SYNTHESIS, STRUCTURE AND REACTIVITIES OF [6]PARACYCLOPHANES

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Abstract—The synthesis, structure and reactivities of [6]paracyclophanes 2a-c, the smallest bridged [n]paracyclophanes so far isolated, are described. The parent hydrocarbon 2a has been efficiently synthesized by oxidative decarboxylation of [6.2.2]propellenecarboxylic acid (7) by lead tetraacetate. The 8-carbomethoxy derivative 2b has been quantitatively synthesized by thermal valence isomerization of the [6.2.2]propellane carboxylation of the [6.2.2]propellane carboxylation of the [6.2.2]propelladiene (4b) (Dewar isomer of 2b). X-Ray structure analysis of the crystalline 2c has revealed that the benzene ring of 2c is severely deformed into a boat conformation with deformation angles of $\alpha = 20.5^{\circ}$ and $\beta = 18.5^{\circ}$. Furthermore, the bond angles of the bridging chain (C(2), C(3), C(4) and C(5)) are considerably expanded from the normal sp^3 angle. Vapor phase thermolysis of 2a gives the spiro triene 12 via homolysis at the benzyl position. Acid-catalyzed isomerization of 2a with trifluoroacetic acid takes place readily to afford the meta and ortho isomers 13a and 14a in a ratio of 1:3. UV irradiation of the ester 2b brings about valence isomerization to the Dewar isomer 4b which isomerizes slowly to the prismane derivative 15a on further irradiation. A [4+2] cycloaddition of 2a with N-phenyl-1,2,4-triazoline-3,5-dione occurs at room temperature to give mainly adduct 16. Addition of bromine to 2a takes place to give the dienone dimer 20 which affords on UV irradiation the cage diketone 21 derived from intramolecular photocycloaddition.

The question "How bent can a benzene be without giving up its aromaticity?" represents one of the most intriguing challenges in molecular design and the synthesis of non-natural products. The most direct and efficient way to answer this question is to bridge the para positions of a benzene ring with a small chain. From this point of view, the chemistry of small bridged paracyclophanes has been extensively developed during the last decade,¹ and many fruitful results have been obtained. [7] Paracyclophane (1a) is moderately strained and exhibits unusual reactivities.² The next smallest homologue, [6]paracyclophane (2a), is the smallest bridged paracyclophane isolated to date³ and has been shown to be highly strained by recent work in our laboratory and that of Tochtermann.4,5 More recently, we and Bickelhaupt succeeded in spectroscopic characterization of [5]paracyclophanes 3a and b as unstable but still aromatic intermediates.⁶ However,



these could not be isolated because of their lability. Therefore, [6]paracyclophane (2a) is the most strained paracyclophane which has sufficient stability for investigating the relationship between aromaticity and non-planarity of a benzene ring. Herein we disclose the efficient synthesis of the parent hydrocarbon of [6]paracyclophane (2a) and that of its 8-carbomethoxy and 8-carboxy derivatives 2b and c, as well as improved X-ray structure analysis of 2c, and novel reactivities of 2a associated with the loss of its aromaticity.

Synthesis of [6] paracyclophanes (2a-c)

[6] Paracyclophane (2a) itself was first synthesized in 1974 by Jones and co-workers by a carbene rearrangement in very low yield (< 5%).^{3a} A few years later, Jones and Bickelhaupt reported an improved method of synthesis of 2a by means of valence isomerization of [6.2.2]propelladiene (4a) (Dewar isomer of 2a).^{3b} Although the isomerization of 4a to 2a takes place quantitatively, the preparation of 4a had not been effectively done, and, therefore, the properties of 2a were not unveiled. In this context, the first object in our program was to develop an efficient way of getting a sufficient quantity of 2a for an investigation of its properties. Recently we found that oxidative decarboxylation of [6.2.2] propellane carboxylic acid (5) with lead tetraacetate gave the bridgehead alkene 6 substituted by an acetoxyl group at the opposite bridgehead position.⁷ Since it is conceivable that similar decarboxylation of propellenecarboxylic acid 7 would afford an acetoxy diene 8 which could be converted to 2a by elimination of acetic acid, this process would offer a ready access to 2a (Scheme 1). Moreover, since 2a itself is liquid, our next challenge would be preparation of a crystalline derivative of



2a which could be submitted for X-ray structure determination in order to obtain definite information about the deformations imposed on this system. Such a derivative could be derived directly from 8carbomethoxy[6]paracyclophane(2b), which would be in turn prepared by using valence isomerization of Dewar isomer 4b, taking into account the facile isomerization of 4a to 2a.^{3b} It would thus be possible to prepare both the parent hydrocarbon 2a and its crystalline derivative bearing a substituent on the benzene ring starting from a common intermediate, methyl propellenecarboxylate 11. After we completed our synthetic work, a series of reports by Tochtermann and co-workers on the synthesis and properties of 8.9disubstituted [6]paracyclophanes 2d and e appeared.⁵

Photocycloaddition of 1,2-dichloroethylene to the bicyclic enone 9 and the subsequent reductive dehalogenation of the ethylene acetal of the photoadduct gave the propellenone 10 in 56% yield. Photo-Wolff rearrangement of the a-diazo ketone derived from 10 in methanol afforded the epimeric esters 11X and 11N in 60% yield in a ratio of 2:1. Alkaline hydrolysis of 11X or 11N gave the corresponding acid 7X or 7N almost quantitatively. Oxidative decarboxylation of 7X was carried out with 1.2 equiv of lead tetraacetate in the presence of 0.5 equiv of cupric acetate in benzene at 80° for 1 h. Fortunately, the desired 2a was obtained directly as the major product (39% yield) which was readily purified by silica gel chromatography, along with the acetoxy diene 8 (21% yield). Decarboxylation of 7N under similar conditions gave 2a and 8 in 23 and 13% yields, respectively. As expected, the acetate 8 was readily converted to 2a by treatment with potassium tbutoxide in dimethyl sulfoxide at room temperature (Scheme 2). Thus, the total yield of 2a amounts to 58% from 7X. The efficiency of this method enables us to obtain a sufficient quantity of 2a for further investigation.



Phenylselenenylation of the enolate generated from 11X or 11N with LDA by diphenyl diselenide, followed by oxidation with hydrogen peroxide, afforded the propelladiene 4b in 64% yield. As expected, thermal valence isomerization of 4b to 2b took place even at room temperature to give 2b quantitatively (Scheme 3). The kinetic parameters for the isomerization were determined by measuring the appearance of the absorption of 2b at 330 nm in cyclohexane. The activation energy of the isomerization of 4b to 2b (E_a = 24.9 kcal mol⁻¹, log A = 12.8) is slightly larger than that of 4a to 2a (19.9 kcal mol⁻¹).^{3b}

As shown in Fig. 1, 2b showed a considerable red shift of its UV absorption (λ_{max} (EtOH) 329 (log s 3.1), 261 (3.7), and 231 (4.3) nm) compared with that of methyl 2,5-dimethylbenzoate indicating severe deformation of the benzene ring.⁸ In the ¹H-NMR spectrum of 2b at -40°, the two bridge methylene protons located over the benzene ring appeared at δ -0.64 as a sharp multiplet due to the shielding effect of the benzene ring. Moreover, 2b exhibited coalescence behavior in the ¹H-NMR spectra owing to the flipping of the methylene bridge. The barrier of this conformational change was estimated to be 13.3 kcalmol⁻¹ ($T_c = 7^\circ$, $\Delta v = 116$ Hz).

Alkaline hydrolysis of 2b gave crystalline acid 2c, m.p. 123-125°, which was used for the X-ray structure analysis. Thus starting from a common intermediate 11, a new and efficient route to both parent hydrocarbon 2a and a crystalline derivative 2c of the [6]paracyclophane system have been developed.



a(1)1,2-Dichtorbethylane, Ar, (ii) ethylene glycol, H*, (ii) No, Nety, (A) H*, 56%, b(1) HODgEL, NoDEL, (ii) TsNy, (iii) Ar, MaOH; 60%, c KOH; quantit, d Pb(OAc)₄, CutOAc)₂, et-BuOK; 9%.



Fig. 1. UV spectra of 8-carboxy[6]paracyclophane (2b) (-----) and methyl 2,5-dimethylbenzoate (- - -) in ethanol.



Fig. 2. Molecular structure of 8-carboxy[6]paracyclophane (2c): (a) top view; (b) side view. The minor component of the methylene bridge includes C(22), C(23), C(24), and C(25). Non-hydrogen atoms are drawn by the thermal ellipsoids at 20% probability level. Hydrogen atoms are shown by the spheres corresponding to the artificial isotropic temperature factor of 1.0 Å².

Structure of 8-carboxy[6]paracyclophane (2c)

Preliminary X-ray analysis of 2c at room temperature indicated considerable deformation of the benzene ring of 2c from planarity.⁴⁴ However, because of the large thermal ellipsoids of the methylene bridge carbons, the distinct structure of 2c was not elucidated. Consequently, we performed the structure determination of 2c at -150° . As shown in Fig. 2, it was found that the structure was disordered, consisting of two conformers arising from the flipping of the methylene chain. Since it is therefore difficult to discuss the structure of the bridge in detail, especially that of the minor conformer, we consider here mainly the structure of the benzene ring. The bond distances and the bond angles are listed in Tables 1 and 2, respectively. The bond distances in the benzene ring are normal, whereas the bond angles of the para carbons (C(8)-C(7)-C(12)) and C(9)-C(10)-C(11)) are contracted from the normal value, indicating that the ring is pulled at the para positions by the short bridge. Concerning the major conformer, it can be noted that, as might be expected, the bond distances of the bridge are longer than normal and the bond angles of the central bridge carbons (C(2), C(3), C(4), and C(5)) are expanded, whereas those of the

Table 2. Bond angles in 8-carboxy[6]paracyclophane (2c)

Bond	Distance (Å)
$\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$	1.499(8) 1.510(7) 1.603(6) 1.555(6) 1.561(5) 1.641(5) 1.518(6)
C(7) - C(8)	1.412(7)
C(7) - C(12)	1.415(7)
C(8) - C(9)	1.399(6)
C(9) - C(10)	1.401(8)
C(10) - C(11)	1.401(9)
C(11) - C(12)	1.376(9)
C(8) - C(13)	1.481(8)
C(13)- O(1)	1.319(7)
C(13)- O(2)	1.238(7)
C(1) - C(22)	1.811(22)
C(22)- C(23)	1.511(26)
C(23)- C(24)-	1.566(23)
C(24)- C(25)	1.523(25)
C(25)- C(6)	1.315(18)

Bond	Angle (deg.)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	109.0(4) 115.4(4) 115.3(3) 115.3(3) 115.6(3) 103.1(3)
$\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$	123.2(4) 115.7(4) 117.1(4) 122.9(5) 116.9(5) 119.8(4) 116.5(5) 119.2(5) 120.8(6) 119.8(6) 120.0(5)
C(8) - C(13)- O(1) C(8) - C(13)- O(2) O(1) - C(13)- O(2)	114.1(5) 124.3(5) 121.5(5)
C(1) - C(22) - C(23) C(22) - C(23) - C(24) C(23) - C(24) - C(25) C(24) - C(25) - C(6)	123.7(14) 117.5(14) 118.8(14) 113.5(14)

Table 1. Bond distances in 8-carboxy[6]paracyclophane (2c)



Fig. 3. Out-of-plane deformation of benzene ring in small bridged [n]paracyclophanes.

benzyl carbons (C(1) and C(6)) are identical with or slightly contracted from the ordinary value.

The most remarkable feature in the structure of 2c is of course the deformation of the benzene ring from planarity, which is represented by the deviation angles of the para carbons (α) from the base plane of the boat shaped benzene ring and those of the benzyl carbons (β) from the bow of the benzene ring as shown in Fig. 3. Table 3 lists the deformation angles of 2c and those of 8,9-dicarbomethoxy derivative 2e recently reported by Tochtermann and co-workers,54 as well as those of 3carboxy[7]paracyclophane (1b).2b Interestingly, the deformation angles of the para carbons of 2c are 20.9° and 20.1° (average 20.5°) and those of the benzyl carbons are 19.2° and 18.1° (average 18.7°). The former is 3.7° greater whereas the latter is about 12° larger than those of [7] paracyclophane 1b. This indicates that the deformation of the para carbons of 2c nearly reaches the limit of non-planarity within which the aromaticity of a benzene can be maintained.⁹ It is also noted that both of the out-of-plane deformation angles, α and β , in 2c are essentially the same as those in 2e within experimental errors. The benzene ring of the [6]paracyclophane system is deformed into a boat form with a bent angle of about 20°. The sum of the bent angles (38.9-41.0°) of this system, as in [5]metacyclophane (38.8°),¹⁰ represents to our knowledge the most highly deformed benzene rings known so far.

Reactivities of [6] paracyclophanes (2a and b)

Even though the benzene ring of the [6]paracyclophanes is highly deformed from planarity, the spectroscopic data indicate that it is still aromatic. Since it is known that strained cyclophanes exhibit unusual reactivities associated with deformation,¹ some reactions of 2a and b were examined in order to find (a) the stability or lability and (b) the unusual reactivities of the [6]paracyclophane system due to deformation of its benzene ring.

First, thermal, acid-catalyzed, and photochemical isomerizations of 2a were examined.¹¹ Vapor phase thermolysis of 2a at 400° under nitrogen afforded the



spiro triene 12 as the major product in 90% yield. The formation of 12 is readily understood by homolysis of the bridge at the benzyl position as shown in Scheme 4. This should be contrasted with the higher homologues of 12 which have been shown to afford [7]- and [8]paracyclophanes on thermolysis.²⁴ Clearly the relative stabilities of cyclophane and spiro systems are reversed on going from the [7] to the [6] systems.

It is well known that acid-catalyzed isomerization of strained cyclophanes takes place under mild conditions. For example, [7]paracyclophane (1a) is isomerized to the meta isomer by fluorosulfonic acid catalysis.2. On treatment with trifluoromethanesulfonic acid (CF₃SO₃H) at room temperature 2a is immediately isomerized to the ortho isomer 14a. By using the milder acid, trifluoroacetic acid (CF₃CO₂H), the meta isomer 13a¹² and the ortho 14a were obtained in a ratio of 1:3. The former remained unchanged on treatment with CF₃CO₂H, whereas it was converted to the latter by CF₃SO₃H. Thus, with CF₃CO₂H catalyst, a 1,2-shift of the bridge in the cation intermediate derived from protonation of 2a first gave protonated 13a, which subsequently afforded 13a by deprotonation or protonated 14a by a further 1,2-shift.



It was reported that photolysis of 2a brought about valence isomerization to the Dewar isomer 4a leading to a photostationary state consisting of a 1:3 ratio of 2a and 4a.^{3b,13} More recently, the diester 2d was reported to isomerize to the Dewar isomer 4c, which on further irradiation gave a prismane derivative 15b.^{5c} Similarly, irradiation of the monoester 2b in hexane through a Pyrex filter with a high pressure mercury lamp initially gave rise to a photostationary state of 2b and its Dewar isomer 4b in a ratio of about 1:4. Prolonged irradiation

Table 3. Deformation angles (α and β) in small bridged [n]paracyclophanes 1b, 2c and e

Cyclophane	α (deg)	β (deg)	Reference
<u>15</u>	18.3, 15.2	5.7, 7.8	2b
<u>2c</u>	20.9, 20.1	19.2, 18.1	This work
2e	19.4, 19.5	21.2, 18.6	5d

gave the prismane isomer 15a which could not be isolated because it readily isomerized to the ortho isomer 14b during purification. The structure of 15a was elucidated on the basis of ¹H-NMR (δ 2.20 (d, J = 5 Hz, 1H), 2.47 (d, J = 5 Hz, 1H), 2.82 (s, 1H)) and offresonance decoupled ¹³C-NMR spectra (singlets at δ 60.4, 41.4, and 39.7; doublets at δ 47.0, 32.6, and 28.9). Irradiation of 2b in a quartz vessel followed by chromatographic purification gave only 14b in 47% isolated yield.



Next, in order to examine unusual reactivities associated with the non-planarity of the benzene ring of the [6]paracyclophane system, addition reactions of a dienophile, bromine, and oxygen to 2a were carried out. It has been well documented that strained cyclophanes undergo facile [4+2] cycloaddition with reactive dienophiles.^{1,2,e,f} The above behavior is thought to be due to the cyclohexatriene character of the deformed benzene. As might be expected, cycloaddition of 1,2,4triazoline-3,5-dione to [6]paracyclophane (2a) readily took place at room temperature to afford the [4+2]adduct 16 as the major product, isolated in 38% yield. The low isolated yield of 16 was due to cycloreversion to the starting material during chromatography and by contamination with the ketone 17 which has a meta bridge (16:17 = 5:2 by ¹H-NMR in the crude reaction product). The structures of 16 and 17 were elucidated on the basis of ¹H- and ¹³C-NMR spectra (Experimental). Since 16 is stable under the reaction conditions, it is deduced that 17 is not an oxidation product of 16. However, we have no explanation to offer for the formation of 17.



Tochtermann and co-workers have reported that addition of bromine to the diester 2d takes place to give a 1,4- and a 1,2-adduct in a ratio of 2:3-3:2.5e On the contrary, bromine addition to 2a (CCl₄, 0°) afforded only the 1,4-adduct 18, m.p. $32-35^{\circ}$ (dec.), almost quantitatively (by ¹H-NMR). The structure of 18 is evident from the ¹H- (four proton singlet at δ 6.99) and ¹³C-NMR (five signals at δ 131.8 (d), 62.4 (s), 45.4 (t), 25.5 (t), 22.7 (t)) spectra. However, 18 decomposed even in the solid state at room temperature giving off fumes of hydrogen bromide and the monobromides of metaand orthocyclophanes 13 and 14c (34% total yield; about 1:1 ratio) and the dibromides of 1-phenylhexane 19a and b (14% total yield; 2:1 ratio) (Scheme 5). The structures of these products were elucidated on the basis of ¹H-NMR spectra and were confirmed by reduction to the corresponding hydrocarbons 13a, 14a, and 1-phenylhexane and by carboxylation to the



corresponding esters 13b and 14b (Experimental). In contrast to the case of the diester 2d, no 1,2-adduct could be detected either during bromine addition to 2a or on standing the 1,4-adduct 18. In view of the acidcatalyzed isomerization of 2a (vide supra), the formation of 13c and 14c may be explained in terms of a 1,2-shift of the bridge in the cation intermediate derived by elimination of the bromide anion from 18. Though the mechanistic pathway leading to 19a and b is uncertain, it is interesting to note that it apparently involves cleavage between phenyl and benzyl carbons.

Finally, oxidation of 2a with *m*-chloroperbenzoic acid (mCPBA) was undertaken. Oxidation of 2a with 1 equiv of mCPBA at 0° immediately afforded the dienone dimer 20, m.p. 160-163°, in quantitative yield after chromatography. The structure of 20 was elucidated from the following spectroscopic properties : two kinds of carbonyl absorption, 1710 (cyclohexanone) and 1600 cm^{-1} (cyclohexenone) in the IR spectrum; three vinyl protons at δ 6.21 and 6.01 (AB, J = 13 Hz, 2H) and 5.52 (dd, J = 10, 2 Hz, 1H) in the ¹H-NMR spectrum; two carbonyl carbons at δ 212.0 (s) and 201.4 (s), four vinyl carbons at δ 152.3 (d), 148.2 (s), 130.5 (d), and 122.7 (d), five methine carbons at δ 61.5 (d), 52.2 (d), 50.6 (d), 49.8 (d), 43.7 (d), and one quaternary carbon at δ 46.7 (s) in the ¹³C-NMR spectrum. Moreover, the structure was confirmed by conversion of 20 to the symmetrical cage diketone 21, m.p. 183-186°, which showed twelve signals in the ¹³C-NMR spectrum, by irradiation in ethyl acetate through a uranium glass filter (92% yield).¹⁴ The formation of 20 is reasonably explained by [4+2] dimerization of a meta bridged dienone derived by epoxidation of 2a followed by rearrangement as shown in Scheme 6.15 Thus is has been demonstrated that 2a is highly reactive toward a dienophile, bromine, and a peracid, indicating clearly the cyclohexatriene character due to non-planarity of the benzene ring.



EXPERIMENTAL

[6.3.2]Propellenone (10). Enone 9 (21.6 g, 0.132 mol) was dissolved in 300 ml of 1,2-dichloroethylene (cis and trans mixture) and was irradiated in a Pyrex vessel with a high pressure mercury lamp under N₂ for 24 h. Evaporation of the excess olefin gave the crude cycloadducts (three isomers in 8:3:2 ratio) as a light brown oil; IR 1730, 750 cm⁻¹. The above adduct was dissolved in 500 ml of benzene and 100 ml of ethylene glycol and to this soln 5 ml of H₂SO₄ was slowly added. The mixture was heated at reflux for 7 days while water was removed with a Dean-Stark trap. Usual workup gave the crude ethylene acetal as a brown oil; IR 1150, 1090, 1040, 820, $790 \,\mathrm{cm}^{-1}$. To the acetal soln in 330 ml of ether cooled at -78° , 1400 ml of ammonia was distilled in. Na cut in small pieces (total 15 g) was added portionwise and the mixture was stirred for 1 h. Excess NH₂Cl was added and ammonia was allowed to evaporate. Extraction with ether gave the crude acetal of 10; IR 1150, 1030, 770 cm⁻¹. Deprotection was carried out in a two phase system consisting of 1000 ml of ether and 200 ml of 1.2 N HCl for 7 days. Workup followed by silica gel chromatography afforded 14.2 g (56% from 9) of 10: m.p. 69-70°; IR (K.Br) 3040, 1720, 770, 745, 730 cm⁻¹; MS m/e 190 (M⁺, 41), 91 (100); ¹H-NMR (CCl₄) δ0.7-2.3 (m, 15H), 2.6-3.1 (m, 1H), 5.95 (d, J = 2 Hz, 1H), 6.15 (d, J = 2 Hz, 1H). Semicarbazone, m.p. 207-208°. (Found : C, 67.78; H, 8.56; N, 16.92. Calc for C14H21ON3: C, 67.98; H, 8.56; N, 16.99%.)

Af ethyl [6 2 2] propellene or how plates (11X and 11N) Ring contraction of 10 was carried out as described previously' to give the esters 11X and 11N in 60% yield from 10 in a ratio of 2:1 which were separated by chromatography on silica gel. 11X: IR 3030, 1730, 1190, 1170, 790, 760, 745 cm⁻¹; MS m/e 220 (M⁺, 16), 95 (100), 91 (92); 'H-NMR (CCl₄) δ 1.2–2.1 (m, 14H), 2.86 (t, J = 8 Hz, 1H), 3.54 (s, 3H), 5.99 (d, J = 2 Hz, 1H), 6.23 (d, J = 2 Hz, 1H), (Found: C, 76.50; H, 9.35. Calc for C₁₄H₂₀O₂: C, 76.32; H, 9.15%) 11N: IR 3030, 1730, 1350, 1195, 1165, 765 cm⁻¹; MS m/e 220 (M⁺, 22), 105 (100), 91 (100); ¹H-NMR (CCl₄) δ 1.2–2.0 (m, 13H), 2.21 (dd, J = 7, 12 Hz, 1H), 2.69 (dd, J = 7, 8 Hz, 1H), 3.60 (s, 3H), 6.28 (br s, 2H). (Found: C, 76.41; H, 9.32. Calc for C₁₄H₂₀O₂: C, 76.32; H, 9.15%.)

[6.2.2] Propellenecarboxylic acids (7X and 7N). A mixture of 11.0 g(49.5 mmol) of 11X and 210 ml of 2% KOH aq was stirred at 60° for 2 days. Workup gave 10.2 g(100%) of 7X which was recrystallized from petroleum ether: m.p. 18°; IR 3500-2300, 1690, 1220, 920, 790, 760 cm⁻¹; MS m/e 206 (M⁺, 74), 105 (96), 91 (100); ¹H-NMR (CCl₄) δ 1.0-1.9 (m, 14H), 2.96 (t, J = 8 Hz, 1H), 6.10 (d, J = 2 Hz, 1H), 6.25 (d, J = 2 Hz, 1H), 11.86 (br s, 1H). (Found: C, 75.49; H, 8.69. Calc for C₁₃H₁₈O₂: C, 75.69; H, 8.80%.) In a similar manner, 7N was obtained from 11N quantitatively: m.p. 72-73°; IR (KBr) 3500-2300, 1690, 1230, 930, 760 cm⁻¹; MS m/e 206 (M⁺, 2), 105 (100), 91 (88); ¹H-NMR (CCl₄) δ 1.0-2.0 (m, 13H), 2.21 (dd, J = 6, 12 Hz, 1H), 2.75 (dd, J = 6, 8 Hz, 1H), 6.30 (2d, J = 2 Hz, 2H), 11.89 (br s, 1H). (Found: C, 75.40; H, 8.78. Calc for C₁₃H₁₈O₂: C, 75.69; H, 8.80%.)

Oxidative decarboxylation of TX and TN. To a soln of 1.03 g (4.85 mmol) of 7X, 192 mg (2.43 mmol) of pyridine, and 499 mg (2.5 mmol) of cupric acetate monohydrate in 50 ml of benzene heated at 80° was added 2.58 g (5.82 mmol) of lead tetraacetate portionwise. The mixture was heated for 1 h and then filtered. The filtrate was washed with 1 N HCl, water, and then dried. The solvent was evaporated and the residue chromatographed on silica gei to afford 230 mg (39% based on consumed 7X) of [6] paracyclophane (2a), 172 mg (21%) of acetate 8, and 280 mg of unreacted 7X. The structure of 1a was confirmed by comparison of ¹H-NMR and UV spectra with those reported.3" Similar oxidation of 7N gave 2a and 8 in 25 and 8% yields, respectively. 2a: ¹³C-NMR (CDCl₃) δ 143.3 (s), 131.8 (d), 36.5 (t), 36.0 (t), 26.8 (t). 8: IR 3020, 1725, 1240, 1020, 1010 cm⁻¹; MS m/e 220 (M⁺, ND), 107 (63), 104 (100); ¹H-NMR $(CDCl_3)\delta 0.7-2.5 (m, 15H, sat 1.97), 2.48 (dd, J = 6, 17 Hz, 1H),$ 2.87 (dt, J = 17, 2 Hz, 1H), 5.68 (dd, J = 2, 6 Hz, 1H), 5.98 (s, 1)2H); ¹³C-NMR (CDCl₃) δ 170.2 (s), 136.6 (s), 131.3 (d), 128.5

(d), 121.3(d), 85.3(s), 37.5(t), 36.1(t), 33.3(t), 29.4(t), 28.8(t), 27.4 (t), 26.7 (t), 22.5 (q). (Found: C, 76.47; H, 9.14. Calc for C₁₄H₂₀O₃: C, 76.32; H, 9.15%.) 9-Carbomethoxy[6.2.2]propelladiene (4b). To a soln of 16.0

9-Carbonethoxy[6.2.2]propelladiene (4b). To a soln of 16.0 mmol of LDA in 40 ml of THF cooled at -78° was added 2.90 g (13.2 mmol) of a mixture of 11X and 11N (2:1) in 13 ml of THF. After being stirred for 30 min, a mixture of diphenyl diselenide (4.99 g, 16.0 mmol) and 2.86 g (16.0 mmol) of HMPA in 13 ml of THF was added and the resulting soln was stirred at that temp for 1 h. Usual workup followed by chromatography on silica gel afforded 4.39 g (89%) of a major selenide and 264 mg (5%) of a minor one. Major (endo) selenide : IR 3020, 1720, 1580, 1265, 1245, 1120, 760, 740, 690 cm⁻¹; ¹H-NMR (CCI₄) δ 1.2-2.3 (m, 13H), 2.48 (d, J = 13 Hz, 1H), 3.46 (s, 3H), 6.05 (d, J = 2 Hz, 1H), 6.33 (d, J = 2 Hz, 1H), 7.1-7.6 (m, 5H). Minor (exo) selenide : IR 3020, 1720, 1580, 1240, 1190, 1125, 765, 735, 690 cm⁻¹; ¹H-NMR (CCI₄) δ 1.0-2.2 (m, 13H), 2.87 (d, J = 13 Hz, 1H), 3.49 (s, 3H), 6.35 (br s, 2H), 7.1-7.6 (m, 5H).

To a soln of 1.10 g (2.94 mmol) of the major scienide and 474 mg (6.0 mmol) of pyridine in 15 ml of CH₂Cl₂ was added 1.02 g (9 mmol) of 30% H₂O₂ and 1 ml of water. The mixture was stirred for 1.5 h and was worked up as usual. Flash chromatography gave 463 mg (72%) of 4b which gradually isomerized to 2b during purification. 4b: IR 3040, 1720, 1600, 1265, 1230, 780, 735 cm⁻¹; ¹H-NMR (CCl₄) δ 1.2–1.8 (m, 8H), 1.8–2.2 (m, 4H), 3.63 (s, 3H), 6.39 (d, J = 2 Hz, 1H), 6.58 (d, J = 2 Hz, 1H), 7.08 (s, 1H); ¹³C-NMR (CDCl₃) δ 163.4 (s), 155.7 (d), 147.3 (s), 145.3 (d), 144.1 (d), 64.0 (s), 62.4 (s), 51.7 (q), 26.6 (t), 26.5 (t), 26.2 (t), 25.5 (t), 25.3 (t), 25.1 (t); UV λ_{max} EtOH (log e) 245 nm (3.3).

8-Carbomethoxy[6]paracyclophane (2b). Isomerization of 4b was carried out by heating a soln of 4b in MeOH at 60° for 12 h to afford 2b quantitatively: IR 1720 (sh), 1710, 1580, 1545, 1260, 1190, 1070, 790, 685 cm⁻¹; MS m/e 218 (M⁺, 46), 162 (100), 159(86); ¹H-NMR (CDCl₃, 24°) δ - 0.6-0.2(m, 2H), 0.5-1.2 (m, 3H), 1.2-1.9 (m, 3H), 2.0-2.5 (m, 2H), 2.5-3.0 (m, 1H), 3.4-3.9 (m, 1H), 3.88 (s, 3H), 7.36 (AB, J = 8 Hz, 2H), 7.92 (s, 1H); ¹³C-NMR (CDCl₃, 60°) δ 167.0 (s), 147.2 (s), 143.3 (s), 134.4 (d), 134.3 (d), 133.7 (d), 131.9 (s), 51.7 (q), 36.9 (t), 36.2 (t), 35.7 (t), 35.5 (t), 26.7 (t, 2C); UV λ_{max} EtOH (log s) 329(3.1), 261 (3.7), 231 (4.3) nm. (Found: C, 76.80; H, 8.35. Calc for C₁₄H₁₈O₂: C, 77.03; H, 8.31%.)

The isomerization rate was determined by measuring the UV absorption at 330 nm in cyclohexane to give $k(40.0^\circ) = 2.50 \times 10^{-5}$, $k(50.0^\circ) = 8.67 \times 10^{-5}$, and $k(60.0^\circ) = 2.77 \times 10^{-4} \text{ s}^{-1}$.

8-Carboxy[6]paracyclophane (2c). A soln of 546 mg (2.50 mmol) of 2b and 1.40 g (25 mmol) of KOH in 20 ml of MeOH was refluxed for 20 h. Workup gave 442 mg (87%) of 2c which was recrystallized from petroleum ether. 2c: m.p. 123–125°; IR (KBr) 3500–2300, 1670, 1575, 1545, 1300, 1280, 1200, 945, 925, 790, 760, 735, 690 cm⁻¹; MS *m/e* 204 (M⁺, 17), 148 (100); ¹H-NMR (CDCl₃, 24°) δ – 0.6–0.3, (m, 2H), 0.4–1.3 (m, 3H), 1.3–1.9 (m, 3H), 1.9–2.6 (m, 2H), 2.6–3.1 (m, 1H), 3.4–4.2 (m, 1H), 7.35 (AB, J = 8 Hz, 2H), 8.00 (s, 1H), 10.97 (br s, 1H); ¹³C-NMR (CDCl₃, 60°) δ 173.1 (s), 148.6 (s), 143.5 (s), 133.1 (d), 134.9 (d), 134.5 (d), 130.5 (s), 37.1 (t), 36.1 (t), 35.9 (t), 35.4 (t), 26.9 (t, 2C); UV λ_{max} EtOH (log ϵ) 328 (3.1), 260 (3.7), 231 (4.3) nm. (Found: C, 76.18; H, 7.90. Calc for C₁₃H₁₆O₂: C, 76.44; H, 7.90%.)

Thermal isomerization of 2a. A soln of 2a in bexane was passed through a heated (400°) Pyrex column packed with Pyrex chips under N₂. Products were collected in a cold trap (-78°) and were analyzed by GLC. The major product 12^{10} (90% yield by GLC) was isolated by preparative GLC. 12: IR (CCl₄) 3020, 1650, 1110, 890, 860 cm⁻¹; MS m/e 160 (M⁺, 64), 116(82), 104 (100); ¹H-NMR (CCl₄) δ 1.2-1.8 (m, 10H), 4.69 (a, 2H), 5.80 (d, J = 10 Hz, 2H), 6.05 (d, J = 10 Hz, 2H).

Acid-catalyzed isomerization of 2a. To a soln of 12 mg of 2a in 1 ml of CHCl₃ was added one drop of CF₃SO₃H via a syringe. The mixture was stirred at room temp for 5 min and worked up to give 12 mg (100%) of the ortho isomer 14a. Similarly, reaction with CF₃CO₂H gave a mixture of 14a and the meta isomer 13a quantitatively in a ratio of 3:1. The latter was identified with an authentic sample prepared independently.11

Photochemical isomerization of 2b. A degassed soln of 2b in cyclohexane- d_{12} was irradiated with a high pressure mercury lamp in a Pyrex tube at room temp and the course of the isomerization was monitored by 1H-NMR spectra. After 7.5 h irradiation, it reached a photostationary state consisting of 2b and 4b in a ratio of 1:4. Similar irradiation of 4b for 2.5 h gave the same mixture. In both cases, new peaks due to prismane 15a appeared by prolonged irradiation. For example, irradiation of 2b in hexane for 96 h gave a mixture of 2b, 4b, and 15a in a ratio of 1:4:12 from which the spectral data of 15a was elucidated: ¹H-NMR (CCl₄) δ 0.6-2.0 (m, 12H), 2.20 (d, J = 5 Hz, 1H), 2.47 (d, J = 5 Hz, 1H), 2.82 (s, 1H), 3.54 (s, 3H); ¹³C-NMR (CDCl₃) & 172.8 (s), 60.4 (s), 51.3 (q), 47.0 (d), 41.4 (s), 39.7 (s), 32.6 (d), 28.9 (d), 27.5 (t), 26.9 (t), 25.5 (t), 25.3 (t, 2C), 23.3 (t). Attempts to isolate 15a by chromatography resulted in the formation of the ortho isomer 14b which was isolated in 47% yield by irradiation of 2b in a quartz vessel followed by silica gel chromatography: IR 1720, 1605, 1575, 1290, 1270, 1210, 1115, 1100, 770, 750 cm⁻¹; MS m/e 218 (M⁺, 100), 159 (49); ¹H-NMR (CCl₄) δ 1.1–1.5 (m, 4H), 1.5–1.9 (m, 4H), 2.76, 2.78 (2t, 4H), 3.81 (s, 3H), 7.10 (d, J = 8 Hz, 1H), 7.7-7.8 (m, 2H).(Found : C, 76.92; H, 8.43. Calc for C₁₄H₁₈O₂: C, 77.03; H, 8.31%.)

[4+2] Cycloaddition of 2a with N-phenyl-1,2,4-triazoline-3,5-dione. A soln of 184 mg (1.15 mmol) of 2m and 241 mg (1.38 mmol) of the triazolinedione in 5 ml of CHCl₃ was allowed to stand at room temp for 24 h. The solvent was evaporated and the residue chromatographed on silica gel to yield 146 mg (38%) of 16 and 72 mg (18%) of 17 which were recrystallized from ether-CH₂Cl₂ (9:1). 16: m.p. 176-179° (dec.); IR (KBr) 1760, 1700, 1495, 1380, 760 cm⁻¹; MS *m/e* 335 (M⁺, 22), 104 (100); ¹H-NMR (CDCl₃) δ 0.2-0.6 (m, 2H), 0.9-1.3 (m, 2H), 1.6–2.2 (m, 6H), 2.3–2.6 (m, 2H), 5.17 (dd, J = 1, 7 Hz, 2H), 6.33 (d, J = 7 Hz, 2H), 7.4–7.6 (m, 5H); 13 C-NMR (CDCl₃) & 157.0 (s), 154.9 (s, 2C), 131.7 (s), 129.0 (d, 2C), 128.2 (d), 125.5 (d, 2C), 123.9 (d, 2C), 58.7 (d, 2C), 35.7 (t, 2C), 29.4 (t, 2C), 26.4 (t, 2C). (Found : C, 71.53; H, 6.53; N, 12.47. Calc for C₂₀H₂₁O₂N₃: C, 71.63; H, 6.31; N, 12.53%.) 17: m.p. 189-192°; IR 1770, 1740, 1710, 1490, 1405, 1240, 1135, 770 cm⁻¹; MSm/e 351 (M⁺ , 100), 94(31); ¹H-NMR (CDCl₃) δ 1.0–2.6 (m, 12H), 2.78 (dt, J = 2, 6 Hz, 1H), 5.05(d, J = 7 Hz, 1H), 5.24(t, J = 2 Hz, 1H), 6.09 (br d, J = 7 Hz, 1H), 7.40 (br s, 5H); 13 C-NMR (CDCl₃) δ 199.4 (s), 156.1 (s), 151.7 (s), 131.3 (s), 124.3 (d, 2C), 128.6 (d), 125.4 (d, 2C), 118.2 (d), 62.7 (d), 59.7 (d), 46.6 (d), 34.1 (t), 28.1 (t), 26.9 (t), 25.3 (t), 24.2(t), 19.0(t). (Found : C, 68.24; H, 5.94; N, 11.88. Calc for $C_{20}H_{21}O_3N_3$: C, 68.36; H, 6.02; N, 11.96%)

Addition of bromine to 2a. To a soln of 320 mg (2.0 mmol) of 2a in 5 ml of CCl₄ cooled at 0° was added 1 equiv of Br₂ in the same solvent (1 ml). The color of Br₂ immediately disappeared. ¹H-NMR analysis of this soln indicated quantitative formation of the 1,4-adduct 18. After 1 min, the soln was washed with NaHSO₃ aq and water. The solvent was dried and evaporated and the residue recrystallized from petroleum ether-ether (10:1) to give a total of 311 mg (49%) of 18 as a white solid. On standing solid 18 at room temp, it decomposed with fuming of HBr. 18: m.p. 32-35° (dec.); IR (KBr) 940, 880, 800 cm⁻¹, ¹H-NMR (CCl.) δ 1.3-1.6 (m, 8H), 2.2-2.4 (m, 4H), 6.99 (s, 4H); ¹³C-NMR (CDCl₃, -12°) δ 131.8 (d), 62.1 (s), 45.4 (t), 25.5 (t), 22.7 (t).

A soln of 18 (306 mg, 0.96 mmol) in CHCl₃ was left at room temp under N₂ for 16 h. The soln was washed with NaHCO₃ aq and water. After being dried, the solvent was evaporated and the residue chromatographed on silica gel to afford 77 mg (34%) of a mixture of 13c and 14c (1:1) and 43 mg (14%) of dibromo-1-phenylhexanes 19a and b (2:1). Since 13c and 14c could not be separated, they were analyzed as a mixture and were confirmed by conversion into 13a and 14a or 13b and 14b. 13c and 14e: IR 1590, 1030, 800 cm⁻¹; MS *m/e* 240, 238 (M⁺), 159 (100); ¹H-NMR (CCl₄) δ 0.2–0.6 (m), 1.0–2.2 (m), 2.3–3.0 (m), 6.63 (dd, J = 1, 7 Hz), 6.8–7.3 (m). (Found: C, 60.03; H, 6.31. Calc for C₁₂H₁₉Br: C, 60.27; H, 6.32%). Lithiation of the mixture (54 mg, 0.23 mmol) with n-butyl lithium in hexane at reflux for 1.5 h followed by quenching by water gave 36 mg

(100%) of 13a and 14a in a ratio of 1:1. When the lithio derivatives derived from 274 mg (1.15 mmol) of the mixture were carboxylated by standing under an atmosphere of carbon dioxide for 18 h, 22 mg (9%) of esters 13b and 14b (7:1) were obtained after treatment with diazomethane. 13b: IR 1725, 1615, 1270, 1130, 1090 cm⁻¹; MS m/e 218 (M⁺, 34), 159 (100); ¹H-NMR (CCl₄) δ -0.1-2.2 (m, 8H), 2.4-3.0 (m, 4H), 3.81 (s, 3H), 6.78 (dd, J = 1, 8 Hz, 1H), 7.23 (d, J = 1 Hz, 1H), 7.72 (d, J = 8 Hz, 1 H). (Found : C, 76.67; H, 8.62. Calc for $C_{14}H_{18}O_2$: C, 77.03; H, 8.31%.) Dibromides 19a and b were separated by careful chromatography. 19a: IR 1070, 1010, 825, 795 cm⁻¹ MS m/e 322, 320 (30), 318 (M⁺), 171, 169 (100); ¹H-NMR $(CCl_4)\delta 1.1-2.0 (m, 8H), 2.54 (t, J = 7 Hz, 2H), 3.32 (t, J = 6 Hz, 2H)$ 2H), 6.96(d, J = 8 Hz, 2H), 7.32(d, J = 8 Hz, 2H). 19b : IR 1070, 1010, 795 cm⁻¹; MS m/e 322, 320 (25), 318 (M⁺), 171, 169 (100); ¹H-NMR (CCl₄) δ 1.2–2.0 (m, 9H, d at 1.64, J = 8 Hz), 2.4-2.8 (m, 2H), 4.04 (dq, J = 6, 8 Hz, 1H), 6.98 (d, J = 8 Hz, 2H), 7.33 (d, J = 8 Hz, 2H). A soln of 46 mg (0.14 mmol) of 19a and 104 mg (0.36 mmol) of tributyltin hydride in 5 ml of THF was irradiated with a low pressure mercury lamp in a quartz tube for 3 h. The solvent was evaporated and the residue chromatographed to give 16 mg (71%) of 1-phenylhexane. Similar reduction of 37 mg(0.12 mmol) of 19b gave 16 mg(85%) of 1-phenylhexane.

Peracid oxidation of 2a. To a mixture of 80 mg (0.50 mmol) of 2a and 355 mg (2.5 mmol) of sodium hydrogenphosphate in 3 ml of CH₂Cl₂ cooled at 0° was added 135 mg (0.55 mmol) of mCPBA (70%) portionwise and the mixture was stirred for 30 min. Usual workup followed by flash chromatography afforded 89 mg (100%) of 20 which was recrystallized from ether: m.p. 160–163°; IR (KBr) 1710, 1660, 1140, 860 cm⁻¹; MS m/e 352(M⁺, 2), 176(100); ¹H-NMR (CDCl₃) δ 1.0–2.4(m, 26H), 2.62 (br s, 1H), 2.79 (d, J = 7 Hz, 2H); ¹³C-NMR (CDCl₃) δ 212.0(s), 201.4(s), 152.3(d), 148.2(s), 130.5(d), 122.7(d), 61.5(d), 52.2(d), 50.6(d), 49.8(d), 46.7(s), 43.7(t), 31.7(t), 30.0(t), 28.1(t), 28.0(t), 26.5(t), 25.7(t), 23.8(t), 23.6(t), 22.4(t), 19.5(t). (Found: C, 81.62; H, 9.17. Calc for C₂₄H₃₂O₂: C, 81.77; H, 9.15%.)

A soln of 60 mg (0.085 mmol) of 20 in 15 ml of EtOAc was irradiated through a uranium glass filter for 15 min. Evaporation of the solvent followed by flash chromatography gave 55 mg (92%) of 21 which was recrystallized from ether: m.p. $183-186^{\circ}$; IR (KBr) 1700, 1200, 800 cm⁻¹; MS m/e 352 (M⁺, 2), 176(100); ¹H-NMR (CDCl₃) δ 1.0–3.0(m); ¹³C-NMR (CDCl₃) δ 214.5 (s), 57.4 (d), 54.1 (d), 46.3 (s), 43.0 (d), 38.7 (d), 38.5 (t), 29.5 (t), 29.2 (t), 28.6 (t), 27.4 (t), 23.5 (t). (Found: C, 81.62; H, 9.17. Calc for C₂₄H₃₂O₂: C, 81.77; H, 9.15%.)

81.62; H, 9.17. Calc for $C_{24}H_{32}O_2$: C, 81.77; H, 9.15%) X-Ray structure analysis of 2c (crystal data). 8-Carboxy[6]paracyclophane, $C_{13}H_{16}O_2$, F.W. = 204.3, tetragonal, P_{4_2}/n , at -150°, a = 16.480(3), c = 7.940(1) Å, U = 2156.4 Å³, Z = 8, $D_c = 1.258$ g cm⁻³.

X-Ray diffraction data were collected on a Rigaku fourcircle diffractometer using graphite-monochromatized MoKa radiation from a rotating anode X-ray generator (40 kV, 200 mA). During the experiment the temp of the crystal was kept constant at -150° by Rigaku low temp equipment using the liquid N₂ gas-flow method. Integrated intensities were measured by the θ -2 θ scan technique at a 2 θ scan rate of 8° min⁻¹ and a scan width of $\Delta 2\theta = (2.0+0.30 \tan \theta)^{\circ}$. The background intensities were measured for 5 s at both ends of a scan. Three standard reflections were measured after every 63 reflections in order to monitor the radiation damage and the change of the crystal orientations. No significant intensity decay of the standard reflections was observed. A total of 4754 reflections were collected up to 70° in 2 θ , among which 2492 were above background $[|F_0| \ge 3\sigma(F_0)]$.

The starting molecular model for the refinement was taken from the structure at room temp^{4*} and was refined by the fullmatrix least-squares procedure (X-RAY SYSTEM). The difference Fourier maps calculated after the anisotropic refinement for non-H atoms revealed four extra peaks suggesting the disordered structure of the bridging methylene carbons (C(2)—C(5)). The occupancy factors for major and minor components of the disordered methylene carbons were estimated from the electron density peaks as 0.7 and 0.3, respectively, and were fixed in successive refinements with anisotropic temp factors. The H atoms attached to the benzene ring were located and refined with isotropic temp factors, but those of the methylene carbons were impossible to locate. The weighting function was $w = [\sigma^2(F_0) + 0.005(F_0)^2]^{-1}$. The final R index was 0.114 for significant reflections. All the calculations were carried out on an ACOS 850 computer at the Crystallographic Research Center, Institute for Protein Research, Osaka University.[†]

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† The atomic coordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Center, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, U.K. Any request should be accompanied by the full literature citation for this communication.

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