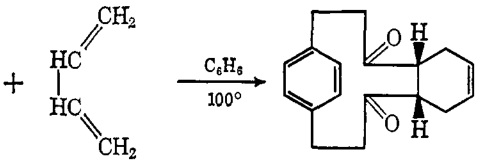
(13) This reaction was patterned after oxidative methanolysis procedures of others as applied to furan compounds: see ref. 4 and M. Clauson-Kaas, *Chem. Abstr.*, 42, 1930*e* (1948).

ketone isomerized to *trans* only slowly at 25° in a solution of 20% sulfuric acid, 30% water, and 50% ethanol. The two isomers probably gave XXIV as a precursor, which under neutral or basic aqueous conditions gives *cis* isomer, but which in the presence of hydrogen bromide and methanol gives a bisketal (XXV) which hydrolyzes to the *trans* isomer when added to water. The yields in the best reactions used for the preparation of XXII and XXIII were about 70%, but in some cases the yields were as low as 30% (50% was average). When the reaction mixture was allowed to come to 20°, the solution spontaneously evolved heat, turned brown, and yielded no product. When the reaction mixture was worked up immediately after the water treatment, a solid was isolated which spontaneously went to a brown gum with evolution of heat. If the aqueous mixture was allowed to stand, the enediones separated slowly from solution. These facts suggest that XXIV is an unstable intermediate.

When heated to 170° for 1 hr, the *cis* isomer went quantitatively to the *trans* isomer. An examination of molecular models of the two isomers leaves little doubt but that the *trans* isomer is the least strained. The nmr spectra of the two isomers are remarkably similar to one another. The four aromatic protons of the *cis* isomer occur at τ 2.95 as a sharp singlet, and of the *trans* isomer at τ 2.90 as a sharp singlet. The two vinyl protons of each isomer occur as a sharp singlet at τ 4.45. The remaining eight methylene hydrogens of each compound exhibit a symmetrical multiplet centered at τ 7.20, recognizable as a A_2B_2 pattern. The coupling constants of the *cis*-methylene hydrogens appear to be somewhat larger than those for the *trans*.

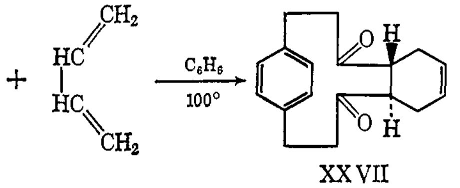
Each isomer when heated to 100° with 1,3-butadiene gave Diels–Alder adducts (XXVI and XXVII). These compounds resisted attempts at aromatization of the new six-membered ring (chloranil, or 30% palladium on charcoal). The nmr spectra of these two adducts exhibited a symmetrical octet centered around τ 2.90 for the adduct (XXVII) from *trans* olefin, and a symmetrical quartet centered around τ 2.95 for the adduct (XXVI) from *cis* olefin. A molecular model of XXVI shows that the two carbonyl groups are over one side of the aromatic ring, causing the underlying two protons to be different from those under the cyclohexene ring. A molecular model of XXVII indicates that one carbonyl group is over a hydrogen on one side of the benzene ring whereas the other carbonyl group is over a hydrogen on the opposite side of the benzene ring. In both XXVI and XXVII, the steric barrier to rotation of the elements of the side chain must be large enough to make rotamer equilibration slow on the nmr time scale. Otherwise the aromatic hydrogens would exhibit a singlet. The two vinyl hydrogens of XXVI occurred as an unsymmetrical doublet centered at τ 4.55, and of XXVII as a multiplet centered at τ 4.50. The methylene hydrogens of both compounds gave complex absorption that ranged from τ 6.7 to 8.6 for XXVII and from τ 6.9 to 8.2 for XXVI.

XXIII
cis-enedione



XXVI

XXII
trans-enedione

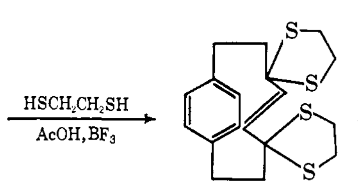


XXVII

The *trans*-enedione (XXII) when treated with 2 equiv of ethanedithiol in acetic acid containing boron trifluoride etherate at 25°[14] gave two compounds, one of which was the dithioketal of 3,6-diketo[8]paracyclophane (XII), and the other was the dithioketal of 3,6-diketo-4-[8]paracyclophene (XXVIII). The reduction of the double bond in formation of XII is reminiscent of the reduction of an α-ketol with ethanedithiol in the presence of acid,[3c] and probably involves a similar mechanism. In an attempt to form the benzene–pyridazine analog of [2.2]paracyclophane, both *cis*- and *trans*-enediones (XXIII and XXII) were treated with hydrazine in either slightly basic or acidic ethanol solution. Only polymeric azines were produced. Polyazine was also the product when XXII was submitted to the Wolff–Kishner reaction. However, the bissemicarbazone (XXIX) of XXII when treated with potassium hydroxide in ethylene glycol at 200° gave a poor yield (9%) of 4-[8]paracyclophene (XIX), identified by its vpc retention time and nmr spectrum.

Molecular models of the *trans*-enedione (XXII) suggest that the plane of the double bond is parallel to that of the benzene ring, and that the steric barrier to rotation of the double bond system with respect to the benzene ring might be great enough to make the substance a resolvable racemate. Accordingly, XXII was treated with *l*-menthyl N-aminocarbamate[15] to yield the bishydrazone (XXIX) in 98% yield. This substance possessed a sharp melting point, and in every respect behaved as a single chemical entity. Neither the melting point nor optical rotation changed with repeated recrystallizations. This experiment suggests that the barrier to rotation in the bishydrazone is low enough to allow the diastereomers to behave as a single compound. Attempts to hydrolyze XXIX failed.

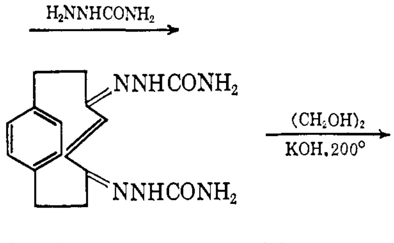
XXII
trans-enedione



+ XII

XXVIII

XXII
trans-enedione



XIX

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(14) L. F. Fieser, *J. Am. Chem. Soc.*, **76**, 1945 (1954).

(15) R. B. Woodward, T. P. Kohman, and G. C. Harris, *ibid.*, **63**, 120 (1941).

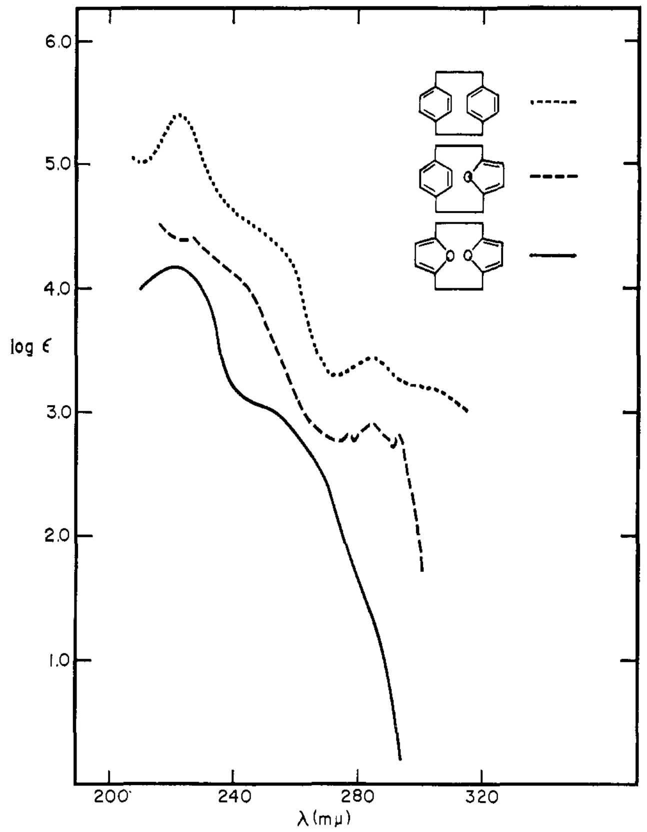
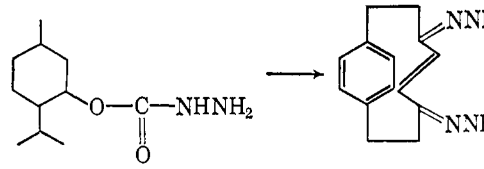


Figure 1. Ultraviolet absorption spectra in absolute ethanol taken on a Cary (Model 14 M) spectrophotometer of difuran compound V, mixed furan–benzene compound III (curve displaced upward by 0.5 log unit), and [2.2]paracyclophane (IV) (curve displaced upward by 1.0 log unit).

XXII
trans-enedione +



XXIX

Infrared and Ultraviolet Spectra. In Table I are compared the carbonyl stretching frequencies as found in the infrared spectra of the various ketones of the [*m*]paracyclophanes. The nonconjugated ketones with one exception all fall in the range 1703–1709 cm^{-1}. These bands are at longer wavelengths than those of normal ketones, and correspond to the frequencies of the bands of cyclononanone and cyclodecanone.[16] The one exception is the *cis*-Diels–Alder adduct XXVI, whose band falls between that of cyclohexanone and cyclopentanone. Molecular models of this substance suggest it to be the most strained of the substances listed, but provide no clue to the reason for this abnormal absorption. No regular change in absorption frequency is observed as the length of the bridge is shortened, as would be expected if the C–C–C bond angles became larger as the methylene belt became tighter.

Table I. Carbonyl Absorption Bands in the Infrared Spectra of [*m*]Paracyclophanes (Carbon Tetrachloride Solution)

Compound	No.	Peak position, cm^{-1}
3-Ketohexahydro[8]paracyclophane	XVII	1707
3-Keto[8]paracyclophane	XIV	1709
Monoketo-monothioketal	XIII	1707
3,6-Diketo[8]paracyclophane	XI	1705
3-Keto-4-[8]paracyclophene	XVI	1687
trans-3,6-Diketo-4-[8]paracyclophene	XXII	1681, 1703
cis-3,6-Diketo-4-[8]-*p*-cyclophene	XXIII	1681, 1703
trans-Diels–Alder adduct	XXVII	1704
cis-Diels–Alder adduct	XXVI	1725
4-Keto[9]paracyclophane[a]	. . .	1703
5-Keto[9]paracyclophane[a]	. . .	1707
5-Keto[10]paracyclophane[a]	. . .	1705
7-Keto[13]-paracyclopane[b]	. . .	1706
8-Keto[15]paracyclophane[b]	. . .	1703
6-Keto-4-[10]paracyclophene[c]		1667, 1709

[a] Reference 3d. [b] C. W. Schimelpfenig, Y.-T. Lin, and J. F. Waller, Jr., *J. Org. Chem.*, **28**, 805 (1963). [c] M. Cordon, Ph.D. Dissertation, University of California at Los Angeles, 1955.

The isomeric enediones XXII and XXIII produce two bands at the same two places, one at 1681 cm^{-1} which is the more intense, and a smaller one at 1703 cm^{-1}. A possible explanation of this phenomenon is that the rigidity of the side chain forces one carbonyl group out of conjugation with the double bond, and the two bands arise from absorption of a conjugated and an unconjugated ketone. These two bands both occur at 6 cm^{-1} shorter wavelength than the bands of the two model compounds, 3-keto[8]paracyclophane (XIV, 1709 cm^{-1}) and 3-keto-4-[8]paracyclophene (XVI, 1687 cm^{-1}). Another interesting comparison involves 6-keto-4-[10]paracyclophene, which, unlike its [8]paracyclophane homolog (XVI), exhibits two carbonyl absorptions, one at 1667 and the second at 1709 cm^{-1}, which occur on either side of the single band of XVI (1687 cm^{-1}). A possible explanation is that the lower homolog whose bridge is relatively rigid exists in a single conformation in which partial conjugation between the carbonyl and double bond is possible. The greater flexibility of the larger homolog provides for two conformations of comparable stability, one in which the two unsaturated groups are conjugated but which involves some compression of methylene hydrogens, and a second in which the unsaturated groups are unconjugated, but which involves less compression of methylene hydrogens.

Figure 1 records the ultraviolet absorption spectra of [2.2]paracyclophane (IV), the difuran analog (V), and the monofuran analog (III). It is interesting that the longer wavelength spectrum of III resembles that of the [*m*]paracyclophanes (see Figure 2) more than that of IV. Furthermore, the total spectrum of III can be described largely as a blend of that of difuran analog V and [8]-paracyclophane. The longest wavelength band of IV is missing in the spectrum of III, and the other transannular band of III at about 244 mμ occurs at much shorter wavelengths than in IV. Thus, transannular electronic effects in the excited state of III appear to be much less important than in that of the hydrocarbon (IV).

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[16] A. T. Blomquist, R. B. Burge, Jr., H. C. Sucsy, L. H. Liu, and J. C. Bohrer, *J. Am. Chem. Soc.*, **74**, 3636, 3643 (1952).

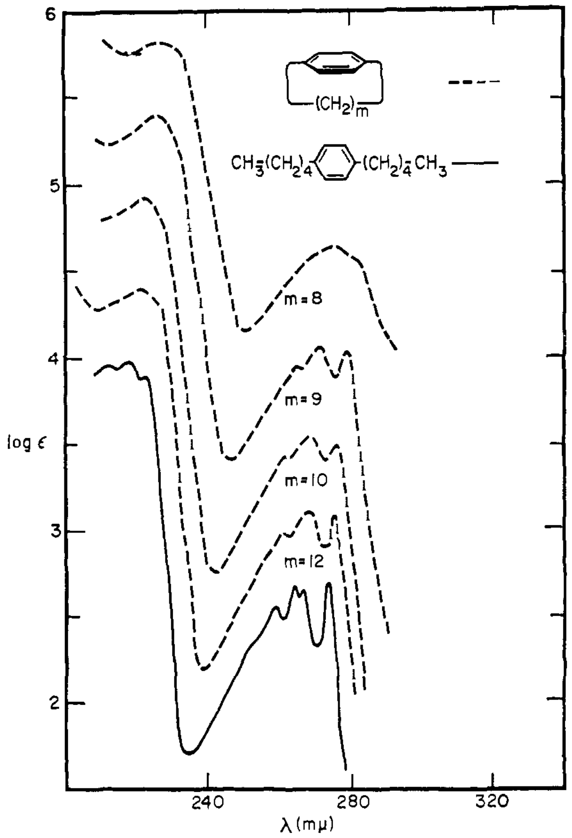


Figure 2. Ultraviolet absorption spectra in absolute ethanol of [8]-, [9]-, [10]-, and [12]paracyclophane, and of open-chain model taken on a Cary (Model 14M) spectrophotometer. The curves are displaced upward successively by 0.5 log unit from the curve immediately below.

Figure 2 contains the ultraviolet spectra of [8]-, [9]-, [10]-, and [12]paracyclophanes. The spectra of the larger cycles resemble that of the open-chain model compound, but as the methylene belt becomes shorter, the fine structure disappears and the bands move toward longer wavelengths, but only by a maximum of about 10 mμ. These effects are clearly associated with deformation of the benzene ring from a planar configuration.[3b] The extent of deformation has been calculated by Allinger, *et al.*,[17] to be about 20°, which is larger than the 13° deformation of the benzene rings from a planar configuration[18] in [2.2]paracyclophane as determined by X-ray crystallography. This comparison justifies the empirical separation of transannular effects from ring deformation effects on the ultraviolet absorption spectra of the smaller [*m.n*]paracyclophanes.[3f]

Figure 3 records the ultraviolet spectra of 6-keto-4-[10]paracyclophene,[3c] 3-keto-4-[8]paracyclophene (XVI), and that of an equal molar mixture of [8]paracyclophene and 2-keto-3-heptene. Comparison of these spectra clearly indicates the presence of transannular electronic effects in the excited state of the two cyclic α,β-unsaturated ketones. The band at 245 mμ in XVI and at 255 mμ in 6-keto-4-[10]paracyclophene is absent in the spectra of model compounds.

Table II records the positions of the absorbing bands in the ultraviolet spectra of some of the other compounds prepared in this study. If 3-hydroxy[8]paracyclophane (XV) is adopted as a reference compound whose benzene ring is bent from a planar configuration by about 20° similar to the parent hydrocarbon,[17] then many of the other compounds of Table II can be judged as being more or less deformed, depending on the position of the absorption bands, particularly those at 224–232 mμ, and the most intense band in the 275-mμ region. The data suggest that introduction of one carbonyl group into the 3 position of the bridge (compound XIV) increases the deformation of the benzene ring slightly, but introduction of two carbonyl groups in the 3 and 6 positions decreases the deformation markedly. By this criterion, fusion of a six-membered ring system either *cis* or *trans* onto the bridge containing two carbonyl groups (compounds XXVI or XXVII) results in less deformation than in the reference alcohol. Molecular models suggest the opposite conclusion. Both the monothioketal (XIII) and bisthioketal (XII) appear to be more deformed than the reference alcohol XV.

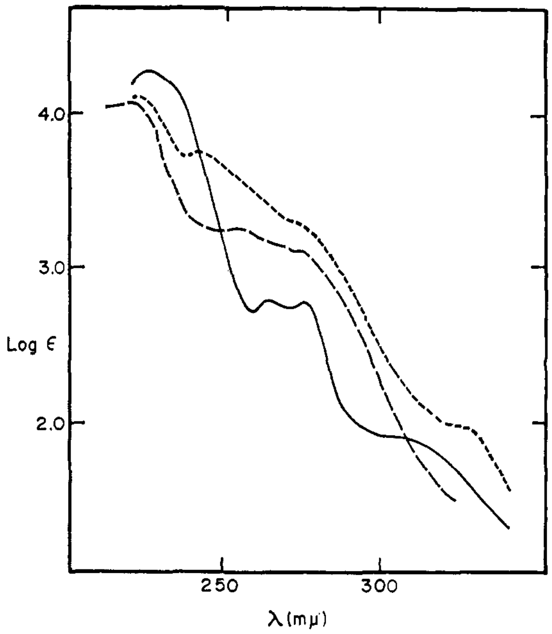
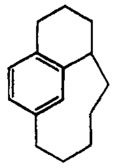
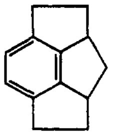


Figure 3. Ultraviolet absorption spectra in absolute ethanol taken on a Cary (Model 14M) spectrophotometer: ———, equimolar mixture of [8]paracyclophane and 2-keto-3-heptene; — — (displaced upward by 0.5 log unit), 6-keto-4-[10]paracyclophene; - - - - (displaced upward by 1.0 log unit), 3-keto-4-[8]paracyclophene.

The fine structure of the *cis*-enedione (XXIII) has been almost completely destroyed, whereas the maxima are distinct in the less hindered *trans* isomer (XXII). The superposition of chromophores makes the positions of the bands unsuitable for judging benzene ring deformation. The ultraviolet spectrum of the ring-alkylated compound (XX) resembles those of the ring-alkylated compounds XXX and XXXI,[19] whose spectra have been compared previously.[3h]



XXX



XXXI

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[17] N. L. Allinger, L. A. Freiberg, R. B. Hermann, and M. A. Miller, *J. Am. Chem. Soc.*, **85**, 1171 (1963).

[18] K. N. Trueblood and D. A. Bekoe, private communication.

[19] H. Rapoport and G. Smolinsky, *J. Am. Chem. Soc.*, **82**, 1171 (1960).

Table II. Bands in the Ultraviolet Spectra of [*m*]Paracyclophanes and Related Compounds[a]

Compound	No.	λ, mμ (log ε)			
3-Keto[8]paracyclophane	XIV	232 (3.17)	272 (2.41)[b]	278 (2.44)	286 (2.46)
3,6-Diketo[8]paracyclophane	XI	224 (3.68) 300 (1.40)[b]	265 (2.41)[b]	270 (2.50)	279 (2.41)
cis-Diels–Alder adduct	XXVI	226 (3.66)	274 (2.42)	282 (2.38)[b]	~300(1.86)[b]
trans-Diels–Alder adduct	XXVII	~225 (3.76)[b] ~296 (1.47)[b]	264 (2.37)[b]	272 (2.40)	280 (2.38)[b]
Monothioketal of diketone XI	XIII	234 (3.45)[b]	272 (2.53)	278 (2.60)	286 (2.47)[b]
Bisthioketal of diketone XI	XII	232 (3.92)	270 (2.52)[b]	276 (2.56)	284 (2.45)[b]
[8]Paracyclophane[c]	X	230 (3.83)	268 (2.43)[b]	276 (2.55)	282 (2.48)
cis-3,6-Diketo-4-[8]paracyclophene	XXIII	219 (4.06)	250 (3.48)[b]	~280 (2.85)[b]	
trans-3,6-Diketo-4-[8]paracyclophene	XXII	223 (3.87)	249 (3.52)	~300 (2.80)[b]	
3-Hydroxy[8]paracyclophane	XV	230 (3.84)	270 (2.44)[b]	276 (2.53)	284 (2.44)[b]
Ring alkylated product	XX	210 (4.39)	226 (3.87)[b]	278 (3.95)[b]	291 (4.03)

[a] Spectra taken in 95% ethanol. [b] Shoulder. [c] Taken in acetonitrile.

Kinetics and Mechanism of Acetolysis of [8]Paracyclophane 3-*p*-Toluenesulfonate (XVIII). The rates of acetolysis of tosylate XVIII (0.01 *M*) were measured as in the study of the next higher homolog,[3h] and the first-order rate constants were calculated from eight to nine points taken over the first 80% of the reaction. The rate constants were determined at 25.01 and 50.02°, and activation parameters were calculated in the usual way. Duplicate runs gave rate constants within probable error of one another: $k = 4.04 \pm 0.10 \times 10^{-6}$ sec^{-1} for the run at 25° and $k = 0.983 \pm 0.013 \times 10^{-4}$ sec^{-1} for the run at 50°, $\Delta H^* = 23.8 \pm 0.7$ kcal/mole and $\Delta S^* = -3.4 \pm 2.4$ eu. In Table III, the relative rates of acetolysis of a number of tosylates are listed for comparison purposes.

Table III. Relative Rates of Acetolysis of Cyclic Tosylates at 50°

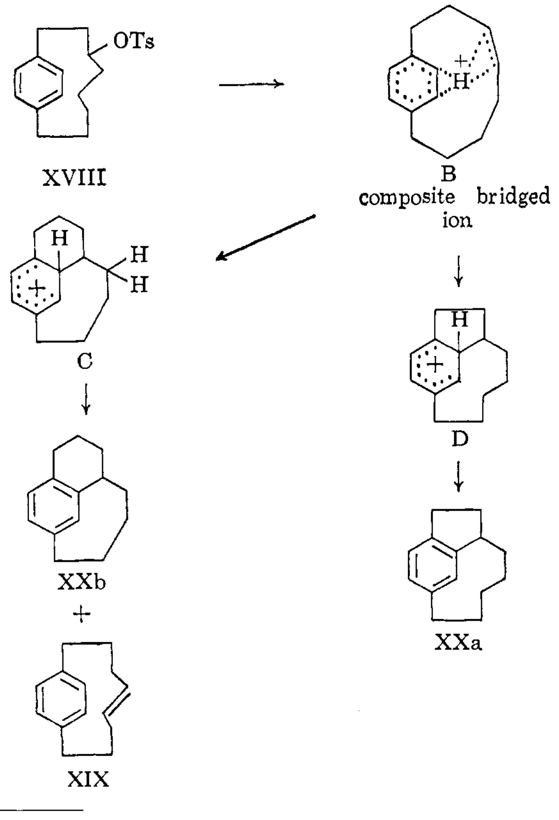
Tosylate	Relative rate
Cyclohexyl	1[a]
Cyclodecyl	539[a]
[10]Paracyclophane-5	15[b]
[9]Paracyclophane-3	60[b]
[9]Paracyclophane-5	170[b]
[9]Paracyclophane-4	1800[b]
[8]Paracyclophane-3	52

[a] R. Heck and V. Prelog, *Helv. Chim. Acta*, **38**, 1541 (1955). [b] Reference 3h.

Unfortunately, [8]paracyclophane 4-tosylate proved too unstable to be isolated. Comparison of molecular models of [9]paracyclophane 3- and [9]paracyclophane 4-tosylates and the corresponding 3- and 4-tosylates in the [8]paracyclophane series suggests that the 4-ester upon ionization should release more strain than the 3-ester in each series. The two hydrogen atoms which most seriously butt into the π clouds of the benzene rings in [9]paracyclophane are in the 4 and 6 positions, and in the 4 and 5 positions of the lower homolog, where steric repulsions are even more serious. The fact that the 4-tosylate was stable in pyridine solution in the [9] but not the [8] homolog suggests that the solvolysis rate of the latter compound is much greater than that of the former, which solvolyzes ~10^3 faster than cyclohexyl tosylate.

Separation of steric and electronic effects are particularly difficult in these compounds. No correlation between solvolysis rates and the infrared carbonyl stretching frequencies (Tables III and I) is evident.[20] Replacement of hydrogen π repulsions in the starting material with carbonium ion π attractive forces in the transition state can be referred to as either steric or electronic effects. The inductive effect of the benzene ring, changes in torsional and other nonbonded interactions, and changes in steric inhibition of solvation also undoubtedly affect the rates. Of these, the replacement of hydrogen π repulsions with carbonium ion π attractions seems to be the effect which varies the most as the structures of the paracyclophane tosylates are changed.

The products of acetolysis support the thesis that hydrogen participation in ionization is responsible for at least some of the rate enhancement of solvolysis of tosylate XVIII. Only hydrocarbon was produced, and the only olefin (60%) was product of hydrogen migration (4-[8]paracyclophene). Two other hydro-



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[20] C. S. Foote, *J. Am. Chem. Soc.*, **86**, 1853 (1964).

carbons were also generated (39 and 1%), the major component being the product of bridge alkylation of the benzene ring (XXa or XXb). Unfortunately, the substance resisted structure elucidation, and structures XXa and XXb were not differentiated, so it is not clear whether this material is also the product of hydrogen migration. Hydrogen migration was also observed when [9]paracyclophane 5-tosylate was acetolyzed, but the product was a mixture of olefins, rearranged acetate, and rearranged bridge-alkylated aromatic product. The simplest way to formulate the products in a way compatible with the facts is to invoke both neighboring hydrogen and transannular phenyl participation in ionization. A composite bridged ion can be envisioned as an intermediate (B) in which a proton is imbedded in the two π clouds, that of the incipient olefin and that of the benzene ring. The presence of a positive charge in the system should reduce the π–π repulsions of the two systems. The ring-alkylated and olefinic products then arise from subsequently formed intermediates (C and D) as formulated.

Experimental Section

Physical Methods. Ultraviolet spectra were recorded on a Cary Model 14M recording spectrophotometer in benzene-free absolute ethanol. Infrared spectra were taken on a Perkin-Elmer 421 grating spectrophotometer or a Beckman IR5 infrared spectrophotometer in either chloroform or carbon tetrachloride solutions or in a fused potassium bromide pellet. The nuclear magnetic resonance spectra were taken on a Varian A-60 analytical nmr spectrometer. Deuteriochloroform solutions containing 2% tetramethylsilane as an internal standard were used.

Vapor phase chromatographic analyses of solvolysis products were done on a 10 ft × 0.25 in. 20% Epon 1001 on 60–80 firebrick column at 180° in an Aerograph Model A-90-P gas chromatograph. Preparative vpc of the solvolysis products was performed on a 6 ft × $^3/_8$ in. 20% Epon 1001 on 60–80 firebrick column. All other analytical vpc was done on a 6 ft or 3 ft × $^1/_4$ in. 20% silicone gum on 60–80 firebrick column in an F and M Model 720 dual-column programmed-temperature gas chromatograph. All other preparative vpc was done on 6 ft × $^1/_2$ in. 20% silicone gum on 60–80 firebrick column.

All alumina chromatography was done with neutral activity I alumina with a 50:1 ratio of alumina to compound. All silica gel chromatography was done with nonactivated silica gel with a 100:1 ratio of silica gel to compound.

Plates used in thin layer chromatography were spread with a 1-mm thick layer of silica gel G and water, and activated in a 140° oven for at least 4 hr before use. Solvents used for developing the chromatograms were various mixtures of cyclohexane and ethyl acetate. Compounds were located by spotting in an iodine chamber. Melting points were uncorrected.

Benzene–Furan Analog (III) of [2.2]Paracyclophane (IV). The substance, 5-methylfurfuryltrimethylammonium iodide, was prepared[4] in 67% yield, mp 158–159°, on a 565-g scale. The original procedure[4] used to prepare *p*-xylyltrimethylammonium hydroxide was modified in the present work as follows.

To a solution of 165 g (1.1 moles) of sodium iodide in 2 l. of dry acetone was added 140 g (1.0 mole) of α-chloro-*p*-xylene in 500 ml of dry acetone. The mixture was stirred overnight and the precipitated sodium chloride was collected. The filtrate was evaporated at reduced pressure and the residual yellow oil was dissolved in 500 ml of dry ether. This solution was added over a period of 2 hr to a solution of 200 g (3.4 moles) of trimethylamine in 2 l. of dry ether. The reaction was kept at 0° during the addition. The precipitate of *p*-xylyltrimethylammonium iodide was collected and dissolved in 3 l. of water. This solution was put through a column containing 454 g of Dowex 1-X8, 50–100 mesh, strongly basic anion-exchange resin which had been converted to the hydroxide form by passing 12 l. of 2 *N* sodium hydroxide solution through it. The resulting quaternary ammonium hydroxide solution was added to a solution prepared by passing 280 g (1.0 mole) of 5-methylfurfuryltrimethylammonium iodide in 2 l. of water through a column containing 454 g of exchange resin which had been prepared in the manner described above. The combined hydroxide solutions were then added in 1-l. portions to a 3-l., three-neck, round-bottom flask containing 1 l. of toluene and fitted with mechanical stirrer and a liquid–liquid extractor in such a manner that the evaporating water was replaced by toluene. Phenothiazine (0.2 g) was added and the mixture was refluxed until all of the water was removed, and for 24 hr more to ensure that the reaction had gone to completion. The reaction mixture then was cooled and filtered to remove the insoluble polymeric material formed during the reaction. The volume of the toluene solution was reduced to 150 ml by distillation at atmospheric pressure, and the remaining solution was allowed to cool slowly. A mixture of soluble polymer and [2.2]paracyclophane, precipitated which on sublimation yielded 12.8 g (12%) of [2.2]paracyclophane (IV), mp 281–283°. The toluene solution then was put through a column of 2 kg of activity I neutral alumina. Pentane eluted 44.5 g (23%) of the benzene–furan analog (III) of [2.2]paracyclophane, mp 68–68.5°. Elution of the column with 5% ether–95% pentane produced 8.1 g (9%) of the difuran analog[4] (V) of [2.2]paracyclophane, mp 180–181°.

Production of [2.2.2]Paracyclophane (VI) from the Benzene–Furan Analog (III) of [2.2]Paracyclophane. A solution of 0.740 g (0.00384 mole) of furan–benzene compound III in 75 ml of cyclohexane was saturated with oxygen and placed in sunlight. Each day oxygen was bubbled through the solution, and the volume was kept constant. A white powder slowly precipitated. After 4 weeks all of the starting material was consumed. The cyclohexane was removed, and the resulting yellow powder was dissolved in dichloromethane. A dark yellow gum remained which was assumed to be polymer because it was nonvolatile and insoluble in all of the usual solvents. The dichloromethane solution was passed through a column of neutral activity I alumina, and a single band of white compound was recovered with 10% ether in pentane as eluent. No more material could be recovered from the column when the eluent was changed to more polar solvents (methanol was the last solvent). The white powder was recrystallized from absolute ethanol to give 0.151 g (39%) of colorless needles, mp 169–170°. The ultraviolet and nmr spectra were identical with those of [2.2.2]paracyclophane, and the product showed no depression of melting point when mixed with authentic [2.2.2]paracyclophane.[5]

***cis*- and *trans*-3,6-Diketo-4-[8]paracyclophene (XXIII and XXII).** A solution of 6.0 g (0.033 mole) of the benzene–furan analog (III) of [2.2]paracyclophane and 7.0 g (0.082 mole) of anhydrous potassium acetate in 150 ml of anhydrous methanol was cooled to 0°. The solution was stirred vigorously, and a solution of 4.8 g (0.033 mole) of bromine in 30 ml of anhydrous methanol was added over a period of 3 hr. The reaction mixture was maintained at 0° during the addition, and the solution was homogeneous until the last stages when a fine, white precipitate formed. When addition of the bromine was complete, the reaction mixture was poured into 600 ml of 5% sulfuric acid and allowed to stand for 8 hr. The resulting solution containing a voluminous white precipitate was extracted three times with dichloromethane. The dichloromethane solution was washed with water, saturated sodium bicarbonate, and saturated sodium chloride, and was dried. The solvent was evaporated, and the resulting yellow solid was dissolved in a minimum amount of boiling 95% ethanol and allowed to crystallize. The colorless crystals were collected, washed with cold 95% ethanol, and dried in a vacuum desiccator, yielding 3.32 g (47%) of *trans*-3,6-diketo-4-[8]paracyclophene (XXIII), mp 132–132.5°. *Anal.* Calcd for $C_{14}H_{14}O_2$: C, 78.50; H, 6.58. Found: C, 78.66; H, 6.82.

When a reaction mixture identical with the one described above was poured into water instead of 5% sulfuric acid, the product was 3.34 g (47.3%) of yellow crystals of *cis*-3,6-diketo-4-[8]paracyclophene (XXII), mp 162.5–163°. *Anal.* Calcd for $C_{14}H_{14}O_2$: C, 78.50; H, 6.58. Found: C, 78.31; H, 6.57.

Diels–Alder Adducts of *cis*- and *trans*-3,6-Diketo-4-[8]paracyclophene and 1,3-Butadiene (XXVI and XXVII). A solution of 0.500 g (0.00234 mole) of *trans*-3,6-diketo-4-[8]paracyclophene (XXII) in 1 ml of 1,3-butadiene and 5 ml of benzene was sealed in a thick-walled glass tube and heated at 100° for 24 hr. The tube was cooled and a white amorphous solid precipitated from solution. The tube was opened and the reaction mixture was warmed to drive off unreacted 1,3-butadiene. The warm solution was diluted with enough cyclohexane to bring the solution to the cloud point. When the mixture was cooled, colorless crystals formed which were collected, washed with cold benzene, and dried to give 0.320 g (51.0%) of the *trans* Diels–Alder adduct (XXVII), mp 175–176°. *Anal.* Calcd for $C_{18}H_{20}O_2$: C, 80.56; H, 7.51. Found: C, 80.74; H, 7.35.

The procedure and quantities were the same for the reaction of *cis*-3,6-diketo-4-[8]paracyclophene (XXIII) with 1,3-butadiene. The *cis* adduct was less soluble than the *trans* and was crystallized from pure benzene, yielding 0.436 g (73%), mp 170–173°. *Anal.* Calcd for $C_{18}H_{20}O_2$: C, 80.56; H, 7.51. Found: C, 80.55; H, 7.48.

No starting material was recovered in either reaction. The balance of material recovered in both reactions was a colorless gum which did not move on thin layer chromatography and was presumed to be polymer.

Disemicarbazone of 3,6-Diketo-4-[8]paracyclophene. A solution of 1.00 g (0.00467 mole) of *trans*-3,6-diketo-4-[8]paracyclophene in 50 ml of absolute ethanol which had been warmed until all solid was dissolved was added to a solution of 1.66 g (0.0148 mole) of semicarbazide hydrochloride and 1.5 g of sodium acetate in 100 ml of 50% ethanol. The solution was allowed to stand for 3 days at room temperature, and large yellow crystals slowly precipitated from solution. The crystals were collected, washed with water and absolute ethanol, and dried under vacuum in a desiccator. This afforded 1.47 g (96.0%) of the disemicarbazone of *trans*-3,6-diketo-4-[8]paracyclophene. The compound had no discrete melting point but slowly turned into a brown gum at temperatures above 240°.

Bishydrazone from *l*-Menthyl N-Aminocarbamate and 3,6-Diketo-4-[8]paracyclophene (XXIX). A solution of 1.00 g (0.00467 mole) of 3,6-diketo-4-[8]paracyclophene, 3.00 g (0.0140 mole) of *l*-menthyl N-aminocarbamate, and 1 ml of glacial acetic acid in 300 ml of absolute ethanol was refluxed for 1 hr. Water was added until the solution became cloudy, and the mixture was kept at 25° for 4 days. During this time fine, hair-like crystals precipitated from the solution. The solid was collected, washed with ether, and dried to give 2.77 g (99%) of the corresponding bishydrazone of 3,6-diketo-4-[8]paracyclophene, mp 242–243° dec, $[\alpha]^{25.5}{}_{546}$ −116.4° (*c* 3.0, $CHCl_3$). *Anal.* Calcd for $C_{28}H_{54}N_4O_4$: C, 71.25; H, 8.97. Found: C, 71.34; H, 8.95.

This material (XXIX) was recrystallized from tetrahydrofuran with a 34% recovery, mp 242–243°, $[\alpha]^{25.5}{}_{546}$ −116.4° (*c* 3.0, $CHCl_3$). A second recrystallization from tetrahydrofuran with a 49% recovery gave mp 242–243°. $[\alpha]^{26.0}{}_{546}$ −117° (*c* 3.0, $CHCl_3$). Similar recrystallizations were done in ethanol with no change in either the melting point or rotation.

3,6-Diketo[8]paracyclophane (XI). A solution of 9.29 g (0.047 mole) of the benzene–furan analog (III) of [2.2]paracyclophane, 54 ml of water, 108 ml of glacial acetic acid, and 3 ml of 10% sulfuric acid was refluxed for 18 hr. The solution was cooled, poured into 400 ml of water, and extracted with three 100-ml portions of dichloromethane. The organic layer was washed with water, saturated sodium bicarbonate solution, and saturated sodium chloride solution and was dried. Removal of the solvent yielded 9.80 g of yellow powder which on crystallization from 95% ethanol gave 8.30 g (82%) of colorless crystalline 3,6-diketo[8]paracyclophane (XI), mp 154–154.5°. *Anal.* Calcd for $C_{14}H_{16}O_2$: C, 77.74; H, 7.46. Found: C, 77.75; H, 7.61.

Monoethanedithioketal (XIII) of 3,6-Diketo[8]paracyclophane. A solution of 5.00 g (0.023 mole) of 3,6-diketo[8]paracyclophane in 200 ml of glacial acetic acid was treated with a solution of 2.18 g (0.023 mole) of ethanedithiol in 110 ml of glacial acetic acid, and to the resulting solution was added 30 ml of 48% boron trifluoride etherate. The reaction mixture was sealed tightly and allowed to stand for 2 days at 25°. The reaction mixture was poured into 1500 ml of water, the mixture was extracted with three 250-ml portions of dichloromethane, and the combined organic layers were washed with water, saturated sodium bicarbonate, and saturated sodium chloride solution. The solution was dried and evaporated, and the residue was taken up in a minimum amount of benzene and subjected to alumina column chromatography. Elution with 10% ether–90% pentane brought through 0.743 g (9%) of the bisethanedithioketal (XII) of 3,6-diketo[8]paracyclophane, which when recrystallized from ethanol gave mp 139–139.5°. *Anal.* Calcd for $C_{18}H_{24}S_4$: C, 58.64; H, 6.57. Found: C, 58.68; H, 6.60.

Elution of the column with 50% ether–50% pentane produced 4.44 g (66%) of the monoethanedithioketal of 3,6-diketo[8]paracyclophane, which when recrystallized from ethanol gave mp 157–157.5°. *Anal.* Calcd for $C_{16}H_{20}OS_2$: C, 65.70; H, 6.89. Found: C, 65.58; H, 6.83.

Elution of the column with pure ether produced 0.549 g of starting material.

Desulfurization of the Monoethanedithioketal (XIII) of 3,6-Diketo-[8]paracyclophane. To a solution of 3.5 g (0.012 mole) of monoethanedithioketal of 3,6-diketo[8]paracyclophane in 200 ml of dioxane was added 35 g of W-2 Raney nickel which had been deactivated by refluxing it in dry acetone for 2 hr. The mixture was refluxed for 10 hr, cooled, and filtered, and the solvent was removed on a rotary evaporator at reduced pressure. The product, a yellow oil, was diluted with pentane and subjected to alumina column chromatography. Elution of the column with 10% ether–90% pentane gave 0.636 g (26%) of 3-keto[8]paracyclophane (XIV), mp 69.0°, purified by sublimation at 50° (0.1 mm). *Anal.* Calcd for $C_{14}H_{18}O$: C, 83.12; H, 8.97. Found: C, 83.10; H, 8.76.

This compound was immediately followed off the column by 0.727 g (30%) of 3-keto-4-[8]paracyclophene (XVI), mp 56–57°, purified by sublimation at 50° (0.1 mm). *Anal.* Calcd. for $C_{14}H_{16}O$: C, 83.96; H, 8.05. Found: C, 83.82; H, 8.01.

3-Ketohexahydro[8]paracyclophane (XVII). A solution of 5.58 g (0.0192 mole) of the monoethanedithioketal of 3,6-diketo[8]paracyclophane in 200 ml of absolute ethanol was refluxed with stirring in a nitrogen atmosphere over 65 g of W-2 Raney nickel for 10 hr. The mixture was cooled and filtered, and the solvent was removed on a rotary evaporator at reduced pressure. The resulting yellow oil was diluted with 10 ml of pentane and subjected to silica gel column chromatography. Elution of the column with pentane afforded 0.682 g (17%) of 3-ketohexahydro[8]paracyclophane (XVII) as a colorless oil. *Anal.* Calcd for $C_{14}H_{24}O$: C, 80.70; H, 11.62. Found: C, 80.70; H, 11.42.

Elution of the column with 10% ether–90% pentane yielded 2.45 g of a colorless oil which was a mixture of nine or more compounds in approximately equal amounts as shown by thin layer and vapor phase chromatography. The infrared spectrum of this mixture showed the presence of hydroxyl groups and the absence of carbonyl groups. No attempt was made to isolate and identify any of these compounds.

3-Keto[8]paracyclophane (XIV). A solution of 8.00 g (0.274 mole) of the monoethanedithioketal of 3,6-diketo[8]paracyclophane in 350 ml of dry acetone was stirred at room temperature with 41 g of W-2 Raney nickel for 1 hr. A very slight warming of the solution was observed during the first 20 min of the reaction. The nickel was collected, stirred with dichloromethane, and again collected. The acetone and dichloromethane filtrates were combined, and the solvent was removed on a rotary evaporator at reduced pressure. The resulting white solid was sublimed at 50° (0.07 mm) yielding 4.43 g (80%) of 3-keto[8]paracyclophane (XIV), mp 69.0°, undepressed by admixture with the sample described above. This was the only product recovered from this reaction.

3-Hydroxy[8]paracyclophane (XV). A solution of 1.97 g (0.0102 mole) of 3-keto[8]paracyclophane in 200 ml of dry ether was added over a period of 2 hr to a mixture of 0.400 g (0.0105 mole) of lithium aluminum hydride in 200 ml of dry ether at 0°. The reaction mixture was stirred during the addition and for an additional 4 hr before it was allowed to warm to room temperature. An excess of ethyl acetate was cautiously added to the mixture and then 100 ml of water was added and the mixture was stirred for 1 hr. The organic layer was removed, and the aqueous layer was washed twice with 20-ml portions of ether. The combined organic layers were washed twice with water, once with saturated sodium chloride solution, and dried. The solvent was removed on a rotary evaporator at reduced pressure. The resulting slightly yellow solid was sublimed at 45° (0.07 mm) yielding 1.73 g (83%) of 3-hydroxy[8]paracyclophane (XV), mp 49–51°. *Anal.* Calcd for $C_{14}H_{20}O$: C, 82.30; H, 9.87. Found: C, 82.22; H, 9.94.

[8]Paracyclophane 3-*p*-Toluenesulfonate (XVIII). To a solution of 0.500 g (0.00245 mole) of 3-hydroxy[8]paracyclophane in 2 ml of dry pyridine was added 0.700 g (0.00368 mole) of *p*-toluenesulfonyl chloride. The mixture was swirled until all of the sulfonyl chloride had dissolved, and then stored at 0° for 24 hr. During this time large crystals of pyridinium hydrochloride precipitated from the solution. The cold mixture was poured into 30 ml of cold water and extracted with three 40-ml portions of 1:1 pentane–ether. The combined organic layers were washed with water, 2 *N* sulfuric acid, 5% sodium bicarbonate, and water, and dried. The drying agent was removed and the solution was evaporated to a volume of 3 ml. The solution was diluted with 3 ml of pentane, and again evaporated to a volume of 3 ml. This was then diluted with 3 ml of pentane and cooled. The white crystals that separated were collected and dried at 25 mm for 15 min to give 0.781 g (89%) of [8]paracyclophane 3-*p*-toluenesulfonate (XVIII), mp 71–72°. *Anal.* Calcd for $C_{21}H_{26}O_3S$: C, 70.35; H, 7.31. Found: C, 70.35; H, 7.21.

This compound was unstable and could not be kept under vacuum, under nitrogen, or under pentane at 0° for any length of time.

Material which was crystallized four times from pentane–ether mixture was stable enough to be dried at 25 mm for 1 hr and this was stable under nitrogen for 1 day before decomposition. Carbon–hydrogen microanalysis was done on this four-times-crystallized material.

Acetolysis of [8]Paracyclophane 3-*p*-Toluenesulfonate (XVIII). A solution of 1.5 g (0.0042 mole) of [8]paracyclophane 3-*p*-toluenesulfonate in 100 ml of glacial acetic acid was heated at 50° for 16 hr. The solution was cooled and poured into 500 ml of water. This mixture was extracted with three 100-ml portions of ether. The combined organic layers were washed with three 100-ml portions of water, two 100-ml portions of 5% sodium bicarbonate solution, and 100 ml of water, and dried. The solvent was evaporated at reduced pressure to give 0.685 g of colorless oil, a mixture shown by spectral analysis (see Discussion) to be 0.406 g (52%) of 4-[8]paracyclophene and 0.279 g (36%) of a mixture of two ring-alkylated hydrocarbons in a ratio of 1:30. Since all three compounds should have had the same empirical formula, the entire sample was distilled and submitted for carbon–hydrogen analysis. *Anal.* Calcd for $C_{14}H_{18}$: C, 90.26; H, 9.74. Found: C, 90.34; H, 9.57.

An identical solvolysis reaction was performed except that the solvent was acetic acid which was 0.2 *N* in sodium acetate. Work-up afforded 0.703 g of oil which was shown to be 0.431 g (55%) of 4-[8]paracyclophene and 0.277 g (35%) of the two ring-alkylated hydrocarbons in a ratio of 1:20.

[8]Paracyclophane 3-*p*-Toluenesulfonate from 4-[8]Paracyclophene (XIX). Under an atmosphere of helium, diborane[12] was generated by dropwise addition of a solution of 0.380 g (0.010 mole) of sodium borohydride in 10 ml of diglyme to a stirred solution of 3.55 g (0.025 mole) of boron trifluoride etherate in 10 ml of diglyme. The generated diborane was bubbled slowly through a stirred solution of 0.858 g of solvolysis product from [8]paracyclophane 3-*p*-toluenesulfonate which contained 0.520 g (0.00279 mole) of 4-[8]paracyclophene in 20 ml of tetrahydrofuran. After generation of diborane was complete the helium flow was increased to sweep the unreacted diborane from the solution. A solution of 0.400 g of sodium hydroxide in 10 ml of water was added slowly to the reaction mixture at room temperature. This was followed by careful addition of 1.2 ml of 30% hydrogen peroxide.

The reduction mixture was extracted with three 30-ml portions of ether. The combined organic layers were washed with water, saturated ferrous sulfate solution, and water, and dried. The solvent was removed at reduced pressure yielding 0.740 g of colorless oil which was subjected to silica gel column chromatography. Elution with pentane afforded 0.240 g of unreacted ring-alkylated hydrocarbon, and elution with 50% ether–50% pentane gave 0.485 g (85%) of an oil whose nmr spectrum indicated it to be a mixture of 3- and 4-hydroxy-[8]paracyclophane.

This material (0.300 g or 0.00147 mole) was treated with *p*-toluenesulfonyl chloride by the procedure recorded above. The reaction yielded 0.173 g (33%) of [8]paracyclophane 3-*p*-toluenesulfonate, mp 71–72°, identical in all respects with material prepared from other starting material (see above). The crystallization filtrates contained 0.169 g (62%) of hydrocarbon which by vpc analysis was shown to be 94% 4-[8]paracyclophene and 6% of unidentified hydrocarbon.

[8]Paracyclophane (X). A solution of 0.75 g of mercuric chloride in 15 ml of water and 2 ml of 6 *N* hydrochloric acid was swirled with 15 g of mossy zinc for 15 min. Heat was evolved and the zinc became shiny. The solution was decanted and the amalgamated zinc was washed with water and drained. The amalgamated zinc was added to a solution of 0.65 g (0.00328 mole) of the benzene–furan analog of [2.2]paracyclophane (III) in 30 ml of acetic acid and 20 ml of concentrated hydrochloric acid, and the resulting mixture was refluxed for 24 hr. After the mixture was heated for 5 hr, 15 g of amalgamated zinc was added to the solution. The mixture was cooled, poured into 100 ml of water, and extracted with three 50-ml portions of dichloromethane. The combined organic layers were washed with water, saturated sodium bicarbonate solution, and saturated sodium chloride solution, and dried over anhydrous magnesium sulfate. The solvent was removed at reduced pressure. The residue was dissolved in benzene and subjected to alumina column chromatography. Elution of the column with pentane afforded 0.339 g (55%) of [8]paracyclophane (X), a camphoraceous smelling colorless oil, followed closely by 0.025 g (4%) of a colorless oil which was not identified but whose infrared spectrum indicated that the substance contained a double bond. Elution with 50% ether–50% pentane yielded 0.105 g (15%) of 3,6-diketo-[8]paracyclophane, mp 154–154.5°. The [8]paracyclophane was distilled and analyzed. *Anal.* Calcd for $C_{14}H_{20}$: C, 89.29; H, 10.71. Found: C, 89.36; H, 10.35.

Kinetics. Acetic acid containing 0.1 *M* acetic anhydride was prepared as described previously.[21] Standard sodium acetate in glacial acetic acid was prepared by accurately weighing the desired amount of Baker Analyzed reagent grade anhydrous sodium carbonate from a freshly opened bottle.

For those rates determined at 25°, a 0.01 *M* solution was prepared in a 50-ml volumetric flask which was immersed in a constant temperature bath. Points were taken by opening the flask and withdrawing 5 ml of solution in a 5-ml automatic pipet and titrating as quickly as possible. The time was taken at the end point of the titration. A zero point was withdrawn 1 hr after immersion in the bath. The infinity point was taken by removing the flask from the 25° bath and immersing it in a 50° bath for 16 hr before sampling.

For those rates determined at 50°, a 0.01 *M* solution was prepared at room temperature in a 50-ml volumetric flask, and 5-ml aliquots were sealed in tubes and immersed in a 50° constant temperature bath. Points were taken by removing a tube from the bath and swirling it for 30 sec in an ice–water bath. The tube then was opened and the solution was titrated in the tube as quickly as possible. The time was noted at the beginning of the ice–water quench. A zero point was withdrawn 15 min after immersion and the infinity point after 24 hr in the bath.

The developing *p*-toluenesulfonic acid was followed by titration with standard sodium acetate in acetic acid, using 7 drops (per 5.00-ml aliquot) of saturated bromphenol blue in acetic acid as indicator. At the end point the solution turned from colorless to a slight yellow.

Diels–Alder Reaction of Difuran Analog of [2.2]Paracyclophane. A mixture of 1.88 g (0.01 mole) of difuran compound V, 2.14 g (0.015 mole) of dimethyl acetylenedicarboxylate, and 1.1 ml of benzene was heated in a sealed tube at 105° for 18.5 hr. The brown product was cooled and crystallized from benzene to give 2.62 g (71%) of colorless, hard, square rods, mp 164–165° (with decomposition and remelting at 156°). *Anal.* Calcd for $C_{18}H_{18}O_6 \cdot 0.5C_6H_6$: C, 68.27; H, 5.74. Found: C, 68.42; H, 5.84. A portion of this material was recrystallized from ethanol to give white needles of polycyclic compound VII, mp 163°. *Anal.* Calcd for $C_{18}H_{18}O_6$: C, 65.45; H, 5.50. Found: C, 65.39; H, 5.38. Examination of the mother liquors from this crystallization (vpc and ultraviolet spectrum) revealed the presence of benzene.

A 0.20-g sample of the Diels–Alder adduct (VII) was heated under nitrogen at 165° for 2 hr and cooled, and the product was crystallized from ether–pentane to give 0.10 g of difuran analog V of [2.2]-paracyclophane, mp 180–181°, undepressed by admixture with authentic material.

Hydrogenation of the Diels–Alder Adduct (VIII) of the Difuran Analog of [2.2]Paracyclophane and Dimethyl Acetylenedicarboxylate. The Diels–Alder adduct (0.384 g), recrystallized from ethanol to eliminate the benzene of solvation, was hydrogenated in 5 ml of glacial acetic acid with 20 mg of platinium oxide at 24° and atmospheric pressure. Hydrogen absorption was rapid and was equivalent to 91% of theory for two double bonds. The mixture was filtered, the solvent was evaporated, and the solid that separated was washed with water and dried. The product (VIII) was recrystallized from ether to give 0.354 g (91%) of white square bipyramidal crystals, mp 229–230°. *Anal.* Calcd for $C_{18}H_{22}O_6$: C, 64.66; H, 6.64. Found: C, 64.84; H, 6.62.

This material was heated as a liquid just above its melting point for 1 hr, cooled, and sublimed to give unchanged starting material.

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(21) A. H. Fainberg and S. Winstein, *J. Am. Chem. Soc.*, **78**, 2770 (1956).