The Cycloaddition of Dispiro[2.2.2.2]deca-4,9-diene with the Styrene Derivatives. The Syntheses and Spectral Properties of the [4.2]Paracyclophane Derivatives

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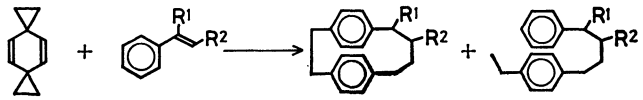
The thermal cycloaddition of dispiro[2.2.2.2]deca-4,9-diene **1** with the styrene derivatives has afforded [4.2]paracyclophane derivatives, **3**. A reaction mechanism by way of the biradical intermediates, involving the initial homolytic cleavage of the cyclopropane ring in **1** followed by the addition to the styrene molecule, is proposed. In the reaction of **1** with styrene, and methyl α-phenylacrylate, the yields of **3** were improved with the dilution of the reactants, while in the reaction with *trans*-stilbene, no appreciable dependence on the reactant concentration was observed. The mass spectra of the substituted [4.2]paracyclophanes show a predominant fragmentation to the substituted *p*-xylene-α,α′-diyl (or elements thereof) ion radical. [4.2]Paracyclophane exhibited a temperature-dependent NMR spectrum which could be ascribed to the rapid equilibration between two structurally equivalent conformers. Bulky substituents on C-1 and C-2 shifted the equilibrium to one side.

We have previously reported the thermal cycloaddition of dispiro[2.2.2.2]deca-4,9-diene **1**[1] with 1,3-butadiene derivatives, which afforded [8]paracycloph-4-enes by way of the biradical intermediate formed through the homolytic cleavage of the cyclopropane ring in **1**.[2] In the course of our continuing study of the cycloaddition reaction of **1**, we found that the thermal cycloaddition of the styrene derivatives, **2**, to **1** gave [4.2]paracyclophanes, **3**, in fair to good yields.[3] Although the chemistry of cyclophanes is currently a subject of considerable interest,[4] relatively few preparation methods of [4.2]-paracyclophanes are known.[5] The present reaction is experimentally simple and provides a convenient route to [4.2]paracyclophanes functionalized at C-1 and C-2. In this report we will describe the preparation and the spectral properties of [4.2]paracyclophane derivatives and will discuss the probable mechanism of this novel cycloaddition reaction.

Results and Discussion

Reaction of Dispiro[2.2.2.2]deca-4,9-diene 1 with the Styrene Derivatives, 2. A solution of **1** (0.16 M) and 1,1-diphenylethylene **2g** (0.37 M) in *t*-butyl alcohol was heated at 150—155 °C for 12 h under argon in a sealed glass ampoule. The subsequent separation of the reaction product by column and preparative gas chromatographies afforded 1-phenyl[4.2]paracyclophane **3g** as colorless crystals in a 67% yield. Analogously, the reaction of **1** with some related styrene derivatives, **2a**—**2f**, gave **3a**—**3f** respectively. The results are summarized in Table 1. Proof of the structures of those products was provided by the elemental analysis and their spectral properties. In the NMR spectra, the signals of the aromatic ring protons appeared at an unusually high field, δ 6.2—6.6, reflecting the shielding effect by the facing aromatic ring,[5b] and in the UV spectra, a bathochromic shift of λ_{max} to 282—283 nm and the disappearance of the fine structure were noted.[5a] The mass spectra of **3** showed prominent peaks which could be explained in terms of the predominant fragmentation to the *p*-xylene-α,α′-diyl (or methylenetropylium) ion radicals. These characteristics clearly show



1 2 3 4

a, $R^1=R^2=H$; b, $R^1=CH_3, R^2=H$; c, $R^1=OSi(CH_3)_3, R^2=H$
d, $R^1=H, R^2=CO_2CH_3$; e, $R^1=CO_2CH_3, R^2=H$
f, $R^1=H, R^2=C_6H_5$; g, $R^1=C_6H_5, R^2=H$; h, $R^1=OH, R^2=H$

TABLE 1. PRODUCTS FROM THE REACTION OF DISPIRO[2.2.2.2]DECA-4,9-DIENE **1** WITH **2** STYRENES[a]

	Styrene		Reactant concentrations		Products (% Yield)[b]		
	R^1	R^2	**1** (mol/l)	**2** (mol/l)	**3**	**4**	Others[c]
a	H	H	0.010	0.038	7.6	0.7	**5**, 3.4
b	CH_3	H	0.05	0.15	46	5.7	
c[d]	$OSi(CH_3)_3$	H	0.10	0.22	4.4		**6**, 7.2
d	H	$COOCH_3$	0.08	0.20	28		
e	$COOCH_3$	H	0.017	0.033	78[e]		
f	H	C_6H_5	0.16	0.40	34[e]	7.0[e]	
g	C_6H_5	H	0.16	0.37	67		

a) The reactions were carried out in *t*-butyl alcohol unless otherwise noted. b) The yields are from the weight of the isolated product unless otherwise noted. c) Besides the characterized products, the formation of a few unidentified minor products was invariably observed. The major part of the residue, however, was an intractable, tarry material. d) Reaction in hexane. e) The yields were determined by GLC.

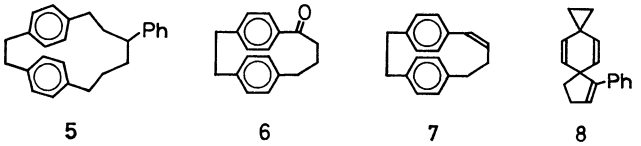
TABLE 2. MELTING POINTS AND SPECTRAL PROPERTIES OF [4.2]PARACYCLOPHANES

Compd	Mp (°C)	UV Spectrum[a] λ_{max} in nm($\varepsilon \times 10^{-2}$)	Mass spectrum[b] *m/e* (Relative intensity)
3a	71.0—72.0[c]	271(4.7), 283(2.7)	236(M^+, 35), 208(18), 145(16), 132(10), 131(20), 130(23), 129(13), 117(32), 116(33), 115(19), 105(18), 104(100), 103(13), 91(21), 78(19), 77(13),
3b	58.1—58.8	271(3.0), 283(1.9)	251(13), 250(M^+, 53), 145(22), 133(51), 132(27), 131(21), 119(14), 118(100), 117(66), 115(11), 105(27), 104(19), 91(17)
3c	82.0—82.8		325(24), 324(M^+, 59), 297(15), 296(49), 252(10), 193(23), 192(100), 178(50), 147(30), 117(13), 73(27)
3d	85.2—86.9	271(4.5), 283(3.1)	294(M^+, 40), 208(29), 189(25), 131(11), 130(11), 129(19), 119(12), 118(9), 117(42), 115(11), 105(30), 104(100), 91(16), 71(10)
3e	70.6—71.7	251(3.9), 271(3.9) 282(sh, 2.7) 292(sh, 0.8)	295(16), 294($M,^+$ 66), 235(21), 189(18), 175(10), 163(28), 162(16), 143(17), 132(14), 131(51), 129(18), 120(10), 119(100), 118(12), 117(40), 115(20), 105(30), 104(82), 103(12), 91(29), 77(12)
3f	148.0—148.5	255(4.0), 262(5.8), 265(6.1), 268(6.8), 283(3.1)	312(M^+, 16), 208(16), 207(22), 118(10), 117(12), 105(15), 104(100), 103(13), 77(15)
3g	70.8—71.8	254(5.3), 263(6.6), 270(7.0), 283(3.6)	313(10), 312(M^+, 30), 194(13), 181(18), 180(100), 179(16), 178(16), 167(19), 165(30), 145(13), 131(11), 117(10),115(13), 104(12), 91(13)
3h	116.3—116.8	271(3.6), 283(2.3)	252(M^+, 3.4), 234(32), 143(17), 131(11), 130(100), 129(58), 128(18), 118(30), 117(10), 115(40)
6	107.3—108.0	250(57)[d]	251(22), 250(M^+, 93), 133(72), 118(32), 117(100), 80(11)
7	102.6—103.0[e]	227(105), 268(53)	234(M^+, 34), 143(16), 131(11), 130(100), 129(55), 128(18), 118(30), 115(45)

a) The spectra were taken in hexane unless otherwise noted. The shoulder was denoted as sh.
b) The ions of each spectrum were normalized to the spectrum's most intense ion set equal to 100. The spectra were taken at an ionizing voltage of 80 eV. c) Reported to be 74.4—75.0°C.[5b] d) The spectrum was taken in 95% ethanol. e) Reported to be 100—101°C.[5d]

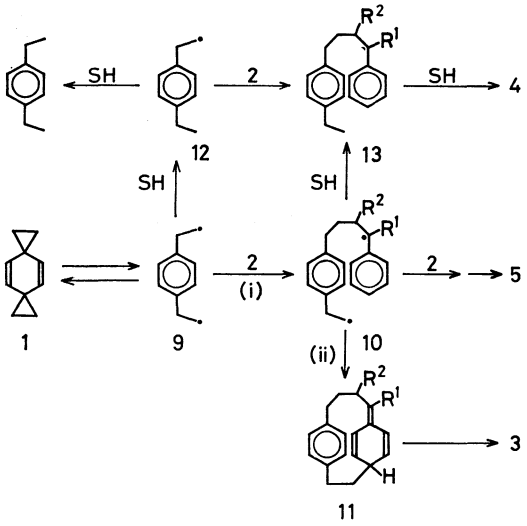
that the products, **3**, have a paracyclophane structure. The spectra and melting point of **3a** also agreed very well with those previously reported.[5a,b]

In the reaction of **1** with **2a**, besides the 1:1 cycloadduct, **3a**, an open-chain addition product, **4a** (0.7%), and a 1:2 cycloadduct, **5** (3.4%), were isolated from the reaction mixture. Open-chain adducts were also produced in the reactions of **2b** and **2f**. The reaction with **2c** proceeded rather anomalously and afforded [4.2]paracyclophan-1-one **6** as the most abundant product, together with **3c**. The alcohol obtained by the $NaBH_4$ reduction of **6** was identical in all respects with the hydrolysis product of **3c**. The application of the present reaction to the acetylenic compound was also examined. The reaction of **1** (0.20 M) with ethynylbenzene (0.40 M) in *t*-butyl alcohol at 160 °C, however, gave [4.2]paracycloph-1-ene, **7**, in only a low yield (2.3%) and was accompanied by the formation of a dispiro[2.2.4.2]dodecane derivative, **8** (13%).



5 6 7 8

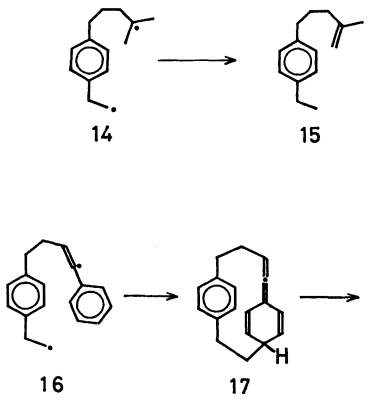
Mechanism. The present reaction may be explained by the pathway outlined in Scheme 1. We have previously demonstrated that the cyclopropane ring in **1** cleaves homolytically at an appreciable rate above 150 °C.[1,6] The biradical, **9**, thus generated reversibly from **1** adds to **2** to give **10**. The intramolecular coupling of the biradical, **10**, at the *p*-position of the benzylic radical moiety leads to the formation of **11** which subsequently rearranges to **3** under the present reaction conditions. Hydrogen abstraction by **9** and/or **10** would result in the formation of *p*-diethylbenzene and the open-chain adduct **4**. The addition of **10a** to another molecule of



Scheme 1.

2a, followed by the ring closure, afforded **5**. The isomerization of 1-methylene-2,5-cyclohexadiene to toluene, which corresponds to the rearrangement of **11** to **3**, has been known to take place at the boiling point of diethyl ether.[7] Interestingly, the reaction of **1** with **2b** did not afford the intramolecular (formally at least) disproportionation product of the biradical intermediate, **10b**, in a detectable yield (<0.5%); this is in contrast to the reaction with isobutene, which gave **15** as the major product, probably *via* **14**.[8] These results imply that the cyclization of **10** at the *p*-position of the benzylic radical moiety is not hampered in the presence of such a potential hydrogen donor in the molecule.

The reaction of **1** with ethynylbenzene resulted in the formation of the dispiro compound, **8**, and the yield of the cyclophane, **7**, was low. In the reaction of **1** with **2**, no adducts with the dispiro[2.2.4.2]dodecane structure were isolated. The different behavior of the biradical, **16**, from that of **10** may be accounted for by the higher structural barrier imposed on the approach of the reaction sites in **16** to give **17** than in **10** to give **11** and/or a higher strain in the cyclized intermediate **17** than in **11**.



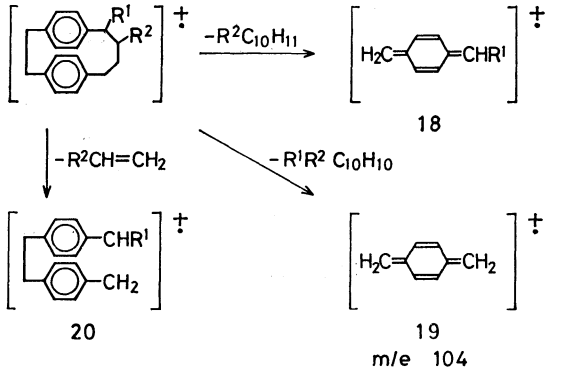
In the reaction of **1** with dimethyl *trans,trans*-2,4-hexadienoate, CIDNP has been observed in the cycloaddition product.[2b] Therefore, one may expect CIDNP in the reaction of **1** with **2** as well. The NMR spectrum recorded during the reaction of **1** and **2g** in biphenyl at 190 °C indeed showed CIDNP, and the characteristic signal of the aromatic protons in **3g**, shifted up-field, appeared as a weak emission substantiating the radical pathway of the reaction. The attempts to detect a signal which could be ascribed to the probable intermediate **11g** have, however, been fruitless thus far.

The addition of the biradical intermediate **9** to **2** is in competition with side reactions including the hydrogen abstraction to **12**, and, to give **3**, the resulting biradical **10** must collapse before side reactions including the addition to another molecule of **2** can take place. Therefore, the concentration of **2** should exert opposite effects on the yield of **3** at Steps (i) and (ii). with a few of the styrene derivatives, the effect of dilution on the yield of **3** was examined. In the reaction of **1** with **2e**, the yield of **3e** increased with the dilution of the reactants, and a similar trend was noted with **2a**. In the reaction with **2f**, however, no clear relationship between the yield of **3f** and the reactant concentration was observed. Since **2e** has a high reactivity toward the alkyl radical,[9] and since the addition of **9** would proceed efficiently even in a dilute solution, the dilution of the reactants might act favorably for the intramolecular cyclization of **10e**. In the case of **2f**, which has a relatively low reactivity, the opposite effects of the olefin concentration at Steps (i) and (ii) might balance. The reaction with **2a**, which very rapidly polymerizes, resulted in a low yield of **3a** probably because the addition of **10a** to another molecule of **2a** rather than the collapse to **11a** might predominate even in a dilute solution.

Although the reaction could be carried out in other solvents, such as benzene and hexane, *t*-butyl alcohol was used simply because of its low reactivity toward hydrogen abstraction. In benzene, the addition of **9** took place and 1-phenyl-2-*p*-tolylethane was formed, though in a small amount.

Mass Spectra of Substituted [4.2]Paracyclophanes. The mass spectra of [4.2]paracyclophane and its derivatives showed a fair generality in the fragmentation pattern and are in good accord with the assigned structures. In the spectrum of **3a**, the most intense peak occurred at *m/e* 104; its origin could be reasonably formulated by the cleavage at the benzylic positions to the *p*-xylene-α,α′-diyl (or methylenetropylium) ion radical, **19**.[10] The above fragmentation appeared common to the [4.2]paracyclophane derivatives. Thus, in the spectra of **3d** and **3f**, the most intense peak occurred at the same *m/e*, and, in those of 1-substituted derivatives, **3b**, **3c**, and **3g**, the fragment corresponding to the substituted *p*-xylene-α,α′-diyl[10] appeared as the base peak. In that of **3e**, the *p*-xylene-α,α′-diyl fragment ion peak was not the most intense, but it was still prominent. The appearance of the most intense peak at *m/e* 130 in the spectrum of **7**, which might be ascribed to **21**,[10] was also in line with the above fragmentation pattern.[11] The spectrum of **6** was distinct from the others and showed two dominant peaks, at *m/e* 117 (base peak) and 133, which could be explained by the cleavage at the ethano-bridge, followed by the McLafferty rearrangement.[12] Besides the above fragments characteristic peaks, though not intense, were observed at *m/e* corresponding to **20**[10] which demonstrated unambiguously the position of the substituent.

10)



Thus, the mass spectrum provides a convenient tool for the structural analysis of [4.2]paracyclophane derivatives.

Temperature Dependence of NMR Spectrum and Conformation of 3. An examination of the NMR spectra of **3** provided information regarding the conformation. The parent [4.2]paracyclophane **3a** shows four peaks in the NMR spectrum at room temperature: two singlets at δ 6.45 (8H, aromatic protons) and 2.96 (4H, H-5, and H-6), and two relatively narrow multiplets at δ 2.22 (4H, H-1, and H-4) and 1.40 (4H, H-2, and H-3). Upon cooling, all the signals broadened from about −40 °C and resharpened again by −110 °C, accompanying the splitting of those signals into two sets of signals equal in intensity: the singlet at δ 6.45 into an AB quartet (J=8 Hz) centered at δ 6.55 and a singlet at δ 6.22, the singlet at δ 2.96 into an AA'BB' multiplet, the multiplet at δ 2.22 into a doublet of doublets (J=4 and 12 Hz) centered at δ 2.54 and a triplet (J=13 Hz) at δ 1.82, and the multiplet at δ 1.40 into two complex multiplets centered at δ 1.89 and 0.67. These observations may be explained in terms of the equilibration between two equally numerous conformers, **25a** and **26a**. A similar conformational equilibration has been invoked by Cram *et al.* to explain the temperature-dependent NMR spectrum of *cis*-2,3-diacetoxy[4.2]paracyclophane.[13] The signals observed at low temperatures can reasonably be assigned as is shown in Fig. 2, which indicates the shielding of Ha and Hd by 0.8 and 0.9 ppm respectively and the deshielding of Hc by 0.3 ppm, while there is no apparent shift of Hb compared with the corresponding protons in propylbenzene. An examination of the molecular models supports the above explanation and also reveals that R^1 in the **25** conformer is less sterically hindered than in **26** and that for R^2 the situation is the same.[14] The NMR spectrum of the 1-methyl derivative, **3b**, exhibited a similar temperature dependence and the characteristic doublet signal of the methyl protons split into two sets of doublets, 3: 1 in intensity, at δ 1.20 and 1.03 upon cooling; these sets of doublets might be ascribed to the conformers, **25b** and **26b**, respectively. More bulky substituents on C-1 and C-2 would displace the equilibrium to one side, and the chemical shifts of protons in the NMR spectra of **3d**—**g** can be explained reasonably on the basis of the **25d**—**g** conformers respectively. The coupling constants in **3d** and **3g** which have been determined thus far are also consistent with the above conformations.

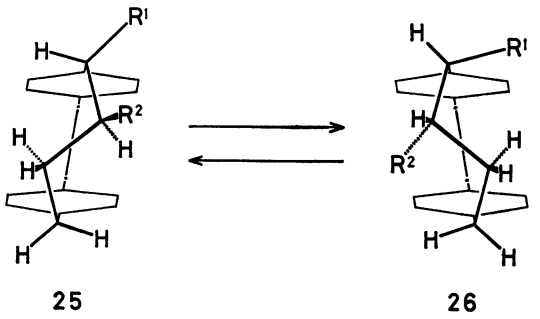


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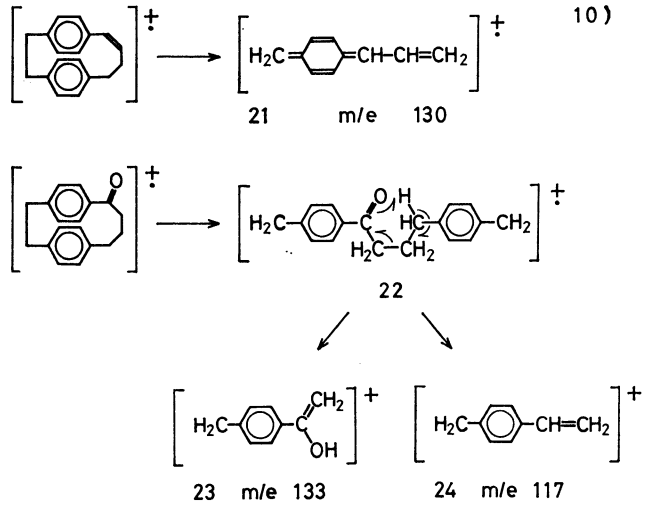
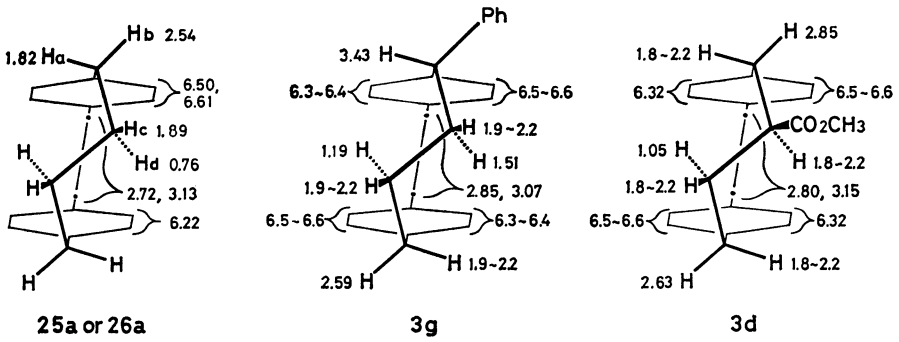
Fig. 1. Conformational equilibration in [4.2]paracyclophane derivatives.



Experimental

General. Melting points are corrected. NMR spectra were obtained with JEOL PS-100 and Hitachi R-24 spectrometers at 100 and 60 MHz respectively; chemical shifts are given in ppm from $Si(CH_3)_4$. IR spectra were taken on a Hitachi Model 215 grating spectrometer and are given in cm^{-1}. Mass spectra were recorded on a Hitachi Model RMU-6E spectrometer at an ionizing voltage of 80 eV; ions of each spectrum were normalized to the spectrum's most intense ion set equal to 100. UV spectra were taken on a



25a or 26a 3g 3d

Fig. 2. Chemical shifts in [4.2]paracyclophane derivatives. Chemical shifts in **25a** were obtained from the spectrum taken at *ca.* −115°C in CS_2 and those in **3d** and **3g** were obtained from the spectra at 23°C in CCl_4.

Cary Model 17 spectrophotometer and are given in nm. GLC work was done on a Hitachi Type 063 gas chromatograph with a thermal conductivity detector, using helium as a carrier gas. The following glass columns were used: A, 3% Apiezon Grease L on Celite 545, 3 mm×70 cm; B, 15% Apiezon Grease L on Celite 545, 3 mm×1 m; C, 20% Apiezon Grease L on Celite 545, 3 mm×1 m; D, 20% PEG phthalate on Celite 545, 4 mm×2 m; E, 20% Silicon DC-550 on Celite 545, 4 mm×1.5 m. Yields were calculated on the basis of **1** used in the reaction.

Materials. The preparation of dispiro[2.2.2.2]deca-4,9-diene **1** was carried out as has been described previously.[1] Styrene, α-methylstyrene, 1,1-diphenylethylene, and methyl cinnamate were obtained from commercial sources and were purified by fractional distillations. α-Trimethylsiloxystyrene was prepared by the method of House *et al.*[15] Methyl α-phenylacrylate was prepared following the procedure of Saquet and Thuillier.[16] *trans*-Stibene was obtained by the $NaBH_4$ reduction of desyl chloride.[17] Ethynylbenzene was prepared through the bromination and dehydrobromination of styrene.[18] *t*-Butyl alcohol was purified by fractional distillation from sodium.

*Reaction of **1** with Styrene **2a**.* A solution of 108 mg of **1** (0.82 mmol) and 345 μl of **2a** (3.0 mmol) in 80 ml of *t*-butyl alcohol was distributed among glass ampoules, bubbled with argon for 10 min, and heated at 160 °C for 10.5 h under argon (50 atm) in an autoclave. After the reaction, only a trace amount of **1** and *ca.* one fifth of the starting **2a** remained. The solvent was then removed and the residue was chromatographed on silica gel. Elution with a petroleum ether–benzene 5: 1 mixture produced an oil which was shown by GLC analysis to consist of one major and three minor components. Separation by preparative GLC (column C, 210 °C) geve 14.7 mg of [4.2]paracyclophane **3a** (7.6%) which when recrystallized from methanol had a mp of 71.0—72.0 °C (lit, 74.4—75.0 °C),[5b] 1.4 mg of **4a** (0.7%) and 3.3 mg of a mixture of two uncharacterized products. Elution with a petroleum ether–benzene 1: 1 mixture and separation by preparative GLC (column A, 210—230 °C) yielded three products in comparable amounts: 8.6, 9.4, and 4.1 mg . The second component was cheracterized as 3-phenyl[6.2]paracyclophane **5** (3.4%) on the basis of its physical properties. Further elutions with benzene and benzene–methanol produced only a polymeric, intractable material. **3a**, NMR (CS_2, 100 MHz): 1.40 (m, 4H), 2.22 (m, 4H), 2.96 (s, 4H), 6.45 (s, 8H). **4a**, NMR (CCl_4, 60 MHz): 1.17 (t, J=7.5 Hz, 3H), 1.4—1.7 (complex m, 4H), 2.2—2.7 (complex m, 8H), 6.90 (s, 4H), 7.02 (br s, 5H); mass: *m/e* 238 (M^+, 34), 131 (32), 120 (17), 119 (100), 117 (19), 115 (12), 105 (21), 104 (21), 92 (12), 91 (84), 78 (13), 77 (16), 65 (16), 41 (17). **5**,[19] NMR (CCl_4, 100 MHz): 0.9—2.6 (complex m, 11H), 3.00 (s, 4H), 6.2—6.7 (m, 8H), 6.9—7.3 (m, 5H); UV (hexane): λ_{max} (ε), 268 (1160), 282 (sh, 400); mass: *m/e* 341 (31), 340 (M^+, 100), 235 (15), 208 (30), 207 (99), 149 (15), 145 (10), 131 (45), 129 (13), 128 (11), 118 (16), 117 (85), 116 (14), 115 (34), 105 (21), 104 (47), 103 (15), 91 (88), 79 (10), 78 (14), 77 (14), 65 (19).

*Reaction of **1** with α-Methylstyrene **2b**.* From a reaction mixture of 133 mg of **1** (1.00 mmol) and 390 μl of **2b** (3.0 mmol) in 20 ml of *t*-butyl alcohol, the solvent was removed after heating at 155 °C for 12 h. Chromatography of the residue on silica gel, with petroleum ether–benzene (4: 1) elution, gave 183 mg of a mixture of four components, two of which were found by GLC analysis to be very minor (less than one hundredth of the major component in the peak area). The isolation of the two major products by preparative GLC (column D, 200 °C) afforded 115 mg of colorless crystals, **3b** (46%), which when recrystallized from methanol had a mp of 58.1—58.8 °C and 14.3 mg of **4b** (5.7%). Further elution with a petroleum ether–benzene 1: 1 mixture and benzene produced 65 mg of a viscous oil whose NMR spectrum indicated it to be a mixture of 1: 1 and 1: 2 adducts which have not yet been separated. **3b**, NMR (CS_2, 100 MHz): 0.9—1.7 (complex m containing d at 1.14, J=7 Hz, 7H), 1.9—2.5 (complex m, 3H), 2.96 (m, 4H), 6.37 (s, 4H), 6.47 (s, 2H), 6.56 (s, 2H). Found: C, 91.15; H, 8.78%. Calcd for $C_{19}H_{22}$: C, 91.14; H, 8.86%. **4b**, NMR (CCl_4, 100 MHz): 1.1—1.3 (t at 1.20, J=7.5 Hz, and d at 1.21, J=7 Hz, 6H), 1.3—1.7 (m, 4H), 2.4—2.8 (complex m, 5H), 6.93 (s, 4H), 6.9—7.3 (m, 5H); mass: *m/e* 252 (M^+,24), 119 (34), 117 (16), 115 (10), 106 (11), 105 (100), 104 (18), 103 (14), 91 (37), 79 (17), 78 (11), 77 (20). Found: C, 90.54; H, 9.58%. Calcd for $C_{19}H_{24}$: C, 90.41; H, 9.58%.

*Reaction of **1** with α-Trimethylsiloxystyrene **2c**.* A solution of 132 mg of **1** (1.00 mmol) and 416 mg of **2c** (2.0 mmol) in 10 ml of hexane was heated at 155 °C for 12 h under argon. The solvent was then removed and the residue was chromatographed on silica gel which had been dried at 150 °C under 1—2 Torr. Elution with dry benzene produced 183 mg of an oily complex mixture which has not been characterized. Further elution with dry benzene produced 21 mg of crystals which, when recrystallized from petroleum ether, gave 15 mg of analytically pure **3c** (4.4%), mp 82.0—82.8 °C. Elution with a chloroform–ethyl acetate 3: 1 mixture produced 70 mg of an oil which contained **6** and acetophenone. Dry air was bubbled in at 100 °C under 1—2 Torr to remove the acetophenone. The subsequent recrystallization of 33 mg of the crystalline residue from petroleum ether gave 18 mg of **6** (7.2 %, mp 104.4—106.8 °C) which, when recrystallized again from petroleum ether, had a mp of 107.3—108.0 °C. **3c**, NMR (CCl_4, 100 MHz): 0.04 (s, 9H), 1.0—1.8 (br s, 4H), 2.27 (br s, 2H), 3.01 (s, 4H), 4.44 (br s, 1H), 6.46 (m, 7H), 6.81 (d, J=8 Hz, 1H). **6**, NMR (CCl_4, 100 MHz): 2.04 (m, 2H), 2.60 (m, 4H), 2.97 (m, 4H), 6.27 (d, J=8 Hz, 2H), 6.45 (d, J=8 Hz, 2H), 6.52 (d, J=8 Hz, 2H), 6.96 (d, J=8 Hz, 2H); IR (KBr): 1665 (C=O). Found: C, 86.21; H, 7.20%. Calcd for $C_{18}H_{18}O$: C, 86.36; H, 7.25%.

*Reaction of **1** with Methyl Cinnamate **2d**.* A mixture of 64 mg of **1** (0.48 mmol) and 191 mg of **2d** (1.18 mmol) in 5.9 ml of *t*-butyl alcohol was placed in a glass ampoule and bubbled with argon. The ampoule was then sealed off and kept at 150 °C for 14 h. After concentration, the residual mixture was chromatographed on silica gel and eluted with benzene. The preparative GLC separation (column B, 220 °C) of the eluted mixture afforded 39.5 mg of **3d** (28%) which when recrystallized from methanol had a mp of 85.2—86.9 °C, besides 68 mg of unreacted **2d**. **3d**, NMR (CCl_4, 100MHz): 1.05 (t, J=13 Hz, 1H), 1.7—3.4 (complex m, 10H), 3.73 (s, 3H), 6.2—6.7 (m, 8H); IR (KBr): 1731 (C=O). Found: C, 81.62; H, 7.55%. Calcd for $C_{20}H_{22}O_2$: C, 81.60; H, 7.53%.

*Reaction of **1** with Methyl α-Phenylacrylate **2e**.* Following the procedure described for the reaction of **1** with **2d**, 103 mg of **3e** (43%) was obtained from the reaction of 108 mg of **1** (0.82 mmol) with 306 mg of **2e** (1.89 mmol) in 5 ml of *t*-butyl alcohol. **3e**, mp 70.6—71.7 °C; NMR (CCl_4, 100 MHz): 0.8—3.2 (complex m, 11H), 3.59 (s, 3H), 6.4—6.8 (m, 8H); IR (KBr): 1743 (C=O). Found: C, 81.57; H, 7.54%. Calcd for $C_{20}H_{22}O_2$: C, 81.60; H, 7.53%.

*Reaction of **1** with* trans-*Stilbene **2f**.* A mixture of 108 mg of **1** (0.82 mmol) and 336 mg of **2f** (1.87 mmol) in 10 ml of *t*-butyl alcohol was heated in a sealed glass ampoule at 150 °C for 14 h under argon. The solvent was then removed *in vacuo* and the partially crystallized, unreacted **2f** was filtered off from the residue. The oily residue was chromatographed on silica gel and eluted with a petroleum ether–benzene 4: 1 mixture to separate the reaction product from **2f**. The con-

centration of the fraction containing the reaction product afforded 48 mg of crystalline **3f** and an oily mixture, which was subjected to preparative GLC (column A, 220 °C) to yield 15.5 mg of **3f** (combined yield, 25%) and 10 mg of **4f** (3.9%). **3f**, mp 148.0—148.5 °C; NMR (CCl_4, 100 MHz): 1.40 (t, J= 12 Hz, 1H), 1.8—3.4 (m, 10H), 6.3—6.8 (m, 8H), 7.24 (s, 5H). Found: C, 92.12; H, 7.72%. Calcd for $C_{24}H_{24}$: C, 92.26; H, 7.74%. **4f**, NMR (CCl_4, 100 MHz): 1.23 (t, J= 7.5 Hz, 3H), 1.98 (m, 2H), 2.40 (m, 2H), 2.55 (quart, J=7.5 Hz, 2H), 2.7—3.0 (complex m, 3H), 6.8—7.3 (complex m, 14H); mass: *m/e* 314 (M^+, 9), 145 (15), 119 (100), 117 (13), 104 (24), 91 (43), 77 (10), 65 (10). Found: C, 91.61; H, 8.44%. Calcd for $C_{24}H_{26}$: C, 91.67; H, 8.33%.

Reaction of ***1*** *with 1,1-Diphenylethylene* ***2g***. A mixture of 108 mg of **1** (0.82 mmol) and 330 μl of **2g** (1.87 mmol) in 5 ml of *t*-butyl alcohol was heated at 150—155 °C for 12 h as has been described above. The subsequent removal of the solvent and chromatography on silica gel with petroleum ether–benzene (4: 1) elution gave 138 mg of unreacted **2g** and then 176 mg of oil. A part of the latter, which was found on the GLC analysis to consist of one major and two minor components was subjected to preparative GLC (column A, 210 °C) and the major component was collected. The viscous oil thus obtained crystallized slowly on standing. The residual oil was seeded with the crystals obtained above to give 172 mg of **3g** (67%) which when recrystallized from ethanol had a mp of 70.8—71.8 °C. Further elution with benzene produced only a polymeric material (115 mg). **3g**, NMR (CCl_4, 100 MHz): 0.9—3.2 (complex m, 10H), 3.43 (d, J=10 Hz, 1H), 6.2—6.6 (m, 8H), 7.18 (s, 5H). Found: C, 92.36; H, 7.71%. Calcd for $C_{24}H_{24}$: C, 92.26; H, 7.74%.

1-Hydroxy[4.2]paracyclophane ***3h***. The treatment of **3c** with methanol containing a trace amount of potassium hydroxide produced **3h** which when recrystallized from petroleum ether had a mp of 116.3—116.8 °C. The reduction of **6** with $NaBH_4$ in 2-propanol as usual gave **3h** (mp 115.5—117.0 °C), which showed no depression of the melting point on a mixed-melting-point measurement with the **3h** obtained above. **3h**, IR (KBr): 3340 (O–H), 1089 (C–O). Found: C, 85.58; H, 8.07%. Calcd for $C_{18}H_{20}O$: C, 85.67; H, 7.99%.

Reaction of ***1*** *with Ethynylbenzene*. A solution of 132 mg of **1** (1.00 mmol) and 220 μl of ethynylbenzene (*ca.* 2 mmol) in 5 ml of *t*-butyl alcohol was heated at 160 °C for 11 h. A GLC analysis of the reaction mixture showed that 71% of the ethynylbenzene was consumed. The solvent was removed and the residue was chromatographed on silica gel. Elution with petroleum ether produced unreacted ethynylbenzene. Further elution with petroleum ether–benzene 5: 1 and 3: 1 mixtures produced 81 mg of the product mixture. Preparative GLC (column B, 200 °C) afforded 29.9 mg of **8** (13%), 6.0 mg of an unidentified product, and 15.3 mg of a mixture which was again subjected to preparative GLC (column D, 210 °C) to give 5.4 mg of **7** (2.3%) which when recrystallized from methanol had a mp of 102.6—103.0 °C (lit, 100—101 °C).[5d] Further elution with benzene produced only a highly viscous polymeric oil (176 mg). **7**, NMR (CCl_4, 100 MHz): 2.2—3.1 (m, 8H), 5.3—5.8 (m, 1H), 6.0—6.8, (m, 9H).[5d] **8**, NMR (CCl_4, 100 MHz): 0.80 (s, 4H), 2.02 (t, J=7 Hz, 2H), 2.45 (t of d, J=2.5 and 7 Hz, 2H), 5.00 (d, J=10 Hz, 2H), 5.33 (d, J=10 Hz, 2H), 5.97 (t, J=2.5 Hz, 1H), 7.06 (m, 3H), 7.38 (m, 2H).

Effect of the Reactant Concentration on the Yield of ***3e***. A solution of *ca.* 7 mg of **1** (0.05 mmol) and 16 μl of **2e** (each accurately weighed) in a specified volume of *t*-butyl alcohol was heated at 155 °C for 14 h in a sealed glass ampoule under argon. The solvent was then removed *in vacuo* and the residue was dissolved in 0.50 ml of benzene. The yield of **3e** was determined on GLC using triphenylethylene as the internal standard.

Run	**1** (mg)	*t*-BuOH (ml)	**1** (mol/l)	**2e** (mol/l)	Yield of **3e**(%)
1	6.6	3.0	0.017	0.033	78
2	6.9	1.0	0.052	0.10	61
3	6.6	0.33	0.15	0.30	59
4	7.4	0.11	0.51	0.90	35

Effect of the Reactant Concentration on the Yield of ***3f***. A solution of *ca.* 10 mg of **1** and *ca.* 36 mg of **2f** in a specified volume of *t*-butyl alcohol was heated at 160 °C for 13.3 h as has been described above. The solvent was then removed *in vacuo* and the residue was dissolved in 1.00 ml of benzene. The yield of **3f** was calculated from the ratio of the peak area on GLC to that of the standard solution of **3f**.

Run	**1** (mg)	*t*-BuOH (ml)	**1** (mol/l)	**2f** (mol/l)	Yield of **3f**(%)
1	10.1	4.0	0.019	0.050	25
2	9.9	2.0	0.038	0.10	27
3	11.1	1.0	0.084	0.20	31
4	10.3	0.50	0.16	0.40	34
5	10.1	0.25	0.31	0.79	32

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