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Preparation, Structure, and Properties of 3*H*-Cyclonona[*def*]biphenylen-3-one, a Potentially Antiaromatic Annulenone

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exo-3*H*-Cyclonona[*def*]biphenylen-3-ol (4) was oxidized to the potentially antiaromatic ketone **3** under Swern conditions. Attempted oxidations of the alcohol with Cr-based reagents gave only the dialdehyde **5**, which has lost a carbon atom. An X-ray structure of the ketone revealed that the dienone system was extremely nonplanar, making the existence of a paratropic ring current unlikely. The lack of conjugation of the carbonyl group with the remainder of the π-system is consistent with the ^{1}H NMR and IR spectra of **3**. Hydride reduction of the ketone unexpectedly gave the exo alcohol **4**. From ^{1}H NMR observations of the reduction process combined with molecular mechanics calculations, it was determined that the endo alcohol **9** forms first, which then, for steric reasons, isomerizes to the exo alcohol.

Introduction

The Hückel $4n + 2$ rule has been successfully extended to annulenones by assuming that their stabilities follow the π-electron count of the resonance structure corresponding to the oxyanion-substituted carbocation. Thus cyclopropenone[1] and cycloheptatrienone,[2] which have carbocation resonance structures with 2 and 6 π-electrons, respectively, are stable compounds. This contrasts with cyclopentadienone[3] and cyclononatetraenone[4] with 4 and 8 π-electrons, which have not been isolated. Both $4n$ and $4n + 2$ higher annulenones, constrained to near planarity by triple bonds, have been synthesized.[5] Depending on the number of π-electrons in the ring, these have shown either paratropic[5b,c] or diatropic[5a] ring currents.

Benzannelation is known to stabilize cyclononatetraene.[6] Several annelated cyclononatetraenones have been made in the hope that they would be stable enough to isolate but still would show antiaromatic properties. Rabinovitz et al.[6c,7] synthesized a dibenzannelated cyclononatetraenone, a stable compound but one that proved to be at most weakly antiaromatic. Molecular models indicate that this compound is tub shaped so that very little cyclic delocalization is possible. A benz-[8] and a naphthannelated[9] cyclononatetraenone have been made by Anastassiou et al. Both compounds were atropic due to nonplanarity.[10]

As part of our continuing study of annelated biphenylenes,[11] we have recently synthesized 3*H*-cyclonona[*def*]biphenylene[12] (1), a neutral homoantiaromatic hydrocarbon, and its aromatic carbanion 2.[13] Although the 9-membered rings in 1 and 2 were *not* planar, the p-orbital interactions were sufficient to allow the ring's fundamental character to express itself. Thus in 1 the inner and outer protons at C3 were split by 2.25 ppm in the ^{1}H NMR spectrum, in keeping with the expected

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† Taken from the Ph.D. dissertation of D.A.B., submitted to the Cornell Graduate School, June 1986.

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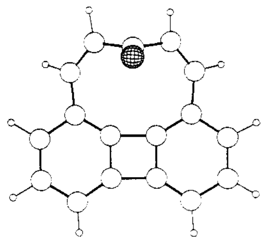
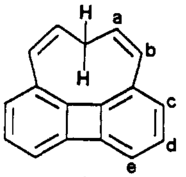


Figure 1. X-ray structure of ketone 3.

paramagnetic ring current in the 8-membered homoring. In 2 the lone proton at C3 pointed in and absorbed at −2.79 ppm, in keeping with a large diamagnetic ring current in the 10-π-electron 9-membered ring. On the basis of this experience, it seemed possible that if 1 or 2 could be converted to the annulenone 3, the latter might prove to be a species with significant antiaromaticity. What was required was that the combined steric and antiaromatic forces inducing nonplanarity could be sufficiently overcome by the sterically constraining influence of the biphenylene ring, combined with whatever electronically stabilizing influence more coplanar benzene rings might have. Although these requirements were very demanding and the prospect of achieving them unpromising, it was also true that 3 stood a better chance of displaying antiaromatic properties than did the previously reported benzannelated cyclononatetraenones and it was judged worth the gamble.



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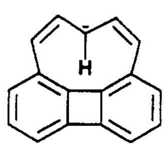

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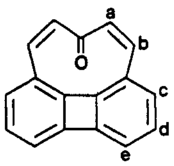

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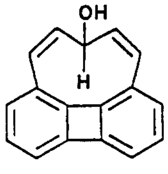
Synthesis and Properties

Several attempts were made to oxidize 1 directly to the ketone, 3. Reaction with selenium dioxide and *tert*-butyl hydroperoxide in CH_2Cl_2[14] resulted mostly in recovery of starting material. After this was removed, the residue contained at least seven compounds by TLC which were not separated. Attempted oxidation with pyridine and chromium trioxide[15] yielded a mixture of starting material and several products, dialdehyde 5 being the only identifiable one (vide infra). Oxidation with pyridinium chlorochromate (PCC)[16] or *N*-bromosuccinimide (NBS) and $CaCO_3$ in moist tetrahydrofuran (THF)[17] gave a complex mixture of compounds, none of which could be identified. As this approach was not successful, the conversion of 4 to 3 was studied.

Alcohol 4 is formed by quenching 2 with O_2 followed by reduction with dimethyl sulfide.[13] Oxidation of 4 with activated MnO_2 for a week resulted in only a trace of the ketone being formed with the rest of the starting material being recovered unchanged. No reaction took place with silver carbonate on Celite.[18] Oxidation with pyridine and chromium trioxide,[15] PCC,[16] or pyridinium dichromate (PDC)[19] gave recovered starting material plus one other compound, 5, which was identical with the compound isolated by direct oxidation of 1. The compound had TLC behavior very similar to that of 1,8-biphenylenedicarboxaldehyde.[12] ^1H NMR showed peaks for two aldehyde protons, a singlet and a doublet. There were also a doublet at 8.5 ppm, two ABC's in the biphenylenic region, indicating an unsymmetrically substituted biphenylene, and a doublet of doublets at 6.5 ppm. By use of information from selective decoupling, structure 5 was assigned. This structure has one less carbon than 4. The double bond was assumed to be (*E*) by the large vinyl coupling constant (J = 16.0 Hz), which is comparable with the vinyl coupling constant of 15.6 Hz for (*E*)-cinnamaldehyde. For comparison the vinyl coupling constant for (*Z*)-cinnamaldehyde is 12 Hz.[20] It is not clear how such a remarkable transformation takes place, particularly the isomerization of the double bond. The cleavage with loss of a carbon is reminiscent of the lead tetraacetate oxidative cleavage of diols.[21] No reaction occurred upon reaction of 3 with PCC under identical conditions, indicating that the ketone is not an intermediate in the reaction. The failure of the Cr-based oxidants was surprising as Anastassiou was able to oxidize 6 to the corresponding ketone in good yield.[8]



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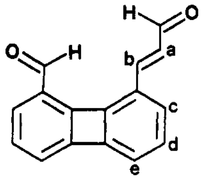

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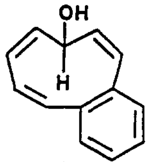

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The oxidation of 4 to 3 was finally realized in 38–55% yield by using the Swern conditions of Me_2SO and oxalyl chloride at low temperature.[22] No starting material or other recognizable compounds were found.

Ketone 3 is a stable orange crystalline solid that slowly decomposes in solution. While total planarity would be the ideal geometry to reveal the expected antiaromatic properties, examination of molecular models suggested that neither of the two possible planar structures would be an energy minimum. The planar structure with the carbonyl pointing into the ring would have severe van der Waals interactions with two of the 4-membered-ring carbons. The planar structure with the carbonyl pointing out suffers from angle strain in the 9-membered ring. To determine the actual geometry, a single-crystal X-ray structure was obtained (Figure 1). The torsional angle between the carbonyl and the flanking double bonds is 67.3°, indicating

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Table I. ^{1}H NMR Chemical Shifts for Ketone 3 and Related Compounds (δ)

proton	1[a]	3	5	(*Z*)-cinnamaldehyde[b,c]
a	5.80	6.02[d]	6.45	6.0
b	5.86	6.15[d]	8.49	7.6
c	6.38	6.36	7.05	
d	6.64	6.63	6.89	
e	6.43	6.39	6.67	

[a] Reference 12. [b] Reference 20. [c] Lettering of protons corresponds to that of 5. [d] These assignments may be switched.

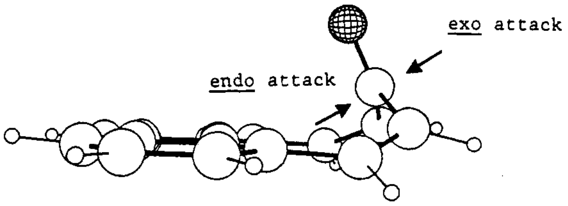


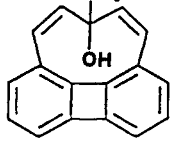
Figure 2. Side view of X-ray structure of ketone 3 showing difference in steric congestion of exo and endo attack.

that the carbonyl must be only weakly conjugated to the rest of the system. The nonplanarity and consequent weak conjugation of the dienone system is reflected in the IR ($CHCl_3$) carbonyl stretch of 1684 cm^{-1}. The ketones of the other known annelated cyclononatetraenones[7-9] absorb at 1600–1625 cm^{-1}, values indicative of more conjugation and more planar dienone systems, a result quite opposite to the initial hopes for this project. Although the biphenylene ring constrains two of the double bonds of cyclononatetraenone to a plane as expected, all of the strain of the system is taken up by rotation of the bonds to the carbonyl group. The bend in the dienone system is so extreme as to preclude any of the cyclic delocalization needed for antiaromaticity.

Another manifestation of the effectively unconjugated carbonyl group is found in the ^{1}H NMR data. For 5 and cinnamaldehyde there are marked shifts of the protons attached to the β-carbon conjugated to the carbonyl group (see Table I), whereas for 3 the conjugated sites are similar to those of hydrocarbon 1 with a small inductive effect at the α-carbon. Further NMR evidence for the lack of carbonyl conjugation in 3 comes from the similarity of the biphenylene protons in 1 and 3.

Chemistry

It was expected that, due to the different steric environments of the two faces of the ketone, incoming nucleophiles would attack from the more accessible exo face (Figure 2). Indeed, reaction of 3 with methylmagnesium chloride in THF gave only one product, which was identified as the expected product, 7, by the NMR shift of 1.4 ppm for the methyl protons. The methyl protons in 8 resonate at 1.1 ppm,[13] and the 0.3 ppm downfield shift in the alcohol is typical for replacing an α-proton by a hydroxyl group.[23]



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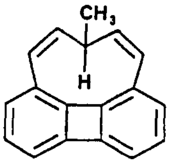

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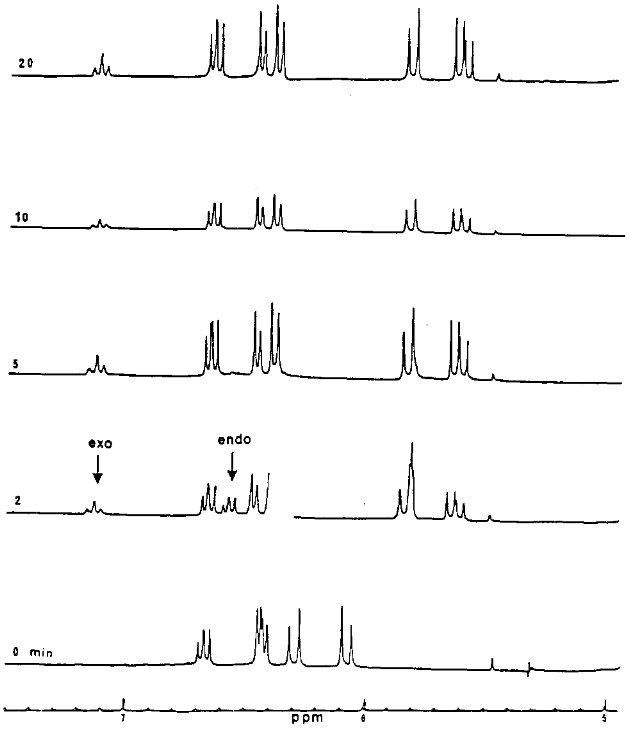
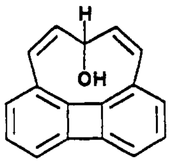


Figure 3. ^{1}H NMR spectra of reduction of ketone 3 as a function of time.

Reduction of 3 with sodium borohydride gave, unexpectedly, only 4, as did reduction with diisobutylaluminum hydride (DIBAL). The exo alcohol could have been formed either directly, by the attack of the hydride on the more hindered endo face of the ketone or by exo attack to give endo alcohol 9 followed by isomerization to 4. The endo attack seemed unlikely, especially in view of the results of the reduction using DIBAL, a highly hindered hydride source.

To test for isomerization, the reaction progress of a sodium borohydride reduction in CD_3OD was monitored by ^{1}H NMR (Figure 3). After 2 min, all of the ketone had reacted. Besides the ethylenic and biphenylenic peaks, there were triplets at 7.14 ppm (J = 9 Hz) and 6.55 ppm (J = 7 Hz). These can be attributed to the protons attached to the carbon with the hydroxyl group of 4 and 9, respectively. The larger coupling constant in 4 is consistent with the larger dihedral angle with the closer ethylenic proton. The spectrum taken after 5 min of reaction time shows only a trace of 9, and after 10 min, only 4 is present.



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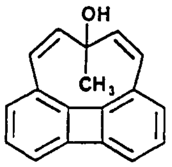

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These results are consistent with the hydride being delivered to the more accessible face of the ketone to form the endo alcohol, which then rapidly isomerizes to the exo alcohol. Molecular mechanics calculations using Allinger's force field[24] indicate that 9 is less stable than 4 by 2.8 kcal/mol, favoring 4 at equilibrium by 99:1 at room temperature. The 1% of endo alcohol would not be detectable by NMR. The higher energy of 9 is due to a bending of

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the carbon framework to move the oxygen away from the carbons in the 4-membered ring. When the carbon skeleton is restricted to C_2 symmetry, an approximate transition-state structure and corresponding energy can be calculated. The heat of formation of this calculated structure is 20.2 kcal/mol above that calculated for **4**. This corresponds to a half-life at room temperature of 74 s for the endo-to-exo isomerization, a number satisfyingly consistent with the NMR data. The endo–exo isomerization of the secondary alcohol **9** is in contrast to the results of the Grignard reaction, where the initially formed product, **7**, is calculated to be more stable than **10** by 4.0 kcal/mol. In this case the larger substituent is initially in the less sterically demanding exo position, so no isomerization takes place.

Experimental Section

General Methods. ^{1}H NMR spectra were recorded on a Brucker WM-300 (300 MHz) spectrometer in $CDCl_3$. Shifts are relative to the residual $CHCl_3$ peak (δ 7.240). ^{13}C NMR spectra were recorded on a JEOL FX-90 (22.49-MHz) spectrometer in $CDCl_3$ with shifts relative to the central peak of the solvent triplet (δ 77.000). Mass spectra were obtained on an AEI MS902 mass spectrometer. UV–vis spectra were recorded on a Hewlett-Packard 8450A double-beam spectrometer. Infrared spectra were recorded on an IBM IR98 spectrometer. Melting points were determined by using a Thomas-Hoover capillary apparatus and are uncorrected. Benzene and THF were freshly distilled from sodium/benzophenone. Me_2SO was distilled from CaH_2 and stored over activated 4-Å molecular sieves. CH_2Cl_2 was washed with acid, distilled, and stored over activated 4-Å molecular sieves. The silica gel used for column chromatography was ICN 32–63 mesh.

***(Z,Z)*-3*H*-Cyclonona[*def*]biphenylen-3-one (3).** A solution of oxalyl chloride (0.35 mL, 2.0 mmol) in CH_2Cl_2 (4 mL) was stirred in an oven-dried flask under an N_2 purge and cooled to −60 °C. Me_2SO (0.4 mL, 5.6 mmol) was added via syringe, and the mixture was stirred for 10 min. Alcohol **4**[13] (13 mg, 5.6×10^{-2} mmol) dissolved in 1.5 mL of CH_2Cl_2 was added dropwise over 5 min, and the mixture was stirred an additional 10 min. Triethylamine (1 mL, excess) was added dropwise over 5 min. The reaction was allowed to warm to room temperature during which time a precipitate formed. Water was added to dissolve the precipitate, and the reaction mixture was extracted with Et_2O, which was washed sequentially with dilute HCl, water, saturated $NaHCO_3$ (aqueous), and again with water. After drying ($MgSO_4$) and filtering, removal of the solvent in vacuo gave an orange solid. Flash chromatography on silica gel with CH_2Cl_2 elution gave 6 mg (47%) of **3**: mp 200–203 °C; R_f (CH_2Cl_2) 0.26; IR ($CHCl_3$) 1684 cm^{-1}; ^{1}H NMR δ 6.63, 6.39, 6.36 (ABC, J = 6.73, 8.29 Hz, 6 H), 6.15 (d, J = 12.3 Hz, 2 H), 6.02 (d, J = 12.3 Hz, 2 H); ^{13}C NMR δ 202.26, 150.95, 149.58, 133.37, 132.24, 130.33, 129.32, 126.40, 116.57; UV (CH_3CN) λ_{max} (log ϵ) 219 s (4.20), 260 (4.20), 280 s (3.95), 416 (3.20); mass spectrum, m/e (rel intensity) 231 (13.23), 230 (M^+, 66.42), 203 (20.94), 202 ($M^+ - CO$, 100.00), 201 (24.42), 200 (32.37), 174 (7.02), 150 (8.47), 149 (16.76); mass spectrum, m/e 230.0735, calcd 230.0732 for $C_{17}H_{10}O$.

***(Z,Z)*-3-Methyl-3*H*-cyclonona[*def*]biphenylen-3-ol (7).** A solution of freshly chromatographed **3** (2 mg, 8.7×10^{-3} mmol) in dry THF (3 mL) was stirred at 0 °C under an N_2 purge in an oven-dried flask, and methylmagnesium chloride (0.1 mL of 2.8 M solution) was added dropwise, causing the color of the solution to turn from orange to yellow. Water was added after 5 min, and after the bubbling ceased, the solution was extracted with Et_2O. The yellow ether layer was washed twice with water, dried ($MgSO_4$), and filtered. Removal of solvent in vacuo gave a yellow oil, which was flash chromatographed on silica gel with CH_2Cl_2 elution to yield <1 mg of **7**: R_f (CH_2Cl_2) 0.39; ^{1}H NMR δ 6.57, 6.38, 6.33 (ABC, J = 6.8, 8.1 Hz, 6 H), 5.73 (d, J = 12.5 Hz, 2 H), 5.67 (d, J = 12.5 Hz, 2 H), 1.43 (s, 1 H), 1.2 (s, 3 H); mass spectrum, m/e (rel intensity) 247 (11.71), 246 (M^+, 48.14), 204 (16.91), 203 (100.00), 202 (73.09), 201 (13.30), 200 (12.82), 149 (11.72); mass spectrum, m/e 246.1040, calcd 246.1045 for $C_{18}H_{14}O$.

Sodium Borohydride Reduction of 3. To a solution of **3** (1 mg, 4.3×10^{-3} mmol) in absolute EtOH (3 mL) was added $NaBH_4$ (1 mg, 2.6×10^{-2} mmol), and the solution was stirred at room temperature for 0.5 h during which time the solution turned from orange to yellow. The reaction mixture was extracted with Et_2O, and the organic layer was washed with dilute HCl followed by water. After drying, the solvent was removed in vacuo, and the resulting yellow solid was passed through a pipet packed with silica gel with CH_2Cl_2 elution. Removal of solvent in vacuo gave 1 mg of a yellow solid identical with **4** by ^{1}H NMR.

DIBAL Reduction of 3. In an oven-dried round-bottomed flask, equipped with a magnetic stirrer and rubber septum, was placed **3** (1 mg, 4.3×10^{-3} mmol) in dry benzene (2 mL). While the solution was stirred at room temperature under a N_2 purge, DIBAL (0.05 mL of a 1.5 M solution) was added. TLC analysis after 1.5 h showed mostly starting material plus one other compound. Two more portions of DIBAL were added over the next 1.5 h, at which time no starting material remained. Addition of MeOH caused bubbling and the formation of a precipitate. The reaction mixture was extracted with Et_2O, and the organic layer was washed with water followed by brine. After drying ($MgSO_4$) and filtering, the solvent was removed in vacuo to give <1 mg of a yellow solid identical with **4** by ^{1}H NMR.

PCC Oxidation of 4. In a 10-mL round-bottomed flask, equipped with a magnetic stirrer and rubber septum, was placed 1 mL of dry CH_2Cl_2. After purging with N_2, PCC (5 mg, 2.3×10^{-2} mmol) was added followed by 2.3 mg (9.9×10^{-3} mmol) of **4** in CH_2Cl_2 (2.5 mL). The solution turned brown and a precipitate formed. After 2 h, TLC showed starting material plus a more polar long-wave UV-active compound. Another 5 mg of PCC was added. After an additional hour of stirring, TLC showed no remaining starting material. The reaction mixture was passed through a pipet filled with silica gel with CH_2Cl_2 elution. The resulting solid was dissolved in Et_2O and washed sequentially with water, saturated $NaHCO_3$ (aqueous), water, dilute HCl, and water. After drying ($MgSO_4$) and filtering, removal of solvent gave 2.1 mg (91%) of **5** as a bright yellow solid: mp 169–171.5 °C; R_f (CH_2Cl_2) 0.07; ^{1}H NMR δ 9.88 (s, 1 H), 9.82 (d, J = 7.7 Hz, 1 H), 8.49 (d, J = 16.0 Hz, 1 H), 7.18, 7.00, 6.84 (ABC, J = 6.9, 8.1 Hz, 3 H), 7.05, 6.89, 6.67 (ABC, J = 6.85, 8.5 Hz, 3 H), 6.45 (dd, J = 7.6, 16.0 Hz, 1 H); ^{13}C NMR δ 194.34, 190.55, 151.65, 148.13, 130.80, 130.15, 129.98, 129.66, 128.36, 127.87, 127.76, 125.55, 121.04, 118.61; mass spectrum, m/e (rel intensity) 235 (21.14), 234 (M^+, 100.00), 233 (32.44), 206 (30.85), 205 (83.08), 178 (30.07), 177 (40.82), 175 (75.72), 152 (18.80), 151 (36.71), 150 (24.58), 149 (14.76); mass spectrum, m/e 234.0665, calcd 234.0681 for $C_{18}H_{10}O$.

CrO_3 and Pyridine Oxidation of 4. In an oven-dried round-bottomed flask, equipped with a magnetic stirrer and rubber septum, were placed pyridine (0.016, 0.20 mmol) and dry CH_2Cl_2 (3 mL). CrO_3 (10 mg, 0.10 mmol) was added, and the mixture was stirred for 70 min under an N_2 purge. Addition of **4** (2.3 mg, 9.9×10^{-3} mmol) in CH_2Cl_2 (2 mL) caused the solution to become cloudy and turn brown. After 2 h of stirring at room temperature, $NaHCO_3$ was added, and the reaction mixture was extracted with Et_2O. The organic layer was washed sequentially with saturated $NaHCO_3$ (aqueous), water, dilute HCl, and again with water. After drying ($MgSO_4$) and filtering, removal of the solvent in vacuo gave an orange solid that was further purified by flash chromatography on silica gel with CH_2Cl_2 elution, giving **5** (2.3 mg), identical by ^{1}H NMR with the sample prepared by PCC oxidation of **4**.

Alcohol **4** was also oxidized with PDC in CH_2Cl_2. The reaction was terminated after a short time when TLC showed that **5** was again being formed.

Single-Crystal X-ray Structure Determination of 3. Crystals of **3** were grown from ethanol solutions. A roughly cubic crystal with edges ca. 0.4 mm was cut from a larger crystal and used in all subsequent experiments. Preliminary X-ray photographs displayed monoclinic symmetry, and accurate lattice constants of a = 17.2542 (21) Å, b = 5.0172 (8) Å, c = 14.2362 (15) Å, and B = 110.492 (84)° were determined from a least-squares fit of 15 diffractometer-measured 2θ values. The crystal density, 1.33 g/cm^3, indicated that four molecules of **3** made up the unit cell. The systematic extinctions were consistent with space group $P2_1/n$. All unique diffraction maxima with $2\theta \leq 114°$ were collected on a computer-controlled four-circle diffractometer using variable-speed 1° ω-scans and graphite-monochromated Cu Kα radiation (1.54178 Å). Of the 1555 reflections measured in this fashion, 910 (58%) were judged observed ($F_o \geqslant 3\sigma(F_o)$) after correction for Lorentz, polarization, and background effects.[25] A phasing model was found without difficulty by using a multisolution tangent formula approach.[25] All non-hydrogen atoms were easily located on the initial E synthesis. Hydrogen atoms were located on a ΔF synthesis after partial refinement of the nonhydrogen positions and thermal parameters. Block-diagonal least-squares refinements with anisotropic non-hydrogen atoms and isotropic hydrogens converged to a crystallographic residual of 0.0369 ($R_w = 0.0461$) for the observed data. Further results of the crystallographic experiments are available and are described in the supplementary material paragraph.

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Registry No. 3, 108058-71-5; 4, 108058-70-4; 5, 108058-73-7; 7, 108058-72-6.

Supplementary Material Available: Tables of fractional coordinates and thermal parameters, anisotropic thermal parameters, interatomic distances and angles, and torsional angles for ketone 3 (5 pages). Ordering information is given on any current masthead page.

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[25] All crystallographic calculations were done on a PRIME 9955 computer operated by the Cornell Chemistry Computing Facility. Principle programs employed were the following: REDUCE and UNIQUE, data reduction programs by M. E. Leonwicz, Cornell University, 1978; MULTAN 78, MULTAN 80, and RANTAN 80, systems of computer programs for the automatic solution of crystal structures from X-ray diffraction data (locally modified to perform all Fourier calculations including Patterson syntheses) written by P. Main, S. E. Hull, L. Lessinger, G. Germain, J. P. Declercq, and M. M. Woolfson, University of York, England, 1978 and 1980; DIRDIF, written by P. T. Beurskens et al., University of Nijmegen, Netherlands, 1981; MITHRIL, an automatic solution package written by C. J. Gilmore, University of Glasgow, Scotland, 1983; BLS78A, an anisotropic block diagonal least-squares refinement written by K. Hirotsu and E. Arnold, Cornell University, 1980; PLUTO78, a crystallographic illustration program by W. D. S. Motherwell, Cambridge Crystallographic Data Centre, 1978; and BOND, a program to calculate molecular parameters and prepare tables written by K. Hirotsu, Cornell University, 1978.

Synthesis, Conformation, and Structure of 8,11-Bis(methoxycarbonyl)[6]paracyclophane

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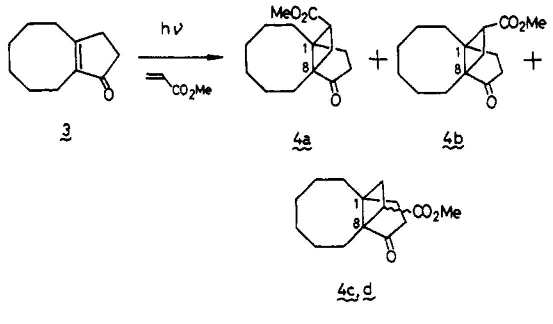
8,11-Bis(methoxycarbonyl)[6]paracyclophane (**1c**), a crystalline derivative of the smallest bridged paracyclophane system with two ester groups at the para position of the aromatic nucleus, has been successfully synthesized by utilizing thermal valence isomerization of its Dewar benzene-type isomer, [6.2.2]propelladiene (**2c**). The rate retardation observed in the above isomerization relative to those of the hydrocarbon **2a** and the monoester **2b** was attributed to development of steric repulsion between the ester groups and the benzyl hydrogens in the transition state. From the dynamic ^{1}H NMR behavior, it has been deduced that **1c** occurs preferentially in conformer A rather than B (20:1 ratio) in solution and $\Delta G^{\ddagger}_c$ for the inversion of the bridge has been estimated to be 12.9 kcal/mol (−24 °C). The X-ray analysis of **1c** not only confirmed the preference of conformer A but also revealed the remarkable deformation imposed on the benzene ring and the methylene bridge. The out-of-plane bending angle of the para carbon (C(7)) is 19.4°, and that of the benzyl carbon (C(1)) is 20.2°. While the bond lengths of the bridge are normal, the bond angles of C(2) and C(3) are remarkably expanded (116.8°) from the normal angle. On the basis of the short nonbonded distance between O(1) and H(11) (2.43 Å), it is deduced that the remarkable conformational bias in favor of conformer A over B is due to the severe nonbonded repulsion between the carbonyl oxygens and the benzyl hydrogens in the latter.

Recently, increasing interest has been focused on the chemistry of small-bridged [*n*]cyclophanes.[1] In the series of [*n*]paracyclophanes so far isolated,[2] the smallest bridged [6]paracyclophane (**1a**) was first synthesized by Jones and co-workers in 1974[3a] and a few years later by Jones and Bickelhaupt et al.[3b] More recently, we have developed a more convenient access route to the parent hydrocarbon **1a** and the 8-substituted derivative such as **1b** by taking advantage of the thermal valence isomerization of the corresponding Dewar benzene-type valence isomers, [6.2.2]propelladienes (**2a** and **2b**).[4] At the same time, Tochtermann and co-workers have explored a different route to 8,9-disubstituted derivatives such as **1d** using the reductive deoxygenation of the bridged oxepine derivatives.[5b] With successful access to this system, we and they have been investigating the structure, especially the out-of-plane bending of the benzene ring (ca. 20°), conformational behavior, and reactivities associated with the de-

Scheme I



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(1) For a recent review: Rosenfeld, S. M.; Choe, K. A. In *Cyclophanes*; Keehn, P. M., Rosenfeld, S. M., Eds.; Academic: New York, 1983; Vol. I, Chapter 5.

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