Tetrahedron. Vol. 31, pp. 2219 to 2227. Pergamon Press 1975. Printed in Great Britain

SYNTHETIC AND STRUCTURAL STUDIES OF [6]-, [7]- AND [10]METACYCLOPHANES

S. HIRANO,* H. HARA, T. HIYAMA, S. FUJITA and H. NOZAKI
Department of Industrial Chemistry, Kyoto University, Yoshida, Kyoto 606, Japan

(*Received in Japan* 18 *December* 1974; *Received in UK for publication* 18 *April* 1975)

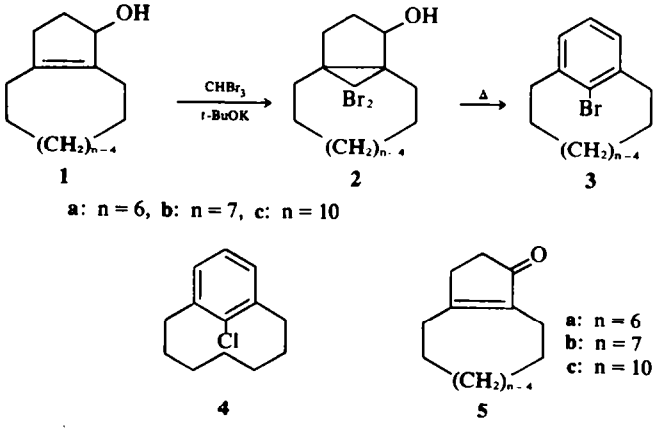
Abstract—A new preparative sequence from 2,3-polymethylene-2-cyclopentenone **5** to 2,6-polymethylenebromobenzenes **3** (n = 6, 7, 10) and 2,6-polymethylenephenyllithiums **6** has been found. The reaction of **6** with various electrophiles produces a number of new compounds to disclose the unique reactivity of the aryl C-Li moiety surrounded by the polymethylene chain. Photolysis of **3a** and **3b** provides transannular products **8**, **10** and **11**, all arising from the proximity between the aromatic bromine and the aliphatic hydrogen intraannularly opposed to be removed as HBr. Spectrometric study gives quantitative data of the dependence of the molecular geometry upon the chain length and the aromatic substituents. The energy barriers $\Delta G_c^{\neq}$ of the conformational flipping are 17·4 kcal/mol (T_c 76·5°) for [6]metacyclophane (**7a**), 11·5 kcal/mol (T_c −28°) for [7]metacyclophane (**7b**), < 8 kcal/mol for [10]metacyclophane (**7c**). The lower-energy process of the aliphatic chain in [6]metacyclophane derivatives is the pseudorotation with substituent-dependent barrier $\Delta G_c^{\neq}$ 11·1 kcal/mol (T_c −31·5°) for **7a**, 12·4 kcal/mol (T_c −4·5°) for **3a** and 12·7 kcal/mol (T_c 1·0°) for **12a**. The rather large rotational barrier is attributed to the compressed structure of each system. The benzene ring distortion of the cyclophanes is deduced from the bathochromic shift of the B-band and the diamagnetic shift of the benzene proton signals in the PMR.

Bridged aromatic compounds[1] now include carbophanes (cyclophanes), heterophanes, heteraphanes, and bridged nonbenzenoid aromatics.[2] Interest has been focused on the conformational analysis of the aliphatic bridge, the characteristic deformation of both aromatic and aliphatic moieties, and on the inclusion of metal cations into hetero-hetera rings.[3] We have synthesized [6]-, [7]- and [10]metacyclophanes to examine the following: (1) the reactivity of the aromatic substituents surrounded by the aliphatic chain with regard to the possible distortion effect and the transannular interaction with the polymethylene bridge,[4] (2) the geometrical change of the carbon bridge induced by variation of the substituent on the benzene ring as well as of the chain length, and (3) the distortion of the incorporated benzene ring.

Synthetic approach to metacyclophanes. Ever since Cram's synthesis of [8]paracyclophanes[5] efforts have been devoted to obtain the lower homologs, [6]- and [7]paracyclophane, both of which have recently been prepared.[6] Little has been known, however, with respect to the meta isomers, [8]metacyclophane being the lowest homolog at the outset of the present research. The synthesis of metacyclophanes given in Scheme 1 is general and applicable even to such highly strained lower homologs as [6]- and [7]metacyclophanes.

The sequence involves the dibromocarbene addition to 2,3-polymethylene-2-cyclopentenol (**1**) and the subsequent thermolysis of the resulting, labile 2,2-dibromocyclopropylcarbinol **2** to produce **3** under ring transformation and elimination. By means of dichlorocarbene reaction (chloroform-potassium t-butoxide) 13-chloro[7]metacyclophane (**4**) was obtained similarly.

The advantages of this route over the recorded ones† are as follows:



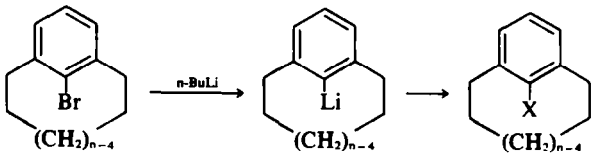
Scheme 1.

†Parham *et al.* have prepared bridged quinolines and naphthalenes in a similar manner from bridged indoles and indenes (see Ref. 7).

(1) Both the gain of the aromatization energy and the release of the cyclopropane strain compensate the strain of cyclophane to be formed. (2) The starting materials **1**

are easily available. (3) Derivatization of the bridged bromobenzenes **3** is easily accomplished via the respective phenyllithiums **6** (Scheme 2).

Preparation of the cyclopentenol **1a** and **1c** was accomplished by the Stobbe condensation[8] providing **5** and the subsequent hydride reduction. The alcohol **1b** was obtained by intramolecular aldol condensation of cyclododecane-1,4-dione[9a,b] (methanolic NaOH) affording **5b** followed by the reduction. Alternatively, **5b** was prepared by the acid catalyzed cyclization of cyclododeca-2,11-dienone ethylene acetal.[9c]



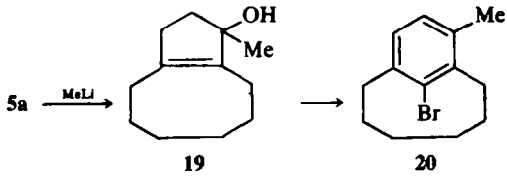
Scheme 2.

Lithiation of 12-bromo[6]metacyclophane (**3a**) with n-butyllithium proceeded smoothly to give 12-lithio[6]metacyclophane (**6**) in spite of the expected steric hindrance of the hexamethylene chain.† The subsequent quenching of **6a** with water gave [6]metacyclophane (**7a**) along with a transannular product, 2a,3,4,5-tetrahydroacenaphthene (**8**). Reduction of **3b** gave [7]metacyclophane (**7b**) and minor transannular products, 2,3,3a,4,5,6-hexahydrophenalene (**10**) and 1,7-tetramethylenehydrindene (**11**), whereas that of **3c** yielded [10]metacyclophane (**7c**)[10] only. Quenching with deuterium oxide afforded **9a** and **9b**.

Treatment of **6b** with excess methyl iodide resulted in the lithium-iodine exchange affording 13-iodo[7]metacyclophane (**12b**). The compound was alternatively prepared by treating **6b** with iodine. The lower homolog, 12-iodo[6]metacyclophane (**12a**), was obtained similarly. Noteworthy is the formation of **12a** in spite of the enhanced strain. In contrast, however, exposure of **6c** to methyl iodide provided 16-methyl[10]metacyclophane (**13c**) besides 16-iodo[10]metacyclophane (**12c**). The methyl derivative **13c** was alternatively prepared by the reaction of **6c** with methyl tosylate. The unusual behaviour of the bridged phenyllithium compounds toward methyl iodide is ascribed to the polymethylene moiety which is forced to solvate intramolecularly and to creat an anomalously nonpolar atmosphere in the vicinity of aromatic C-Li moiety‡ and/or to the perturbation of the reaction path by the steric compression.

Carbonation of **6b** or **6c** gave the benzoic acid derivatives **14b** or **14c**. Autoxidation (bubbling O_2) of **6b** yielded a bridged phenol **15b**[2c,12] albeit in a low yield along with **7b** and transannular products **10** and **11**. Reactivity of **6b** toward carbonyl compounds has been examined. Benzaldehyde reacted with **6b** to form a carbinol **16b** as well as a benzophenone derivative **17b**, which is ascribed to the Cannizzaro type reaction.[7d] Remarkably acetone reacted at the carbonyl site to give the normal t-alcohol **18b**. The α-proton abstraction by **6b** is a minor process, if any, in spite of the enhanced basicity of **6b** due to the hindrance.[7d]

An attempt to obtain a chiral metacyclophane involved the reaction of **5a** with methyllithium producing an alcohol **19**, which was directly subjected to dibromocarbene addition and the adduct was exposed to silica gel. The resolution of thus obtained 12-bromo-8-methyl [6]metacyclophane (**20**) could not be attained due to the small amount.



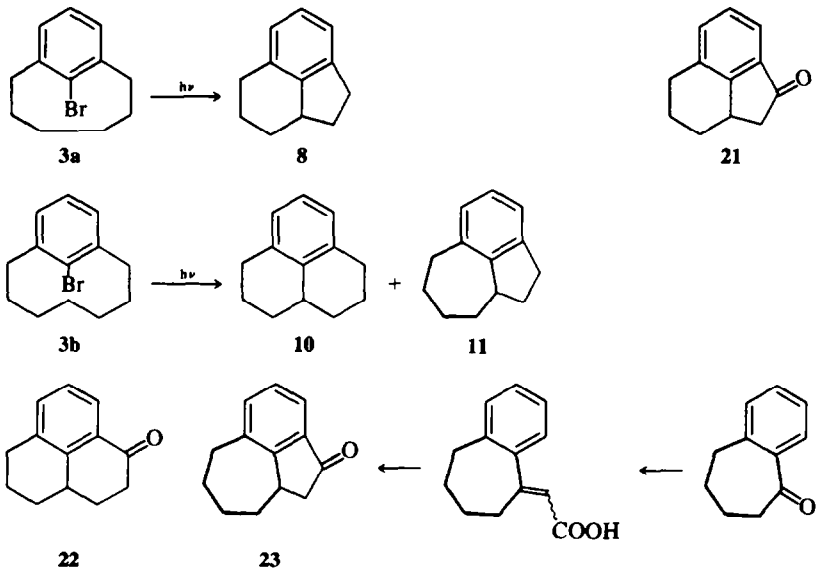
Photochemical transannular reaction of **3a** *and* **3b**. Irradiation of the ethanol solution of **3a** with a Pyrex-filtered mercury lamp afforded a transannular product **8** (Scheme 3).[7c,13] Photolysis of **3b** gave a 1:1 mixture of **10** and **11**. The structures were confirmed by unambiguous syntheses of the authentic samples.[12,14] The formal, "reverse" Friedel-Crafts type reaction is without precedent and is rationalized in terms of the release of the inner-strain energy attained by the transannular C–C bond formation

Conformational studies of metacyclophanes. (*a*) 2,6-*Polymethylenebromobenzenes*, **3a**, **3b** *and* **3c**. The PMR spectrum of 12-bromo[6]metacyclophane (**3a**) (Fig. 1) clearly shows the non-equivalence of the benzylic protons. This observation indicates that the hexamethylene chain is located on the one side of the benzene ring and the conformational flipping does not occur at room temp. The lower-field signal (δ 3·38) of the benzylic protons is ascribed to the inner protons H_A (Fig. 2), the observed deshielding effect being due to the anisotropy of benzene ring and possibly of the Br atom.[15a] The 2H peak ascribed to H_X and $H_{X'}$, of the enantiomeric conformers A and B (Fig. 2) indicates that a rapid equilibrium between them is set up at room temp by pseudorotation.§ This is supported by the PMR vicinal coupling constants between the benzylic protons and homobenzylic ones (J_{AB} = 13·2, J_{AC} = J_{AD} = 7·0, J_{BC} = 4·7, J_{BD} = 6·8 Hz).[16] At −57° the pseudorotation was frozen and a 1H signal (H_X or $H_{X'}$) appeared at δ −1·68 (Fig. 1), the lower-field counterpart ($H_{X'}$ or H_X) probably being hidden behind the signals of other methylene protons. These two signals coalesced at −4·5° and reappeared as an average signal at δ −0·03 (2H). The energy barrier of the pseudoro-

†The unforeseen susceptibility to the lithiation is perhaps due to front side attack to **3** forming a four-centered transition state.

‡The bridging effect would influence the degree of association[11] of **6** at the same time.

§The dynamic process established by the hindered rotation of C(3)–C(4) bond through the loop of the bridge extremely suffers the non-bonded repulsion between the aromatic ring and the C(3) and C(4) protons. This inference is applicable to **7a** and **12a**.



Scheme 3.

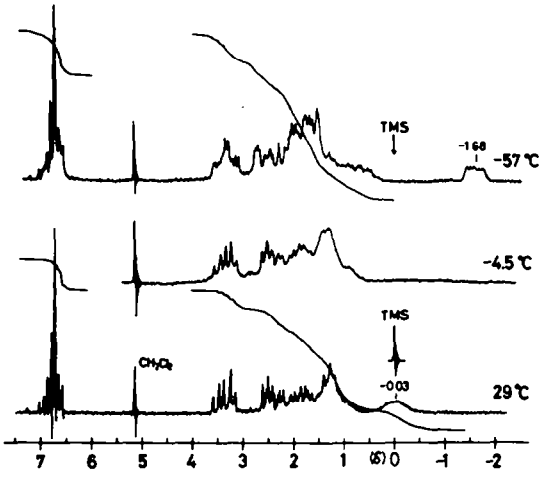


Fig. 1. Temperature dependent PMR spectra of **3a** (60 MHz, $CFCl_3$).

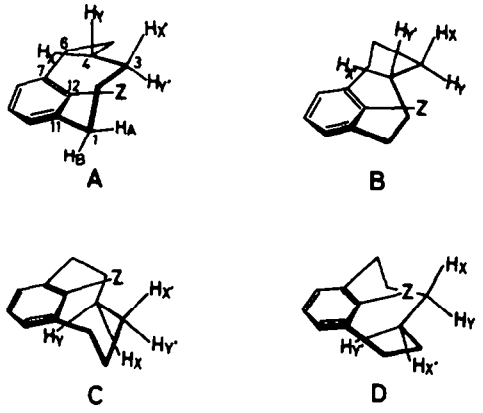


Fig. 2. Conformational equilibrium of [6]metacyclophanes established by pseudorotation (A ⇌ B, C ⇌ D) and flipping (A,B ⇌ C,D).

tation was estimated to be 12·4 kcal/mol at $T_c - 4·5°$.[17] The large value is explained by the compressed structure due to the non-bonded interaction between the aromatic π-cloud and the short aliphatic bridge. The higher energy barrier of the iodo derivative (Table 2) indicates the much severer compression in **12a**.

The heptamethylene bridge of 13-bromo[7]metacyclophene (**3b**) exhibited well-resolved PMR signals (Fig. 3). The chemical shift difference of the methylene protons suggests the conformational rigidity of the methylene bridge, every proton of which suffers the diamagnetic anisotropy of the benzene ring to the varying extent. The highest-field signal (δ −1·86, 1H) was assigned to one of the C-4 protons in comparison with that of the frozen spectrum of [7]metacyclophane (**7b**) (Fig. 6, *vide infra*). Another C-4 proton signal seems to be buried in the three-proton signal at ca δ 1·0. The non-equivalence of C-4 methylene protons unambiguously reveals that the heptamethylene bridge is located on the one side of the benzene ring to give an extreme conformer E. The H_X in E is forced to reside close to the π-cloud of the benzene ring and to suffer the strong diamagnetic shielding effect. The conformational stability of heptamethylene bridge was supported again by the splitting pattern (AB part of ABCD-type signal) of the benzylic protons (C(1)–H and C(7)–H). The inner benzylic protons H_A are considerably deshielded by the anisotropy of the benzene ring as well as the bromine atom (see **3a**). The parameters observed (first order approximation) are collected in Table 3 to indicate the *gauch* relationship between benzylic and homobenzylic methylenes. Table 3 lists further the values observed in 13-substituted derivatives. The flipping of the heptamethylene bridge of these derivatives appears to be frozen at room temperature.

The PMR spectrum (Experimental) of **3c** displayed the benzylic protons appearing as an AB part of ABCD pattern to suggest that the decamethylene bridge is again located on the one side of the benzene ring. The situation did not change even at 200°.† The bromine atom at C(16)

†The similar phenomenon has been observed in 16-bromo-2,9-dithia[10]metacyclophane (Ref. 18a).

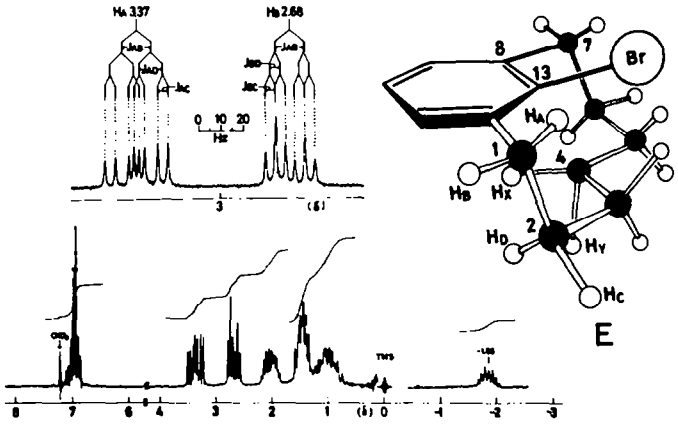


Fig. 3. PMR spectrum of **3b** (100 MHz, $CDCl_3$, 31°).

Table 1. Physical properties of metacyclophanes

Compound	b.p. (°/mm) or m.p. (°)	Formula	Calcd C% (exact mass P^+)	Calcd H%	Found C% (exact mass P^+)	Found H%
3a	97/0·18	$C_{12}H_{15}Br$	60·3	6·3	60·0	6·4
3b	47·5–48·5[a]	$C_{13}H_{17}Br$	61·7	6·8	61·5	6·9
3c	160/0·2	$C_{16}H_{23}Br$	65·1	7·9	65·1	8·2
4	110–120/2	$C_{13}H_{17}Cl$	74·8	8·2	74·7	8·3
7a	120/5	$C_{12}H_{16}$	89·9	10·1	90·0	10·1
7b	115/4	$C_{13}H_{18}$	89·6	10·4	89·3	10·5
7c	130/0·15	$C_{16}H_{24}$	88·8	11·2	88·8	11·4
12a	130/0·16	$C_{12}H_{15}I$	(286·0217)		(286·0235)	
12b	85·5–87[a]	$C_{13}H_{17}I$	52·0	5·7	52·3	5·7
12c	160–170/0·1	$C_{16}H_{23}I$	(342·0843)		(342·0824)	
13c	130–140/0·1	$C_{17}H_{26}$	88·6	11·4	88·8	11·1
14b	146–147[b]	$C_{14}H_{18}O_2$	77·0	8·3	76·9	8·3
14c	166–167[c]	$C_{17}H_{24}O_2$	78·4	9·3	78·5	9·3
15b	120/2	$C_{13}H_{18}O$	(190·1357)		(190·1355)	
16b	117–118[d]	$C_{20}H_{24}O$	85·7	8·6	85·6	8·4
17b	92–93[a]	$C_{20}H_{22}O$	86·3	8·0	86·4	8·0
18b	110–110·5[a]	$C_{16}H_{24}O$	82·7	10·4	82·6	10·6
20	95/0·03	$C_{13}H_{17}Br$	61·7	6·8	61·4	6·8

[a] Recrystallized from *n*-hexane. [b] Recrystallized from benzene. [c] Purified by sublimation. [d] Recrystallized from n-hexane: benzene = 3:2.

thus proved to be even more bulky than the cavity of the *meta* decamethylene bridge.

(*b*) *Metacyclophanes*, **7a**, **7b** *and* **7c**. The PMR spectrum (Fig. 4) of [6]metacyclophane (**7a**) at room temp. is characterized by the non-equivalence of the benzylic protons and the 2H intensity of the most shielded signal (δ 0·35, H_X and H_X). This clearly indicates that a rapid equilibrium between conformers A and B (or C and D) (Fig. 2) exists at room temp. The freezing of the process is demonstrated by the low temp. PMR (Fig. 5) similarly as 3a.* The peak at δ 0·35 (2H) disappeared at $T_c - 31·5°$ and reappeared at $\delta - 1·27$ as a 1H peak at lower temp. ($-82·5°$). At 76·5°, however, the peak disappeared, and a 4H peak (115°) was observed at δ 0·79 (average signal of H_X, $H_{X'}$, H_Y and $H_{Y'}$), whereas the benzylic proton signal appeared as a triplet. The PMR change suggests that the hexamethylene bridge of **7a** is now flipping up and down the benzene ring. The estimated energy barrier of the pseudorotation is collected in Table 2 and that of the flipping in Table 4. The coalescence temp. of the flipping in 12-deuterio[6]metacyclophane (**9a**) was by 3·5° lower than that of **7a**. The considerable steric isotope effect arises from the significant interaction between the C(12)–H and the methylene chain in the transition state for the flipping.† It is noteworthy that the energy barrier $\Delta G_c^{\neq}$ of the conformational flipping of **7a** is comparable to the corresponding one for the racemization of *trans* cyclononene derivative‡ and that the pseudorotation barrier of **7a** is much larger than that of cycloalkenes.§

The aliphatic PMR spectrum of **7b** at room temp. (Fig.

*This is in sharp contrast to the conformational change of 2,5-dithia[6]metacyclophane, whose aliphatic bridge is flipping up and down the benzene ring at room temp. (Ref 18a). The intervening two sulphur atoms make the system more flexible because of the longer C–S bond and the low bending energy of C–S–C.

†A similar conformational kinetic isotope effect of [2·2]metaparacyclophane has been analyzed more precisely (see Ref. 19).

‡The free energy of activation ($\Delta G_{-10°}^{\neq}$) for the racemization of *trans*-cyclononene has been recorded to be 19·1 ± 0·2 kcal/mol (Ref. 20a), while 2-bromo (or 2-chloro)-3-methoxy-*trans*-cyclononene has T_c 92° (100 Mhz) (Ref. 20b).

§For example, 5·8 kcal/mol for cyclooctene, 6·3 kcal/mol for cyclooctanone were reported (see Ref. 21).

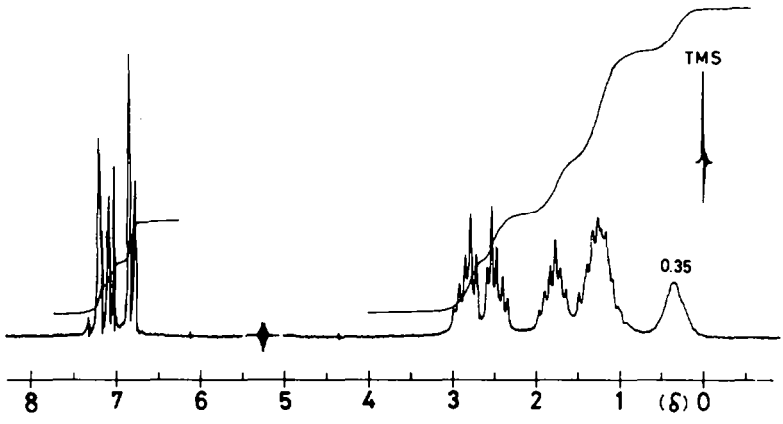


Fig. 4. PMR spectrum of **7a** (100 MHz, $CDCl_3$, 31·5°).

6) exhibits a remarkably high-field 2H signal (δ −0·18) which is assigned to the protons on C-4 on the analogy of [7](2,6)pyridinophane.[22] Above room temp. the heptamethylene bridge appears to be flipping up and down the benzene ring, the protons showing the average signal of the extreme conformers F and G. In these conformers one proton (H_X or $H_{Y'}$) on C-4 is forced in the shielding cone of the benzene ring. The C-4 proton signal disappeared at T_c − 28°, and reappeared at δ − 1·33 as a 1H peak at lower temp. (− 73·5°). The lower-field counterpart was possibly concealed behind the multiplets of the other methylenes. The energy barrier ($\Delta G_c^{\neq}$) of the conformational change was estimated to be 11·5 kcal/mol (T_c − 28°). The barrier is larger than that of [7](2,6)pyridinophane[22] and 2,6-dithia[7]metacyclophane[18] and this indicates the effect of the incorporation of hetero atoms on the steric factors (bulkiness,[23] bond angle,[24] etc.).

Table 2. Coalescence temperature and energy barrier of the pseudorotation of [6]metacyclophanes (in $CFCl_3$)

Compound	$\Delta\nu$[a] (Hz)	T_c (°)	k_c (sec^{-1})	$\Delta G_c^{\neq}$ (kcal/mol)
3a	199	−4·5	443	12·4
7a	194	−31·5	431	11·1
12a	210[b]	1·0	467	12·7

[a] $k_c = \pi\Delta\nu/\sqrt{2}$, $\Delta G_c^{\neq} = 2{\cdot}303\,RT_c\,(10{\cdot}319 - \log k_c + \log T_c)$, assumption; $\Delta\nu = 2(\nu_{high} - \nu_{average})$, see Refs. 17 and 22;
[b] $\Delta_{\nu} = \delta$ 0·04 (at 27°) and $\nu_{high} = -1{\cdot}71$ (at −77°).

The PMR spectrum of [10]metacyclophane (**7c**) exhibited a triplet signal for the benzylic protons. Apparently the decamethylene bridge is flipping and this movement is not frozen even at − 119°.

The distortion of benzene ring in metacyclophanes. The chemical shifts of aromatic protons of the metacyclo-

Table 3. The PMR spectral data of C(4)–Hx and benzylic protons of 13-substituted-[7]metacyclophanes (100MHz, 31·5°, in $CDCl_3$)

Compound	C(13)–X	C(4)–Hx (δ)	ν_A (δ)	ν_B (δ)	J_{AB}	J_{AC}	J_{AD}	J_{BC}	J_{BD}	(Hz)
3b	Br	−1·86	3·37	2·68	13·0	4·6	10·5	4·5	4·5	
4	Cl	−1·80	3·36	2·58	13·0	4·6	10·7	4·4	4·5	
7b	H	−0·18	(ca 2·7)							
12b	I	−1·92	3·34	2·83	13·0	4·7	10·5	4·5	4·5	
14b	COOH	−2·11	3·70	2·67	12·9	4·8	9·8	4·6	4·6	
15b	OH	−1·41	3·07	2·49	13·7	4·5	9·9	4·6	4·6	

Table 4. Coalescence temperature and energy barrier of the flipping of [6]- and [7]metacyclophanes and related compounds (measured at 60 MHz)

Compound	Solvent	$\Delta\nu$ (Hz)	T_c (°)	k_c (sec^{-1})	$\Delta G_c^{\neq}$ (kcal/mol)
7a	$CFCl_3$	53	76·5	117	17·4[a]
9a	$CFCl_3$	49	73	109	17·2[a]
2,5-dithia-[6]metacyclophane	$CDCl_3$-Py	—	−20[b]	—	12·4[b]
7b	$CDCl_3$	138	−28	307	11·5[a]
9b	$CDCl_3$	136	−31·5	301	11·3[a]
[7](2,6)-pyridinophane	$CFCl_3$	194	−75·5	432	9·0[c]
2,6-dithia-[7]metacyclophane	CH_2Cl_2	196	−50[d]	435	10·2

[a] See footnote *a* of Table 2. [b] This was determined by the coalescence of benzylic protons (see Ref. 18a). [c] See Ref. 22. [d] Measured at 100 MHz (see Ref. 18b).

phanes are summarized in Table 5. The shorter the methylene bridge, the higher is the chemical shift of the aromatic proton. This is consistent with the expectation that the shortening of the methylene bridge induces the distortions of the benzene ring, reduces the diamagnetic ring current, and increases the olefinic character of the benzene ring.[6d] Exceptionally C(13)–H of [7]metacyclophane (**7b**) is deshielded by *ca.* 0·3 ppm as compared with the corresponding protons of other [n]metacyclophanes. The down field shift is attributed to the van der Waals effect[15b] of the surrounding heptamethylene chain, whose C(4)–H and/or C(3)– and C(5)–H are possibly located close to the aromatic C(13)–H to exert a steric compression on it.†

The distortion of the benzene ring of metacyclophanes discussed above is also demonstrated by the red-shift of UV absorptions (Table 6). In each case the red-shift appeared to be larger as is the methylene bridge shorter.‡[26]

†The similar steric effect has recently been observed in the CMR of [2·2]metacyclophanes (Ref. 25).

‡The cyclohexatriene-like behaviour of the strained benzene ring of paracyclophane is demonstrated by the Diels-Alder reaction with dienophiles (Ref. 27). Attempted cycloaddition of dienophiles on [6]metacyclophanes failed.

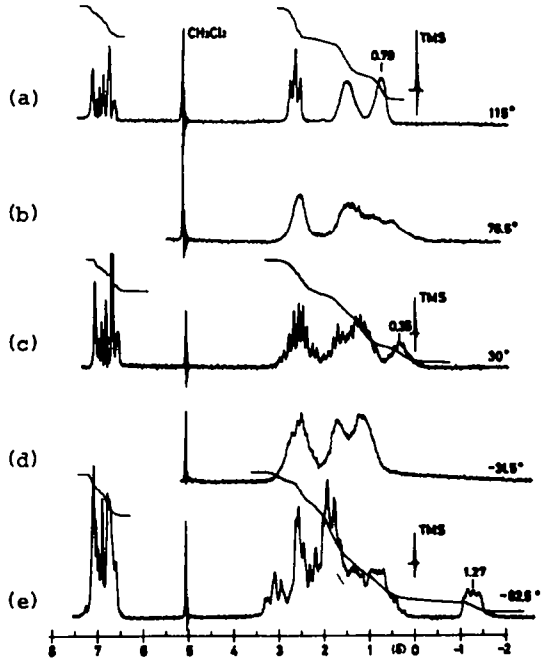


Fig. 5. Temperature dependent PMR spectra of **7a** (60 MHz, a-b in C_4Cl_6 and c-e in $CFCl_3$).

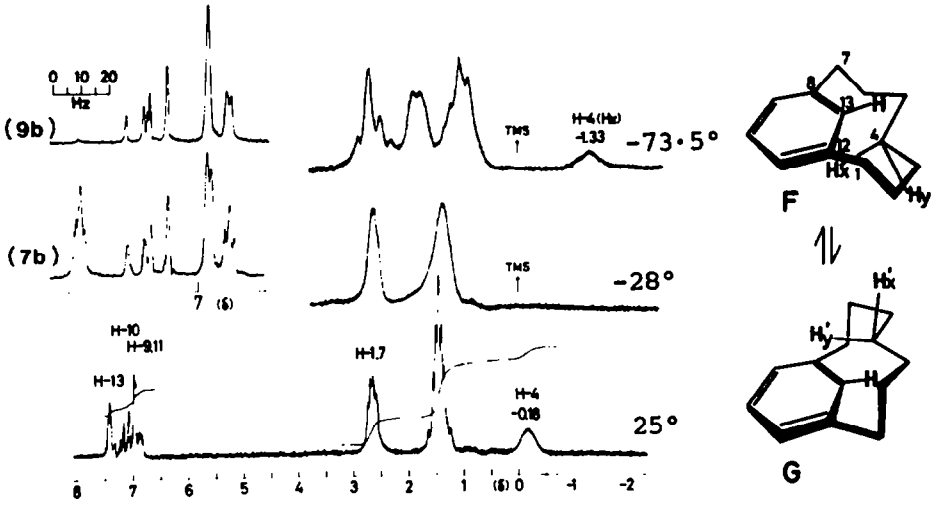
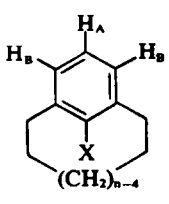


Fig. 6. Temperature dependent PMR spectra of **7b** (60 MHz, $CDCl_3$) and the aromatic part of **7b** and **9b** (100 MHz, $CDCl_3$, 31°).

Table 5. Chemical shift of aromatic protons of [6]-, [7]- and [10]metacyclophanes (measured at 100 MHz)

Compound	X	n	H_A (δ)	H_B (δ)
3a	Br	6	6·97	6·78
3b	Br	7	7·03	6·93
3c	Br	10	[a]	[a]
7a	H	6	7·09	6·81
7b	H	7	7·17	6·92
7c	H	10	7·11	6·89
12a	I	6	6·94	6·67
12b	I	7	7·00	6·84
12c	I	10	7·07	6·96



[a] As the difference of the chemical shift between H_A and H_B is so small that a simple analysis of the AB_2 pattern is impossible. [b] H_x = δ 7·21. [c] H_x = δ 7·43. [d] H_x = δ 7·03.

Table 6. UV spectra of metacyclophanes (in *n*-hexane)

Compound	λ_{max} [nm] (log ϵ)	Compound	λ_{max} [nm] (log ϵ)
3a	210·5 (4·35), 224 (4·20) 253 (3·43), 295 (2·64)	**12a**	219 (4·27), 246 (3·95) 297 (2·94)
3b	209 (4·43), 220sh (4·26) 243 (3·44), 280 (2·52)	**12b**	216 (4·33), 241 (3·99) 284 (2·87)
3c	204·5 (3·88), 260 (2·39) 268 (2·37), 275 (2·26)	**12c**	210 (4·36), 233 (3·94) 263 (2·82), 272 (2·76) 281·5 (2·59)
2,6-Dimethyl-bromobenzene	269 (2·62), 277 (2·57)[a]	2,6-Dimethyl-iodobenzene	258 (3·06)[a]
7a	209 (3·88), 223sh (3·59) 280 (2·48)	**14b**	213 (4·41), 260 (3·59) 304 (3·15)
7b	203 (4·5), 218sh (3·95) 271 (2·40)	**14c**	204 (4·24), 277 (2·82)
[8]Metacyclophane	266 (2·4)[b]		
7c	215 (3·88), 256 (2·57) 263 (2·55), 273 (2·44)		
m-Xylene	212 (3·86), 264·5 (2·48)[c]		

[a] H. Conrad-Billroth, *Z. Physik. Chem.* B 25, 217 (1934).
[b] A. J. Hubert and J. Dale, *J. Chem. Soc.* 86 (1963).
[c] This is taken in 25% MeOH, L. Doub and J. M. Vandenbelt, *J. Am. Chem. Soc.* 71, 2414 (1949).

EXPERIMENTAL

All the temps. are uncorrected. The IR spectra were obtained on a Shimadzu spectrometer 27-G, UV on a Shimadzu MPS-50L, and MS on a Hitachi RMU-6L spectrometer at 70 eV. The PMR spectra were obtained on a JEOL C-60-H and a Varian HA-100 D spectrometer, and the dynamic PMR were recorded on JEOL C-60-H (60 MHz). Exact mass spectra were taken on a Hitachi RMU-6D equipped with Nihon Denshi JEC-6 computer system.

2,3-*Hexamethylene*-2-*cyclopentenone* (**5a**). The compound was prepared according to the reported procedure[8a] for **5c** in 28% overall yield, b.p. 96–101°/4 mm, IR (neat): 1694 and 1646 cm^{-1}, MS: *m/e* 164(P^+). (Found: C, 80·4; H, 9·9. Calcd for $C_{11}H_{16}O$: C, 80·4: H, 9·8%).

2,3-*Heptamethylene*-2-*cyclopentenone* (**5b**). A mixture of cyclododecane-1,4-dione (6·5 g, 33 mmol) and 4% methanolic NaOH (10 g of NaOH and 300 ml of MeOH) was heated at reflux for 4 hr under N_2. Work-up gave **5b** (5·13 g, 87%), b.p. 95°/2 mm. IR(neat): 1696 and 1646 cm^{-1}, MS: *m/e* 178 (P^+). (Found: C, 80·7; H, 10·5. Calcd for $C_{12}H_{18}O$: C, 80·9; H, 10·2%).

2,3-*Hexamethylene*-2-*cyclopentenol* (**1a**). To LAH (1·9 g, 50 mmol, four-fold excess) suspended in ether (100 ml) with magnetical stirring **5a** (8·2 g, 50 mmol) in ether (50 ml) was added dropwise under N_2 over a period of 1 hr. Stirring for 1 hr at room temp. and then at reflux for 40 min, followed by work-up, gave an acid-sensitive oil (**1a**, 7·8 g, 94%), b.p. 95°/0·3 mm. IR(neat): 3320 and 1037 cm^{-1}, MS: *m/e* 148 ($P^+ - H_2O$) (Found: C, 79·6; H, 10·7. Calcd for $C_{11}H_{18}O$: C, 79·5; H, 10·9%).

2,3-*Heptamethylene*-2-*cyclopentenol* (**1b**). The enone **5b** (4·4 g, 25 mmol) was reduced with LAH (0·93 g, 25 mmol) to yield **1b** (3·8 g, 86%), b.p. 96°/0·1 mm. IR(neat): 3320, 1054 and 1030 cm^{-1}, MS: *m/e* 162 ($P^+ - H_2O$). (Found: C, 79·8; H, 11·5. Calcd for $C_{12}H_{20}O$: C, 79·9; H, 11·2%).

12-*Bromo*[6]*metacyclophane* (**3a**). To a vigorously stirred mixture of **1a** (5·0 g, 30 mmol), t-BuOK (150 mmol), and n-hexane (250 ml) a soln of $CHBr_3$ (25 g, 99 mmol) in n-hexane (150 ml) was added during 3 hr at −20° under N_2 and stirring was continued overnight at room temp. Work-up afforded a crude carbene-adduct, which was subjected to destructive distillation from a Claisen flask filled with glass-wool at 170–180°/0·1 mm under dropwise addition in the period of over 3 hr. Redistillation gave **3a** (1·8 g, 25%), IR(neat): 3063, 3044, 1562, 1421 and 1012 cm^{-1}, MS: *m/e* 240 ($P^+ + 2$), 238 (P^+), 130 (100%).

13-*Bromo*[7]*metacyclophane* (**3b**). Treatment of **1b** (3·1 g, 17 mmol) with $CHBr_3$ (13 g, 52 mmol) and t-BuOK (87 mmol) in n-hexane (200 ml) followed by distillation (135°/0·5 mm) gave **3b** (1·5 g, 32%). Recrystallization from n-hexane gave an analytical sample, m.p. (Table 1). IR (KBr): 3070, 3055, 1572, 1425, 1005 and 774 cm^{-1}, MS: *m/e* 254 ($P^+ + 2$), 252 (P^+), 131 (100%).

16-*Bromo*[10]*metacyclophane* (**3c**). The enone **5c** was reduced with LAH to **1c** (91% yield), IR(neat): 3330, 1046 and 973 cm^{-1}. The alcohol **1c** was subjected to carbene addition and the adduct was thermolyzed to **3c** (22%). IR(neat): 3072, 3048, 1575, 1425, 1024 and 783 cm^{-1}, PMR(CCl_4): δ 7·18–6·92 (m, 3H), 3·4–3·12 (m, 2H), 2·76–2·5 (m, 2H), 2·35–1·9 (m, 2H), 1·65–0·6 (m, 12H), and 0·65–0·2 (m, 2H) MS: *m/e* 296 ($P^+ + 2$), 294 (P^+), 131 (100%).

13-*Chloro*[7]*metacyclophane* (**4**). To a mixture of **1b** (0·68 g, 3·8 mmol), t-BuOK (30 mmol) and n-hexane (50 ml) a soln of $CHCl_3$ (2·3 g 19 mmol) in n-hexane (40 ml) was added at 0° under N_2. Thermolysis followed by preparative TLC purification on silica gel (n-hexane, $R_f = 0·8$) afforded **4** (0·19 g, 24% yield). IR(neat): 3070, 3050, 1573, 1059 and 780 cm^{-1}, UV: λ_{max} (n-hexane) (log ϵ) 212·5 (4·52), 233 (3·75) and 279 nm (2·32).

12-*Bromo*-8-*methyl*[6]*metacyclophane* (**20**). To a soln of **5a** (1·64 g 10·0 mmol) in ether (20 ml) an ethereal soln (20 ml) of MeLi (prepared from Li (0·28 g, 40 mmol) and MeI (2·8 g, 20 mmol) was added at 0° under N_2. After 0·5 hr the mixture was worked up to give an alcohol **19** (1·78 g, 99%), IR(neat): 3380 cm^{-1}. The crude **19** was directly subjected to the carbene addition and the product was purified on a silica gel column to afford **20** (1·37 g, 55%). PMR($CDCl_3$): δ 6·81 (d, J = 7·4 Hz, 1H), 6·64 (d, J = 7·4 Hz, 1H), 3·5–3·15 (m, 2H), 3·0–2·7 (m, 1H), 2·6–2·3 (m, 1H), 2·26 (s, 3H), 2·1–0·8 (m, 6H), 0·35 (br s, 1H), and −0·3 (br s, 1H), MS: *m/e* 254 ($P^+ + 2$), 252 (P^+), 173 (100%), UV: λ_{max} (n-hexane) (log ϵ) 215 (4·02), 227 (3·89), 257 (3·09), and 304 nm (2·47).

[6]*Metacyclophane* (**7a**). A soln of **3a** (0·29 g, 1·2 mmol) and n-BuLi (2·4 mmol) in n-hexane (10 ml) was heated at reflux for 2 hr under N_2. The resulting mixture was quenched with H_2O and worked up. Distillation gave 163 mg of a mixture (3:1) of **7a** and **8**. Lithiation at room temp. during 7·5 hr increased the ratio to 5:1. The two products were separated by preparative TLC on SiO_2–$AgNO_3$ (n-hexane/CH_2Cl_2 = 4:1) to give a pure sample of **7a** ($R_f = 0·2$), IR(neat): 3098, 3055, 3034, 1608, 1585, 1487, 786, 762, 729 and 711 cm^{-1}, MS: *m/e* 160(P^+), 145, 131, 117, 105, 104 (100%) and 91. **8** ($R_f = 0·5$).

[7]*Metacyclophane* (**7b**). (*vide infra*). This was prepared by reducing **3b** with n-BuLi in 70% yield along with a small amount (total 2%) of a 2:3 mixture of **10** and **11** (*vide infra*). Preparative GLC gave **7b**, IR(neat): 3105, 3061, 3030, 1610, 1590, 1490 and 783 cm^{-1}, MS: *m/e* 174 (P^+), 104 (100%).

12-*Deuterio*[6]*metacyclophane* (**9a**). Bromide **3a** (0·29 g,

1·2 mmol) was lithiated with n-BuLi (2·4 mmol) and the mixture quenched with D_2O (2 ml) to yield a mixture of **9a** (61%) and **8** (15%). Preparative GLC (SE 30) gave a pure sample of **9a**, IR(neat): 2268 (C-D) cm^{-1}, MS: *m/e* 161 (P^+).

13-*Deuterio*[7]*metacyclophane* (**9b**). This was obtained in 63% yield, b.p. 135°/5 mm, IR(neat): 2258 cm^{-1}, MS: *m/e* 175 (P^+). Byproducts were **10** and **11** (total 2%).

[10]*Metacyclophane* (**7c**). Lithiation of **3c** with n-BuLi and quenching with H_2O gave **7c** (72%). IR(neat): 3055, 3024, 1606, 1588, 1486 and 783 cm^{-1}, PMR (CCl_4): δ 7·2–6·82 (m, 4H), 2·64 (t, J = 6 Hz, 4H), 1·8–1·54 (m, 4H) and 1·4–0·75 (m, 12H), MS: *m/e* 216 (P^+).

12-*Iodo*[6]*metacyclophane* (**12a**). Lithiation of **3a** (0·24 g, 1·0 mmol) with n-BuLi (2·0 mmol) at 69° for 1 hr and treatment with I_2 (0·51 g, 2·0 mmol) at room temp., followed by work-up and preparative TLC (three elutions with isopentane), gave **12a** (R_f 0·78, 103 mg, 36%). IR(neat): 1556, 1415 cm^{-1}, PMR ($CDCl_3$): δ 7·02–6·64 (AB_2, 3H), 3·5–3·2 (m, 2H), 2·8–2·5 (m, 2H), 2·1–1·8 (m, 2H), 1·6–1·0 (m, 4H), 0·03 (br s, 2H), Ms: *m/e* 284 (P^+), 159, 130, 117 (100%). Byproducts were **8** (R_f 0·70, 15 mg, 10%) and **7a** (R_f 0·73, 25 mg, 16%).

13-*Iodo*[7]*metacyclophane* (**12b**)

(*a*) *Reaction of* **6b** *with methyl iodide.* Lithiation of **3b** (0·27 g, 1·05 mmol) with n-BuLi (3·2 mmol) and treatment of the resulting **6b** with freshly distilled MeI (2·0 g, 14 mmol) at 0° gave a crude solid, which was recrystallized from n-hexane to afford **12b** (0·23 g, 74%). IR (KBr): 1563, 1417 cm^{-1}, MS: *m/e* 300 (P^+), 173, 131, 117 (100%). The mother liquor contained small amount of **7b**, **10** and **11**.

(*b*) *Reaction of* **6b** *with iodine.* Quenching of **6b** from **3b** (0·22 mmol) and n-BuLi (0·75 mmol) with I_2 (1·0 g, 4 mmol) at 0° gave **12b** (57 mg, 86%).

16-*Iodo*[10]*metacyclophane* (**12c**). Quenching of **6c** from **3c** (0·15) g, 0·51 mmol) and n-BuLi (1·2 mmol) with MeI (0·40 g, 2·8 mmol) followed by GLC (SE 30, 10% on Chromosorb, 1 m purification gave **12c** (60 mg, 34%). IR(neat): 1574, 1416 cm^{-1}, MS: *m/e* 342 (P^+). Byproducts were **7c** (4 mg, 4%), **13c** (12 mg, 10%) and **3c** (8 mg, 5%).

16-*Methyl*[10]*metacyclophane* (**13c**). Lithiation of **3c** (0·15 g, 0·51 mmol) with n-BuLi (1·2 mmol), followed by treatment with MeOTs (0·22 g, 1·2 mmol) and preparative TLC (SiO_2, n-hexane, R_f 0·9), gave a mixture (83 mg) of **7c** and **13c** (10:17). Preparative GLC (SE 30, 18% on Chromosorb) gave pure **13c**. PMR (CCl_4): δ 7·0–6·85 (m, 3H), 3·05–2·76 (m, 2H), 2·65–2·35 (m, 3H), 2·33 (s, 3H), 2·1–1·6 (m, 2H), 1·65–0·3 (m, 14H), MS: *m/e* 230 (P^+).

[7]*Metacyclophane*-13-*carboxylic acid* (**14b**). Into **6b** prepared from **3b** (0·40 g, 1·6 mmol) with n-BuLi (4·7 mmol) in n-hexane (20 ml) CO_2 gas was bubbled at 0° for 1·5 hr, then at room temp. for 1·5 hr. Preparative TLC (SiO_2, ether) gave colourless needles **14b** (0·10 g, 30%), IR (KBr): 3200–2500, 1677 cm^{-1}. PMR ($CDCl_3$): δ 11·90 (br s, 1H), MS: *m/e* 218 (P^+), 173, 131, 117, 105, 91 (100%). The byproducts were **7b**, **10** and **11** (13 mg).

[10]*Metacyclophane*-16-*carboxylic acid* (**14c**). A mixture of **6c** prepared from **3c** (0·12 g, 0·42 mmol) and n-BuLi (1·2 mmol) was stirred overnight at room temp. under a CO_2 atmosphere. Preparative TLC (benzene/ether 2:1) gave **14c** (R_f 0·5, 32 mg, 30%), IR (Nujol): 3200–2500 cm^{-1}, PMR (CCl_4): δ 11·9 (br, s, 1H), MS: *m/e* 260 (P^+).

13-*Hydroxy*[7]*metacyclophane* (**15b**). To a hexane soln of **6b** O_2 was bubbled for 1 hr at −78°. Preparative TLC (SiO_2, n-hexane/benzene 1:1) gave **15b** (R_f 0·4, 34 mg, 18%). IR(neat): 3550, 1188 cm^{-1}, MS: *m/e* 190 (P^+), 120 (100%), UV: λ_{max} (n-hexane) (log ϵ) 211 (4·40), 228 sh (3·81), 282 nm (3·05). Byproducts were **7b** (15%), **10** (12%) and **11** (7%).

Reaction of **6b** *with benzaldehyde.* To a hexane soln of **6b** obtained from **3b** (0·65 mmol) and n-BuLi (1·3 mmol) PhCHO (0·35 g, 3·3 mmol) was added. The mixture was stirred at room temp. for 2 hr and then heated to reflux for 0·5 hr. Preparative TLC gave **16b** and **17b**. The carbinol **16b** (R_f 0·5, ether/n-hexane 1:10, 146 mg, 80%) exhibited IR (Nujol): 3550 cm^{-1}, MS: *m/e* 280 (P^+), 171 (100%), UV: λ_{max} (n-hexane) (log ϵ) 218·5 (4·41) and 289·5 nm (2·67). The ketone **17b** (R_f 0·4, benzene/n-hexane 1:1, 33 mg, 18%), IR (Nujol): 1664 cm^{-1}, MS: *m/e* 278 (P^+), 105 (100%), UV: λ_{max} (n-hexane) (log ϵ) 207·5 (4·39), 248 (4·10), 279 nm (3·69).

Reaction of **6b** *with acetone.* The phenyllithium **6b** obtained from **3b** (0·50 mmol) and n-BuLi (1·5 mmol) was treated with acetone (0·12 g, 2·0 mmol) at −78° for 1 hr and then at room temp. for 0·5 hr. Preparative TLC (SiO_2, n-hexane/ether 4:1) gave **18b** (R_f 0·4, 60 mg, 52%), IR (Nujol): 3350 cm^{-1}, MS: *m/e* 214 ($P^+ - H_2O$). A fraction (26 mg) at R_f 0·9 contained **7b**, **10** and **11**.

Photolysis of **3a**. A degassed soln of **3a** (0·12 g, 0·50 mmol) in 95% EtOH (12 ml) was placed in a Pyrex tube and irradiated with a 200-W high pressure Hg lamp for 3·5 hr. Distillation (85°/3·5 mm) gave a single product **8** (52 mg, 66%), IR(neat): 1609, 824, 760 cm^{-1}, PMR (CCl_4): δ 7·1–6·6 (m, 3H), 3·1–2·4 (m, 5H), 2·4–1·0 (m, 6H), MS: *m/e* 158 (P^+). The compound was identical with the authentic sample.[14a]

Photolysis of **3b**. Irradiation of the ethanolic soln of **3b** (0·25 g, 1·0 mmol) and distillatory work-up gave a mixture of **10** and **11** (0·15 g, 86%, 1:1 mixture). Preparative GLC (Dowfax 9N9 30% on Neopak 1A, 2 m) gave pure samples. **10**, IR(neat): 1586, 840 cm^{-1}, MS: *m/e* 172 (P^+), 144 (100%). **11**, IR(neat): 1597, 766 cm^{-1}, MS: *m/e* 172 (P^+), 130 (100%). These compounds were identical with the authentic samples.[12,14]

3,4-*Tetramethyleneindanone* (**23**). A mixture of benzosuberone (4·0 g, 25 mmol), $BrCH_2COOEt$ (5·9 g, 35 mmol), active Zn powder[28] (4·6 g, 70 mmol), and benzene (150 ml) was heated for 2 hr in the presence of I_2 (catalytic amount). Usual work-up afforded a β-hydroxyester (7·2 g), which was hydrolyzed with KOH (5 g) in 80% aq EtOH. Acidification and extraction gave a mixture of β-hydroxycarboxylic acid and α,β-unsaturated acid, which was subjected to dehydrative hydrogenation (H_2 130 kg/cm^2, 10% Pd-C (1·0 g), 70% $HClO_4$ (5 drops) in EtOH (100 ml), 60°)[29] to afford 1-carboxymethylbenzosuberane (3·7 g, 73%). The carboxylic acid (1·1 g, 5·1 mmol) was treated with 115% polyphosphoric acid (150 g) at 100° for 2 hr. Work-up gave **23** (0·18 g, 19%), m.p. 117–118·5° (95% EtOH). IR (Nujol): 1704 cm^{-1}, MS: *m/e* 186 (P^+). (Found: C, 83·6; H, 7·6. Calcd for $C_{13}H_{14}O$: C, 83·8; H, 7·6%).

1,7-*Tetramethylenehydrindene* (**11**). A mixture of the toluene soln of **23** (15 mg, 0·081 mmol), 6N-HCl (4 ml) and Zn amalgam (0·2 g) was heated under reflux for 2 hr during which additional 4 ml of 12N-HCl was added. Work-up gave **11** (13 mg).

Acknowledgement—Financial support from the Ministry of Education, Japanese Government, is acknowledged with pleasure.

REFERENCES

[1]For the reviews of bridged aromatic compounds, see: [a]B. H. Smith, *Bridged Aromatic Compounds*, Academic Press, New York (1964); [b]R. W. Griffin, Jr., *Chem. Rev.* **63**, 45 (1963); [c]S. Fujita and H. Nozaki, *Yuki-Gosei Kagaku Kyokai-shi* (*J. Syn. Org. Chem. Japan*), **30**, 679 (1972). For the nomenclature of phanes, see: [d]F. Vögtle and P. Neumann, *Tetrahedron Lett.* 5329 (1969); *Tetrahedron* **26**, 5847 (1970).

[2a]R. E. Harmon, R. Suder and S. K. Gupta, *J. Chem. Soc. Perkin I*, 1746 (1972); [b]S. Bradamante, A. Marchesini and G. Pagani, *Tetrahedron Lett.*, 4621 (1971); [c]T. Hiyama, Y. Ozaki and H. Nozaki, *Chem. Lett.*, 963 (1972); *Tetrahedron*, **30**, 2661 (1974).

[3a]D. J. Cram and J. M. Cram, *Science* **183**, 803 (1974); [b]F. Vögtle and E. Wever, *Angew. Chem.* **86**, 126 (1974).

[4]For the preliminary reports, see [a]S. Fujita, S. Hirano and H. Nozaki, *Tetrahedron Lett.* 403 (1972); [b]S. Hirano, T. Hiyama, S. Fujita and H. Nozaki, *Chem. Lett.* 707 (1972).

[5a]D. J. Cram and G. R. Knox, *J. Am. Chem. Soc.* **83**, 2204 (1961); [b]T. Tsuji and S. Nishida, *J. Am. Chem. Soc.* **95**, 7519 (1973).

[6a]V. V. Kane, A. D. Wolf and M. Jones, Jr., *J. Am. Chem. Soc.* **96**, 2643 (1974); [b]A. D. Wolf, V. V. Kane, R. H. Levin and M. Jones, Jr., *J. Am. Chem. Soc.* **95**, 1680 (1973); [c]N. L. Allinger and T. J. Walter, *J. Am. Chem. Soc.* **94**, 9267 (1972); [d]N. L. Allinger, T. J. Walter and M. G. Newton, *J. Am. Chem. Soc.* **96**, 4588 (1974).

[7a]W. E. Parham and J. K. Rinehart, *J. Am. Chem. Soc.* **89**, 5668 (1967); [b]W. E. Parham, R. W. Davenport and J. B. Biasotti, *Tetrahedron Lett.* 557 (1969); [c]W. E. Parham, D. R. Johnson, C. T. Hughes, M. K. Meilahn and J. K. Rinehart, *J. Org. Chem.* **35**,

1048 (1970); [d]W. E. Parham, R. W. Davenport and J. K. Rinehart, *Ibid.* **35**, 2662 (1970).

[8a]K. Biemann, G. Büchi and B. H. Walker, *J. Am. Chem. Soc.* **79**, 5558 (1957); [b]H. Nozaki, T. Mori, R. Noyori and M. Kawanishi, *Can. J. Chem.* **45**, 1804 (1967).

[9a]B. Camerino and B. Patelli, *Experientia*, **20**, 260 (1964); [b]T. Mori, K. Matsui and H. Nozaki, *Tetrahedron Lett.* 1175 (1970); [c]S. Hirano, T. Hiyama, and H. Nozaki, *Ibid.* 1429 (1974).

[10]A. T. Blomquist, R. E. Stahl, Y. C. Meinwald and B. H. Smith, *J. Org. Chem.* **26**, 1687 (1961).

[11]P. West and R. Waack, *J. Am. Chem. Soc.* **89**, 4395 (1967).

[12]W. Treibs and E. Heyner, *Chem. Ber.* **94**, 1915 (1961).

[13]J. T. Pinhey and R. D. G. Rigby, *Tetrahedron Lett.* 1267 (1969).

[14a]J. v. Braun and G. Kirschbaum, *Chem. Ber.* **55**, 1682 (1922); [b]R. Huisgen and G. Seidl, *Tetrahedron* **20**, 231 (1964); [c]J. v. Braun and J. Reutter, *Chem. Ber.* **59**, 1922 (1926): [d]J. v. Braun and E. Rath, *Ibid.* **60**, 1182 (1927); [e]W. S. Johnson, H. C. E. Johnson and J. W. Petersen, *J. Am. Chem. Soc.* **67**, 1360 (1945).

[15a]L. M. Jackman and S. Sternhell, *Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry*, 2nd Ed, Pergamon Press, London (1969), p. 80; [b]*Ibid.* p. 71.

[16a]H. S. Gutowsky, M. Karplus and D. M. Grant, *J. Chem. Phys.* **31**, 1278 (1959); [b]M. Karplus, *J. Am. Chem. Soc.* **85**, 2870 (1963); [c]H. S. Gutowsky and C. Juan, *J. Chem. Phys.* **37**, 120 (1962).

[17a]G. Binsh, in *Topics in Stereochemistry* (Edited by E. L. Eliel and N. L. Allinger), Vol. 3, pp. 97–192. Interscience Publishers, New York (1968); [b]I. C. Calder and P. J. Garratt, *J. Chem. Soc. B*, 660 (1967); [c]A. Allerhand, H. S. Gutowsky, J. Jonas and R. A. Meinzer, *J. Am. Chem. Soc.* **88**, 3185 (1966).

[18a]F. Vögtle, *Tetrahedron* **25**, 3231 (1969); [b]R. H. Mitchell and V. Boekelheide, *Tetrahedron Lett.* 2013 (1969).

[19]S. A. Sherrod, R. L. da Costa, R. A. Barnes and V. Boekelheide, *J. Am. Chem. Soc.* **96**, 1565 (1974).

[20a]A. C. Cope, K. Banholzer, H. Keller, B. A. Pawson, J. J. Whang and H. J. S. Winkler, *Ibid.* **87**, 3644 (1965); [b]C. B. Reese and A. Shaw, *Chem. Commun.* 1367 (1970).

[21]F. A. L. Anet, in *Conformational Analysis—Scope and Present Limitations* (Edited by G. Chiurdoglu), p. 15. Academic Press, New York (1971).

[22]S. Fujita and H. Nozaki, *Bull. Chem. Soc. Japan* **44**, 2827 (1971).

[23a]I. Gault, B. J. Price and I. O. Sutherland, *Chem. Comunn.* 540 (1967); [b]J. R. Fletcher and I. O. Sutherland, *Ibid.* 1504 (1969); [c]V. Boekelheide, I. D. Reingold and M. Tuttle, *Ibid.* 406 (1973).

[24]S. Hirano, T. Hiyama, S. Fujita, T. Kawaguti, Y. Hayashi and H. Nozaki, *Tetrahedron* **30**, 2633 (1974).

[25]T. Sato, T. Takemura and M. Kainosho, *Chem. Commun.* 97 (1974).

[26a]N. L. Allinger, L. A. Freiberg, R. B. Hermann and M. A. Miller, *J. Am. Chem. Soc.* **85**, 1171 (1963); [b]N. L. Allinger, J. T. Sprague and T. Liljefors, *Ibid.* **96**, 5100 (1974).

[27a]E. A. Truesdale and D. J. Cram, *Ibid.* **95**, 5825 (1973); [b]E. Ciganek, *Tetrahedron Lett.* 3321 (1967).

[28]M. Toda, M. Hayashi, Y. Hirata and S. Yamamura, *Bull. Chem. Soc. Japan* **45**, 264 (1972).

[29]A. C. Cope and S. S. Hecht, *J. Am. Chem. Soc.* **89**, 6920 (1967).