Carbene Insertion into [2.2]Metacyclophane-1,10-dione: A Convenient Route to [3.2]- and [3.3]-Metacyclophanes

By **Daniel Krois** and **Harald Lehner,*** Institut für Organische Chemie der Universität, Währingerstrasse 38, A-1090 Wien, Österreich

Ring enlargement of [2.2]metacyclophane-1,10-dione (1) with diazomethane conveniently affords [3.2]- and [3.3]-metacyclophanes. The homologues [3.2]metacyclophane-1,11- and -2,11-diones (2a and b), thus obtained, were used for the synthesis of [3.2]metacyclophane-1,10-diene (5) and the parent hydrocarbon [3.2]metacyclophane (4). [3.3]Metacyclophane-1,12-, -1,11-, and -2,11-diones (6a—c), prepared by regioselective carbene insertion into (2a) and (2b) with diazomethane, served as intermediates in the synthesis of [3.3]metacyclophane (8). The reactivity of the carbonyl groups of oxometacyclophanes decreases with ring size and thus correlates with ring strain. In contrast to (6a—c), the [3.2]metacyclophanediones (2a and b) form hemiacetals when dissolved in methanol.

We have previously reported on the conformation of oxo[2.2]metacyclophanes [1,2] and their enhanced carbonyl reactivity, which in the case of [2.2]metacyclophane-1,10-dione (1) permitted the isolation of a stable dihydrate. This singular behaviour towards nucleophiles has been attributed to a relief of steric strain on changing the co-ordination number at C-1 from three in the dione (1) to four in the adducts, with a concomitant conformational change. In order to gain more insight into the strain-dependent carbonyl reactivity, we needed higher homologues of (1), *i.e.* oxo-[3.2]- and -[3.3]-metacyclophanes.

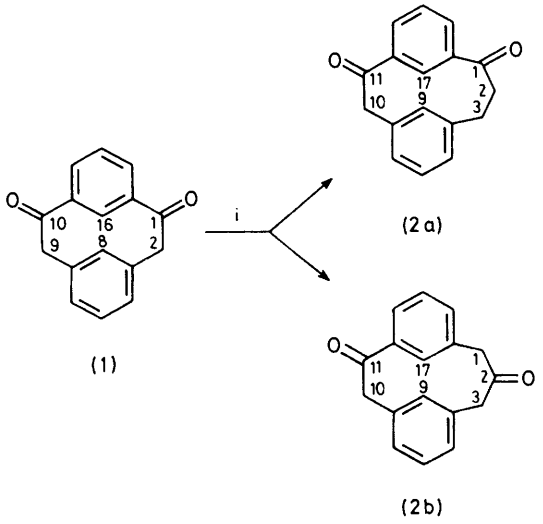
[3.2]Metacyclophanes have been prepared by Griffin *et al.* in a seven-step synthesis from *m*-bromotoluene and ethyl malonate.[3] This procedure has an overall yield of *ca.* 1% and makes no allowance for an access to oxo-derivatives. By this method only 2- and 2,2-substituted [3.2]metacyclophanes can be prepared, the parent [3.2]metacyclophane (4) being still unknown.

[3.3]Metacyclophane (8) was first synthesized by Shinmyozu *et al.* (four steps, 2% overall yield).[4] Later routes *via* dithia[4.4]metacyclophanes and arene complexes were described by several authors.[5,6] However, as in the case of [3.2]metacyclophanes, oxo[3.3]metacyclophanes cannot be prepared simply by the procedures described in the literature.

The lack of a more general route to [3.2]- and [3.3]-metacyclophanes prompts us to describe a synthesis of oxo-[3.2]- and -[3.3]-metacyclophanes, and the use of these ketones as precursors of various derivatives.

RESULTS AND DISCUSSION

[3.2]*Metacyclophanes.*—[2.2]Metacyclophane-1,10-dione (1) dissolved in a mixture of chloroform and propan-2-ol (20% v/v) and treated with ethereal diazomethane, gave 1,11- and 2,11-dioxo-[3.2]metacyclophanes (2a and b) (product ratio 1 : 1) in 90% yield free from higher homologues or oxirans. In propan-2-ol–ether the ratio of (2a) to (2b) is shifted to almost 5 : 3. If methanol is added as catalyst, or if larger proportions of propan-2-ol are used, the reaction proceeds too fast, is insufficiently specific, and cannot be controlled; oxo-[3.3]metacyclophanes (6a—c) and higher homologues are formed as well. On the other hand in the absence of any protic solvent the reaction is too slow and the yield much lower. The isomers (2a and b) can easily be separated by p.l.c. on silica gel or by column chromatography.



SCHEME 1 *Reagent:* i, CH_2N_2

The position of the carbonyl groups in the bridges follows from the ^1H n.m.r. spectra. For (2a) an ABCD multiplet due to the protons on the three-carbon bridge and an AB quartet from the protons of the two-carbon-bridge are observed. For (2b) three chemically non-equivalent AB systems are apparent (Table 1). In addition, the lack of any symmetry element (as revealed by the ^1H n.m.r. spectra) is evidence that the inversion of the eleven-membered ring is slow on the n.m.r. time scale.

[3.2]Metacyclophane (4) was obtained by treatment of (2a) and/or (2b) with propane-1,3-dithiol, followed by reductive desulphurisation of the thioacetals (3a) and/or (3b) with Raney nickel [overall yield from (1) 60%]. The route from 1,3-bis(bromomethyl)benzene and the bis(propylene thioacetal) of isophthalaldehyde [7,8] *via* (1)

and the reaction paths described above resulted in an overall yield of 21%.

For the preparation of the diene (5) the diketones (2a) and/or (2b) were successively treated with lithium aluminium hydride and mesyl chloride. As in the procedure given by Boekelheide *et al.* for the synthesis of [2.2]metaparacyclophane-1,9-diene,[7] the mesyl groups were then eliminated with potassium t-butoxide in t-butyl alcohol, yielding (5) [29% from (2a) or (2b)].

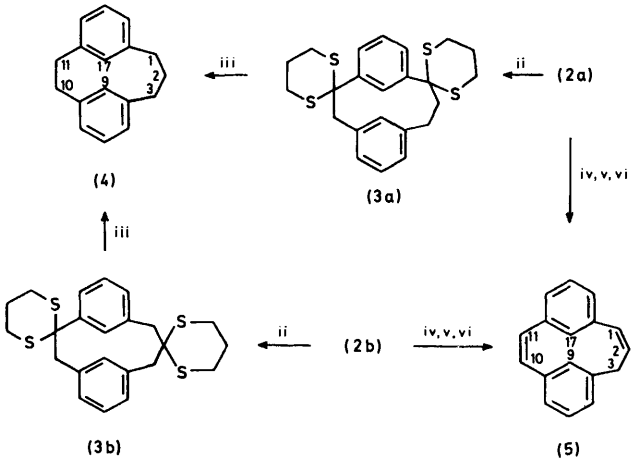
TABLE 1

^{1}H N.m.r. data [a] for [3.2]- and [3.3]-metacyclophanes

Compound	Bridge [b]	Aromatic nuclei: Intra-annular	Aromatic nuclei: Extra-annular	Apparent symmetry
(2a) [c]	4.26 and 4.03 (ABq, *J* 16, 2 H, H-10), 3.81, 3.33, 2.84, and 2.79 (ABCDm, 4 H, H-2, H-3)	7.82 (s, 1 H) 7.59 (s, 1 H)	7.70—6.59 (6 H)	C_1
(2b) [d]	3.90 and 3.72 (ABq, *J* 15, 2 H, H-10), 3.66 (' s ', 2 H, H-1 or H-3), 3.59 (' s,' 2 H, H-3 or H-1)	6.27 (s, 1 H) 5.38 (s, 1 H)	7.45—7.10 (6 H)	C_1
(4) [d]	3.03 and 2.16 ($AA'BB'$m, 4 H, H-10, H-11), 2.76, 2.32, and 1.93 ($A_2B_2C_2$m, 6 H, H-1, H-2, H-3)	5.09 (s, 2 H)	7.22—7.00 (6 H)	C_2
(5) [d]	6.75, 6.00, 3.20, and 2.96 (ABXYm, 4 H, H-1, H-2, H-3), 6.60 (' s,' 2 H, H-10, H-11)	6.81 (s, 1 H), 6.63 (s, 1 H)	7.31—6.88 (6 H)	C_1
(6a) [c,e]	3.28 and 3.09 ($AA'BB'$m, 8 H, H-2, H-3, H-10, H-11)	7.82 (s, 1 H), 7.51 (s, 1 H)	7.90—6.45 (6 H)	C_{2v} [e]
(6b) [d]	3.63 (s, 2 H, H-10 or H-12), 3.60 (s, 2 H, H-12 or H-10), 3.11 and 2.88 ($AA'BB'$m, 4 H, H-2, H-3)	6.75 (s, 1 H), 6.47 (s, 1 H)	7.65—6.93 (6 H)	C_s
(6c) [d]	3.54 (s, 8 H, H-1, H-3, H-10, H-12)	5.80 (s, 2 H)	7.33—7.20 (6 H)	D_{2h}
(8) [d]	2.77 and 2.07 (A_4B_2m, 12 H, H-1, H-2, H-3, H-10, H-11, H-12)	6.90 (s, 2 H)	6.82—6.64 (6 H)	D_{2h}

[a] δ values; *J* in Hz; 20 °C; solvent deuteriochloroform; for (2a) and (2b) 50% (v/v) [$^2H_4$]methanol was added. [b] Assignment of partial spectra by double resonance; note that the carbons in the bridge mostly carry two chemically different protons; the sequence of chemical shifts of a multiplet does not necessarily conform with the location of protons. [c] 360 MHz. [d] 250 MHz. [e] 40 °C.

[3.3]Metacyclophanes.—The [3.3]metacyclophanes (6a—c) were synthesized by prolonging the reaction of (1) with diazomethane. The isomers (6a and b) were formed in approximately equal amounts (40% each), while the diketone (6c) was obtained in smaller quantities (15%). Compound (6c) could be separated from (6a) and (6b) by p.l.c. on silica gel. For further separation, the mixture of (6a) and (6b) was treated with propane-1,3-dithiol, yielding the thioacetals (7a) and (7b), which could be separated by column chromatography on acetals (7b) and (7c). The mixture of (6a) and (6b) obtained from pure (2a) however, could not be separated by chromatography.

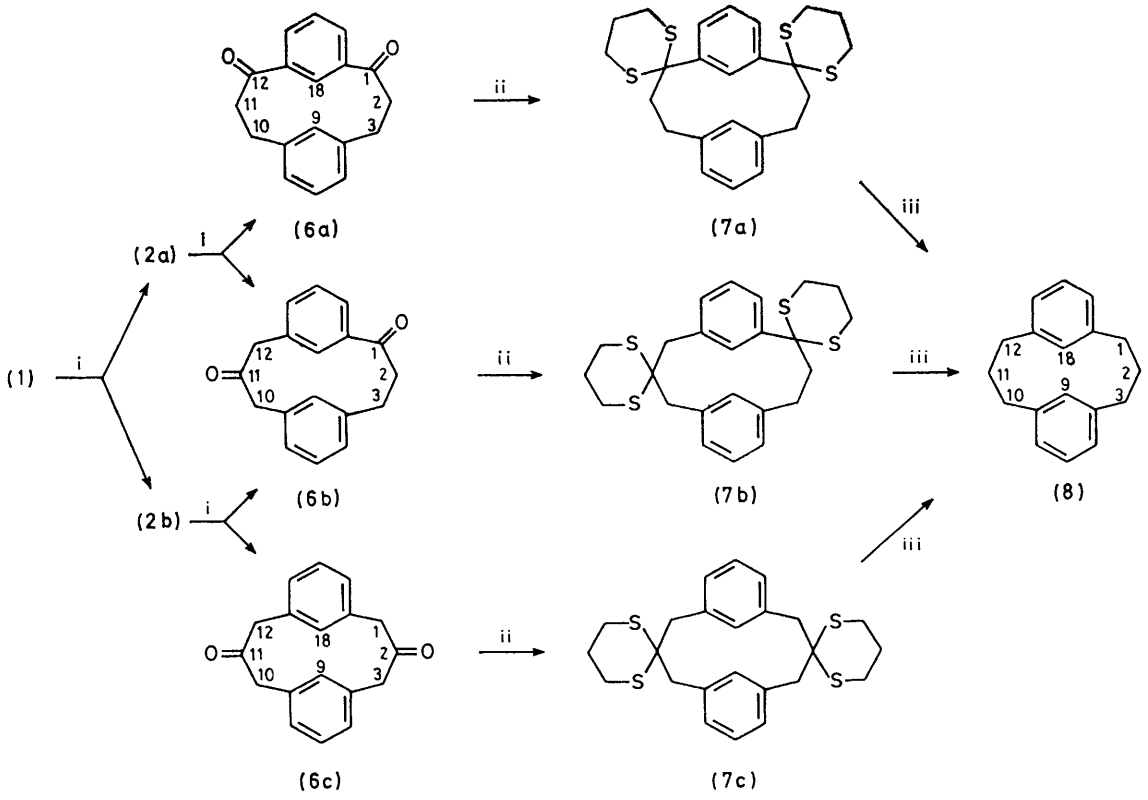


SCHEME 2 *Reagents:* ii, propane-1,3-dithiol; iii, Raney nickel; iv, lithium aluminium hydride; v, mesyl chloride; vi, potassium t-butoxide

The rate of insertion into (2a) and (2b) is much less than for (1). No [4.2]metacyclophanes were isolated, thus showing that carbene is inserted regioselectively into the C_2 bridge of (2a) and (2b). The [3.3]metacyclophanes (6a—c) do not react with diazomethane under the conditions employed. Only by performing the reaction under forcing conditions (pure methanol; large diazomethane excess) and after long reaction times (24 h) could we detect isomeric mixtures of [4.3]- and [4.4]-metacyclophanes (g.l.c.–mass spectrometry), accompanied by increasing amounts of decomposition products. At room temperature, the ^{1}H n.m.r. spectra of (6b) and (6c) exhibit C_s and D_{2h} symmetry, respectively (Table 1); thus inversion of the twelve-membered rings must be fast. For (6a) the absorptions due to the aliphatic systems are broad and unstructured. At 40 °C these signals become a well resolved $AA'BB'$ system and (6a) exhibits an apparent C_{2v} symmetry. From the coalescence temperature (293 K) and the n.m.r. parameters (at 250 MHz) the barrier of ring inversion of (6a) is estimated to be 56 kJ mol^{-1}.

[3.3]Metacyclophane (8) was obtained in 62% yield from the dione (1) *via* the isomeric ketones (6a—c), by desulphurisation of the thioacetals (7a—c). Since the dione (1) can be prepared in 35% yield,[7,8] the synthesis of (8) proceeds in an overall yield of 22%. Hence the yield of compound (8) is much higher than that previously reported.[4,5]

Reactivity of the Carbonyl Groups in Oxometacyclophanes.—The ease of carbene insertion into the oxo-



SCHEME 3 *Reagents:* see Schemes 1 and 2

[2.2]- and -[3.2]-metacyclophanes (1), (2a), and (2b) merits further discussion. For (1) it had been shown that the enhanced reactivity towards nucleophiles can be attributed to a relief of steric strain on rehybridisation ($sp^2 \longrightarrow sp^3$).[1] A similar driving force should be operative in the carbene insertion, since the intermediate in the reaction of diazomethane with a carbonyl group has a tetracovalent carbon atom.[9] Analogously, the reactivity of (2a) and (2b) is indicative of the strain still present in the [3.2]metacyclophane system. The regioselectivity of the carbene insertion in (2a) and (2b) must be attributed to the different relief of strain on rehybridisation of one or the other of the two oxo-functions present. A comparison of the rates of carbene insertion into (1), (2a), (2b), and (6a—c) indicates that the strain inherent to the pertinent cyclophane decreases in the order [2.2]-, [3.2]-, and [3.3]-metacyclophane. This is also reflected in the time-dependent electronic absorption spectra of the [3.2]metacyclophanediones (2a and b) in methanol (Figure), due to hemiacetal formation as reported for (1). These changes are fully reversible on evaporation of the solvent. As expected, none of the [3.3]metacyclophanediones (6a—c) exhibits similar behaviour. These results parallel the ring-size-dependent reactivity of paracyclophane ketones towards diazomethane observed by Cram *et al.*[10]

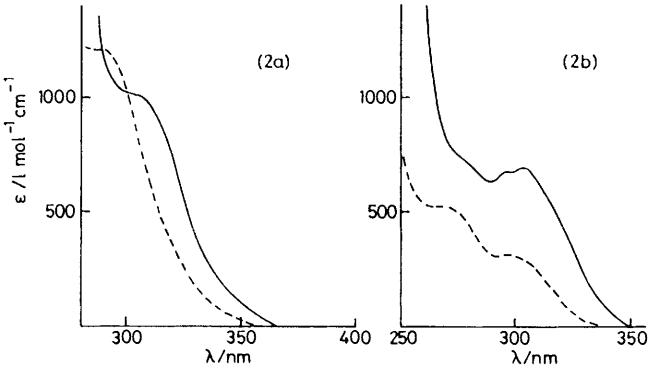


FIGURE Electronic absorption spectra of 1.2×10^{-3}M-solutions of (2a) and (2b) in methanol (——) immediately after dissolution, (– – – –) after 4 h (no further change)

EXPERIMENTAL

M.p.s were taken with a Kofler–Reichert hot-stage apparatus. ^{1}H N.m.r. spectra were recorded with a Bruker WH 360 (360 MHz; Fourier transform mode), a Bruker WM 250 (250 MHz; Fourier transform mode), or a Varian XL 100 (100 MHz; continuous wave mode), using spectroscopic grade deuteriochloroform, with tetramethylsilane as internal standard at 20 °C unless stated otherwise. I.r. spectra were recorded with a Perkin-Elmer 377 spectrometer for solutions in carbon tetrachloride. Electronic absorption spectra were measured with a Cary 15 spectrometer at ambient temperature for solutions in spectroscopic grade cyclohexane or methanol (Uvasol, Merck). Mass spectra were taken with a Varian MAT CH7 instrument at 70 eV. P.l.c. was performed on Kieselgel HF_{254} (Merck), and column chromatography on Kieselgel 60 (Merck, 70—230 mesh) or Aluminiumoxid 90 (Merck, Aktivitätsstufe

II—III, 70—230 mesh). G.l.c. analysis was performed with a Varian Aerograph 1400 chromatograph [5 ft × 1/8 in column of 2% OV 17 on Anakrom ABS (Analabs) at 215 °C].

For preparation of diazomethane, *N*-nitrosomethylurea was decomposed with aqueous potassium hydroxide in ether. The organic layer was dried over potassium hydroxide pellets and distilled. The ethereal solutions thus obtained contained diazomethane at a concentration of 1.3 mol l^{-1} (by titration).

[3.2]*Metacyclophane*-1,11- (2a) *and* -2,11-*dione* (2b).—(*a*) The ketone (1) [7,8] (500 mg, 2.1 mmol) was dissolved in a mixture of chloroform (36 ml) and propan-2-ol (8 ml) and maintained at 0 °C. Then ethereal diazomethane (3.5 ml, 4.5 mmol) was added in one portion. After 20 min the excess of diazomethane was removed by addition of acetic acid, The solvent was evaporated off *in vacuo* and the residue chromatographed on silica gel (70 g; eluant dichloromethane). The ketone (1) (50 mg) was eluted first, then (2b) (200 mg, 42%) and (2a) (230 mg, 48%); overall yield 90%.

(*b*) Substitution of ether (36 ml) for chloroform in procedure (*a*) with a reaction time of 30 min afforded the ketone (1) (62 mg), then (2b) (150 mg, 32%) and (2a) (250 mg, 54%); overall yield 86%. *Compound* (2a) had m.p. 125—128 °C (from n-hexane); $\nu_{max.}$ 1 702 and 1 683 cm^{-1} (CO); $\lambda_{max.}$ (cyclohexane) 335s (ε 195), 299 (955), 252s (7 500), and 220s nm (21 200); (Found: C, 81.4; H, 5.6%; M^+, 250. $C_{17}H_{14}O_2$ requires C, 81.6; H, 5.6%; *M*, 250). *Compound* (2b) had m.p. 109—112 °C (from ether), $\nu_{max.}$ 1 708 cm^{-1} (CO); $\lambda_{max.}$ (cyclohexane) 330s (ε 260), 316 (470), 307 (590), 297 (610), 278 (663), and 235s nm (10 100) (Found: C, 81.3; H, 5.6%; M^+, 250).

[3.2]*Metacyclophane* (4).—(*a*) To a boiling solution of the thioacetals (3a) and/or (3b) (200 mg) in tetrahydrofuran (3 ml), Raney nickel T1 [11] (2 g) was added. After 2 h the slurry was filtered and the solvent evaporated off *in vacuo*. This afforded the *hydrocarbon* (4) (85 mg, 83%), m.p. 59—61 °C (from methanol); $\lambda_{max.}$ (cyclohexane) 274s (ε 300), 268 (380), 262s (320), 238s (1 680), and 225s nm (10 600) (Found: C, 91.7; H, 8.3%; M^+, 222. $C_{17}H_{18}$ requires C, 91.8; H, 8.2%; *M*, 222).

(*b*) *Without isolation of intermediates.* Ring enlargement of (1) (200 mg) was performed as described for the synthesis of (2a) and (2b), except that the reaction time was extended to 30 min. The product contained 1% (1), 80% [(2a) + (2b)] and 15% [(6a) + (6b) + (6c)] as revealed by g.l.c. It was dissolved in glacial acetic acid (5 ml), and propane-1,3-dithiol (0.4 ml) and boron trifluoride–ether (0.05 ml) were added. Usual work-up (see thioacetals) gave a waxy material (350 mg), which was dissolved in tetrahydrofuran (4 ml); Raney nickel T1 (2 g) was added. The mixture was kept at reflux for 2 h, when treated as described in procedure (*a*). P.l.c. (hexane) afforded (8) (15 mg) as a by-product and (4) (95 mg, 50%) as the main fraction.

[3.2]*Metacyclophane*-1,10-*diene* (5).—To a stirred solution of (2a) and/or (2b) (200 mg) in ether (20 ml), lithium aluminium hydride (50 mg) was added. After 1 h water (1 ml) was added and the ethereal layer decanted. The solvent was evaporated off *in vacuo* and the crystalline residue dissolved in chloroform (4 ml). To this stirred solution was added at 0 °C methanesulphonyl chloride (0.3 ml) in one portion, followed dropwise by collidine (0.5 ml) within 5 min. After 20 min chloroform (10 ml) was added and the organic layer extracted with aqueous sodium hydrogen carbonate (10 ml) and water (10 ml). The solution was dried over sodium sulphate and evaporated off *in vacuo*. The residual mixture of mesylates dissolved in t-butyl alcohol (20 ml) containing potassium t-butoxide (2 g) was then refluxed for 2.5 h under argon. After cooling to room temperature, water (20 ml) was added and the mixture extracted with ether. The ethereal solution was washed twice with water and dried over sodium sulphate. Evaporation of the solvent and p.l.c. (hexane) yielded *compound* (5) (50 mg, 29%), m.p. 60—62 °C (from methanol); $\lambda_{max.}$ (cyclohexane) 315s (ε 2 310), 304 (2 660), 293s (2 570), 285s (2 610), 253 (13 700), and 223 nm (11 900) (Found: C, 93.2; H, 6.6%; M^+, 218. $C_{17}H_{14}$ requires C, 93.5; H, 6.5%; *M*, 218).

[3.3]*Metacyclophane*-1,12- (6a), -1,11- (6b), *and* -2,11- (6c) *diones*.—(*a*) To the ketone (1) (500 mg, 2.1 mmol) dissolved in chloroform (25 ml) and propan-2-ol (7 ml) was added ethereal diazomethane (7 ml, 9 mmol) at 0 °C. Work-up after 20 h as described for (2a)/(2b) and chromatography on silica gel (70 g) gave (6c) (80 mg, 14%) as the first eluted fraction and a mixture of (6a) and (6b) (400 mg, 72%). The mixture (6a)/(6b) was transformed into the thioacetals, which were separated to yield (7a) (200 mg) and (7b) (300 mg). The thioacetal (7a) (200 mg) was then dissolved in a mixture of tetrahydrofuran (8 ml) and water (0.8 ml) and maintained at 0 °C. Then *N*-bromosuccinimide (810 mg, 4.5 mmol) in acetone (6 ml) and water (0.8 ml) was added within 3 min. After 20 min, water (50 ml) and ascorbic acid (100 mg) were added. Extraction with ether and evaporation of the extract *in vacuo* yielded (6a) (90 mg). The same procedure afforded (6b) (108 mg) from (7b) (300 mg) (overall yield 50%).

(*b*) *The diones* (6b) *and* (6c) *from* (2b). Compound (2b) (57 mg, 0.23 mmol) dissolved in chloroform (5 ml) and propan-2-ol (1.5 ml) was cooled to 0 °C, and ethereal diazomethane (1.0 ml, 1.3 mmol) was added. The usual work-up after 4 h and p.l.c. yielded (6b) (29 mg) and (6c) (17 mg); overall yield 75%.

(*c*) *The diones* (6a) *and* (6b) *from* (2a). The same procedure with (2a) (60 mg) after 10 h gave a mixture of (6a) + (6b) (51 mg, 80%); for separation see (*a*).

Compound (6a) had m.p. 153—157 °C (from cyclohexane); $\nu_{max.}$ 1 682 cm^{-1} (CO); $\lambda_{max.}$ (cyclohexane) 305 (ε 1 200), 298 (1 260), 240s (11 200), and 228s nm (15 100) (Found: C, 81.8; H, 6.0%; M^+, 264. $C_{18}H_{16}O_2$ requires C, 81.8; H, 6.1%; *M*, 264). *Compound* (6b) had m.p. 88—90 °C (from ether); $\nu_{max.}$ 1 708 and 1 683 cm^{-1} (CO); $\lambda_{max.}$ (cyclohexane) 325s (ε 170), 294 (1250), and 240s nm (7 500) (Found: C, 81.6; H, 6.1%; M^+, 264). *Compound* (6c) had m.p. 197—199 °C (from ether); $\nu_{max.}$ 1 710 cm^{-1} (CO); $\lambda_{max.}$ (cyclohexane) 325 (ε 127), 315 (315), 305 (442), 295 (443), 278 (453), 263 (426), 235s (5 450), and 220s nm (9 020) (Found: C, 81.7; H, 6.2%; M^+, 264).

Thioacetals.—To the appropriate ketone or ketonic mixture (1.5—3 mmol) dissolved in glacial acetic acid (10—20 ml) were added successively propane-1,3-dithiol (0.5—1 ml, 5—10 mmol) and boron trifluoride–ether (0.1—0.2 ml). After 1 h at room temperature chloroform (20 ml) was added. The organic layer was washed with aqueous sodium hydrogen carbonate and water and dried over sodium sulphate. After evaporation the thioacetals were obtained in 90—95% yield. For the preparation of the hydrocarbons (4) and (8) the crude thioacetals were used in the desulphurisation step without further purification. Separation of isomeric mixtures and purification of the crude thioacetals was achieved by column chromatography

on alumina (170—340 g) using dichloromethane–hexane (1 : 3 v/v) as eluant. Relative retention times: t_r(3a) < t_r(3b); t_r(7a) < t_r(7b) < t_r(7c). The properties of the individual thioacetals are listed in Table 2.

TABLE 2

Bis[propylene thioacetals]; physical and analytical data

Compound	M.p. (°C)	Formula	Analysis Found (required) (%)	M^+ (= M)
(3a)	208—212 [a]	$C_{23}H_{26}S_4$	C, 64.0 (64.1) H, 6.2 (6.1) S, 29.6 (29.8)	430
(3b)	211—215 [b]	$C_{23}H_{26}S_4$	C, 63.9 (64.1) H, 6.2 (6.1) S, 29.7 (29.8)	430
(7a)	233—236 [b]	$C_{24}H_{28}S_4$	C, 64.5 (64.8) H, 6.4 (6.3) S, 28.7 (28.8)	444
(7b)	183—186 [b]	$C_{24}H_{28}S_4$	C, 64.6 (64.8) H, 6.4 (6.3) S, 28.4 (28.8)	444
(7c)	280—284 [a]	$C_{24}H_{28}S_4$	C, 64.6 (64.8) H, 6.3 (6.3) S, 28.9 (28.8)	444

[a] Recrystallization from benzene–hexane. [b] Recrystallization from acetone.

[3.3]*Metacyclophane* (8).—Ring enlargement of the ketone (1) (200 mg) was performed as described for the synthesis of the [3.3]metacyclophanediones (6a—c). The resulting mixture was transformed into the thioacetals (7a—c) and the dithian groups were removed by Raney nickel T1 [11] as in the synthesis of (4) [procedure (*b*)]. This afforded the hydrocarbon (8) (124 mg, 62%), m.p. 79—80 °C (from methanol) (lit.,[4] 79—80 °C; lit.,[5] 81—82 °C); identical (electronic spectrum and elemental analysis) with the material reported.[4,5]

We thank Mr. G. Verhegge and Professor M. Anteunis (Rijksuniversiteit Gent, Belgie) for the 360 MHz n.m.r. spectra. All other n.m.r. spectra were run by Mr. W. Silhan (this institute). We acknowledge financial support by the Hochschuljubiläumsstiftung der Stadt Wien and by the Fonds zur Förderung der wissenschaftlichen Forschung.

[1/1075 *Received*, 7*th July*, 1981]

REFERENCES

[1] D. Krois, E. Langer, and H. Lehner, *Tetrahedron*, 1980, **36**, 1345.
[2] For the nomenclature of phanes see F. Vögtle and P. Neumann, *Tetrahedron*, 1970, **26**, 5847.
[3] R. W. Griffin, jun., and R. A. Coburn, *Tetrahedron Lett.*, 1964, 2571; *J. Am. Chem. Soc.*, 1967, **89**, 4638.
[4] T. Shinmyozu, T. Inazu, and T. Yoshino, *Chem. Lett.*, 1976, 1405.
[5] T. Otsubo, M. Kitasawa, and S. Misumi, *Chem. Lett.*, 1977, 977; *Bull. Chem. Soc. Jpn.*, 1979, **52**, 1515; L. Rossa and F. Vögtle, *J. Chem. Res.* (*S*), 1977, 264; (*M*) 3010.
[6] H. A. Staab, C. P. Herz, and A. Döhling, *Chem. Ber.*, 1980, **113**, 233; M. F. Semmelhack, Y. Thebtaranouth, and L. Keller, *J. Am. Chem. Soc.*, 1977, **99**, 959.
[7] V. Boekelheide, P. H. Anderson, and T. A. Hylton, *J. Am. Chem. Soc.*, 1974, **96**, 1558.
[8] H. Lehner, *Monatsh. Chem.*, 1974, **105**, 895.
[9] C. D. Gutsche in *Org. React.*, 1954, **8**, 364.
[10] D. J. Cram and R. C. Helgeson, *J. Am. Chem. Soc.*, 1966, **88**, 3515.
[11] X. A. Dominguez, I. C. Lopez, and R. Franco, *J. Org. Chem.* 1961, **26**, 1625.