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NONAMETHYLENE-BRIDGED PHENOLS AND TROPONES

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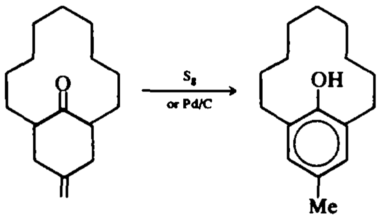
Abstract—Novel phenols (**4** and **6**) having the OH group surrounded by nonamethylene chain were prepared from cyclododecanone. 2,7-Nonamethylene bridged tropone (**11**) was obtained by stepwise bromination-dehydrobromination of bicyclo[9.4.1]hexadecan-16-one (**7**). The aliphatic chain of these phanes has been proved to reside on the one side of the respective aromatic ring. Spectroscopic studies indicate that the phenol **6** belongs to "intermediately hindered" phenol. The reactivity of the hindered OH group and of the strained benzene ring was examined with respect to **6**, which is susceptible to methylation and acetylation but not to isopropylation. 12-Methyl[9]metacyclophane (**15**) was obtained by mesylation of **6**, followed by the reduction of the resulting sulfonate. The constraint caused in the conjugate base of **6** by the nonamethylene bridge possibly is responsible for the selectivity in the dichlorocarbene addition giving **16** exclusively. Reaction of **6** with monochlorocarbene afforded bridged tropylidene **24** which was easily thermolysed to 3,4-bridged toluene **25** under ring-contraction.

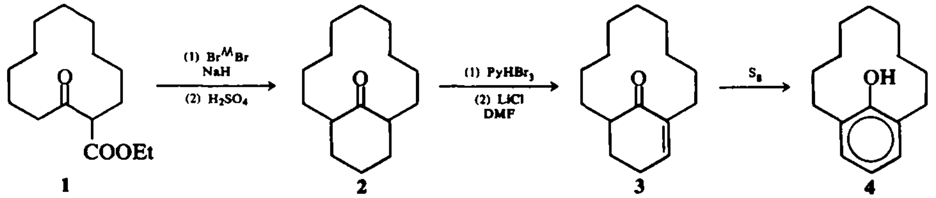
Cyclophanes[1] or bridged aromatics[2] are fascinating compounds owing to their unique physical and chemical properties. The territory of "phanes"[3] now includes heterophanes[4] and bridged nonbenzenoid aromatics.[5] Twenty-five years ago Prelog *et al* examined the effect of the size of the bridge on the UV absorptions of 2,6-polymethylene-4-nitrophenol[6a] and on the reduction potential of 2,6-polymethylenebenzoquinones.[6b] These studies were solely devoted to the static character of the bridged phenols. Recent theoretical and methodological development prompted us to investigate dynamic aspects of the chemistry of bridged phenols. This article describes the synthesis of 2,6-nonamethylenephenols and 2,7-nonamethylene bridged tropone.[7] Furthermore the reactivity of these strained systems are discussed.

15-*Hydroxy*[9]*metacyclophane* (4)

Alkylation of 2-ethoxycarbonylcyclododecanone (**1**)[8] with 1,3-dibromopropane, followed by hydrolysis and decarboxylation, afforded the bicyclic ketone **2**. Bromination with pyridinium hydrobromide perbromide (PyHBr$_3$) and subsequent dehydrobromination (LiCl-DMF) gave the bicyclic enone **3**. Dehydrogenative aromatization of **3** was accomplished by heating with sulphur to afford 15-hydroxy[9]metacyclophane (**4**). 12-Me substituted derivative **6** was obtained from the enone **5** by simple dehydrogenation with sulphur or Pd-C. Both **4** and **6** gave no coloration with ferric chloride. This negative phenol test[9] as well as the IR spectrum of **6** shown in Fig 1 suggests that the steric hindrance of the OH group of **6** is intermediate between 2,6-xylenol and 2,6-di-t-butyl-*p*-cresol (**20**). The bathochromic absorption of **6** (λ_{max} (EtOH) 286 nm (log ϵ 3·28)) compared with those of 2,4,6-trialkylphenol (λ_{max} 275–278 nm)[10] should be ascribed to the constraint by the nonamethylene chain bridging the 2- and 6-position of the phenol. UV absorptions in alkaline ethanol are shown in Fig 2 which indicates that as much as 0·5 M NaOH concentration is required for the extensive ionization of the phenol **6**. The difference of the absorption wave length between the phenolic and phenolate forms is 23 nm. These facts also support



5 **6**



1 **2** **3** **4**

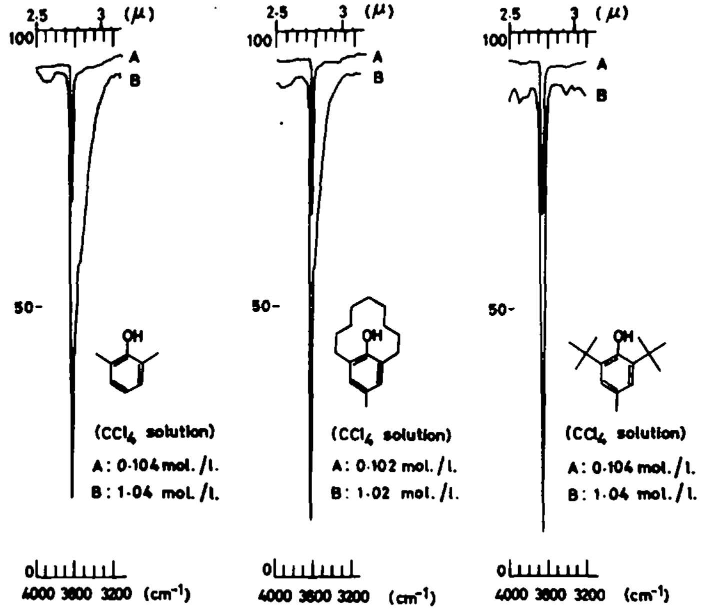


Fig 1. IR spectra of 2,6-xylenol, **6**, and **20**.

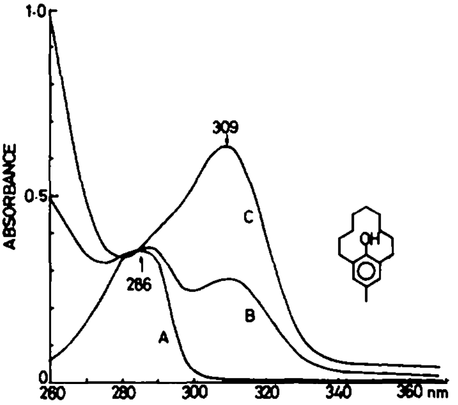


Fig 2. UV spectra of **6** in alkaline ethanol solution. (A: EtOH, B: 0·1 M NaOH/EtOH, C: 0·5 M NaOH/EtOH).

that **6** should be regarded as a partially hindered phenol according to the definition of Coggeshall *et al.*[10]

The PMR spectra of **6** as well as **4** are shown in Fig 3. Non-equivalence of the benzylic protons indicates that the nonamethylene chain resides only on the one side of the aromatic ring. This conformation appeared to be maintained up to 196° because the non-equivalence of the benzylic protons remained unchanged. As molecular models suggest, multiplet at δ 0·4–0·5 (2 H) supposedly is ascribed to one of methylene hydrogens on C-4 and C-6. PMR study using a shift reagent was attempted. Addition of 0·1 equivalent of $Eu(fod)_3$ to **6** in carbon tetrachloride caused a slight down-field shift of the polymethylene signals (0·17 ppm for benzylic and 0·09 ppm for average methylenes). The saturation was observed already at molar ratio of as much as 0·3. The non-linear relationship between the chemical shift change and the amount of $Eu(fod)_3$ suggests that the coordination of the oxygen atom in **6** to Eu is hindered by the nonamethylene chain.

2,7-*Nonamethylene bridged tropone* (**11**)

While bridged benzotropones have been recorded by Heilbronner *et al*[11] and recently by American[12] and French[13] chemists, the bridged tropone itself has been unknown. In continuation of our investigation on bridged aromatics, we have synthesized 2,7-nonamethylene bridged tropone and examined its spectroscopic characteristics.

Bromination of bicyclo[9.4.1]hexadecan-16-one (**7**)[14] with $PyHBr_3$ gave the monobromo ketone **8**. Dehydrobromination (LiCl in DMF) afforded the enone **9**. Allylic bromination (NBS) gave the unstable dienone **10** which rapidly polymerized on standing at room temperature. The dienone **10** was immediately subjected to the subsequent bromination ($PyHBr_3$) and neutralization (sodium bicarbonate) to yield 2,7-nonamethylenetropone (**11**).* IR and UV spectra (Experimental) of the compound were consistent with those reported on 2,7-dialkyltropones.† PMR spectra of **11** shown in Fig 5

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*Alternative preparation of the compound **11** has been reported recently. See Ref 15*a*.

†We are indebted to Prof. R. Noyori and Dr. H. Takaya for supplying the spectral data of the troponoids. *Cf* Ref 15*b*.

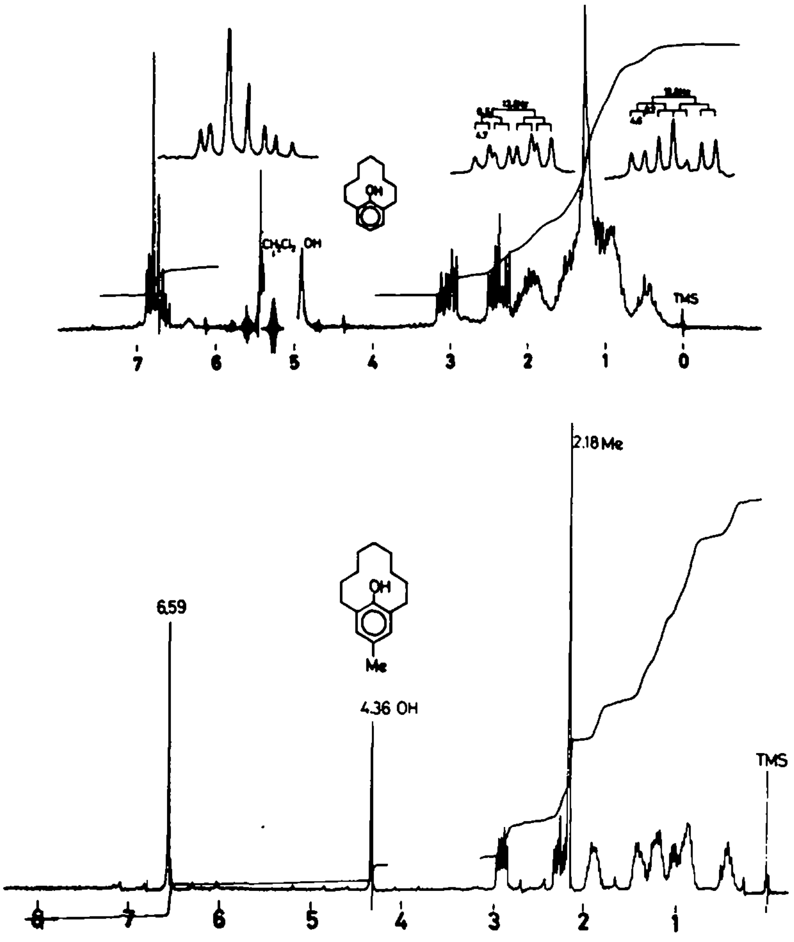

Fig 3. PMR of **4** (upper, 100 MHz, CCl_4, TMS, CH_2Cl_2 standard, r.t.) and **6** (below, 220 MHz, CCl_4, TMS, r.t.).

indicate the non-equivalence of the two benzylic protons. This implies that the nonamethylene chain is fixed to the one side of the tropone ring. Apparent ring current effect of tropone ring was not observed.[*] In contrast, addition of a little more than one equivalent of trifluoroacetic acid caused down-field shift of the olefinic (0·92 ppm) and benzylic (0·12–0·41 ppm) protons, owing to the formation of the tropylium cation (**12**). The diamagnetic ring current of the tropylium cation was evidenced by the splitting of the polymethylene signals and by the new peaks appearing at δ 0·75 and 0·93 ppm. The diamagnetic ring current was also observed in the ^{13}C-NMR (CMR) spectra of **11** summarized in Table 1. Upon addition of CF_3COOH peaks at 26·452 and 26·634 ppm shifted to higher field (*ca* 0·12–0·30 ppm) in spite of the resulting positive charge[†] of the tropylium cation.

Reaction of 6 *with electrophiles*

Since the phenol **6** is more easily prepared than **4**, the reactivity of the OH group surrounded by nonamethylene chain was examined with respect to **6**. Treatment of **6** with sodium hydride and then with methyl iodide provided the methyl ether **13**, while the reaction with isopropyl bromide failed. The more bulky isopropyl group cannot approach the phenoxy anion sheltered by the nonamethylene chain. Meanwhile, acetylation of **6** was accomplished with acetic anhydride-pyridine.

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[*] Tropone is recorded not to exhibit appreciable aromatic character. See Ref 16.

[†] No report on the diamagnetic shielding effect by nonbenzenoid aromatics by means of CMR has appeared yet. Levin and Roberts (Ref 17) have observed the ring current effect (*ca* 0·3 ppm) on the chemical shift of the methylene carbons in [12]paracyclophane, but the value of the contribution depends on the selection of the reference compound. In our case the reference compound is the bridged tropone **11** itself and no ambiguity exists.

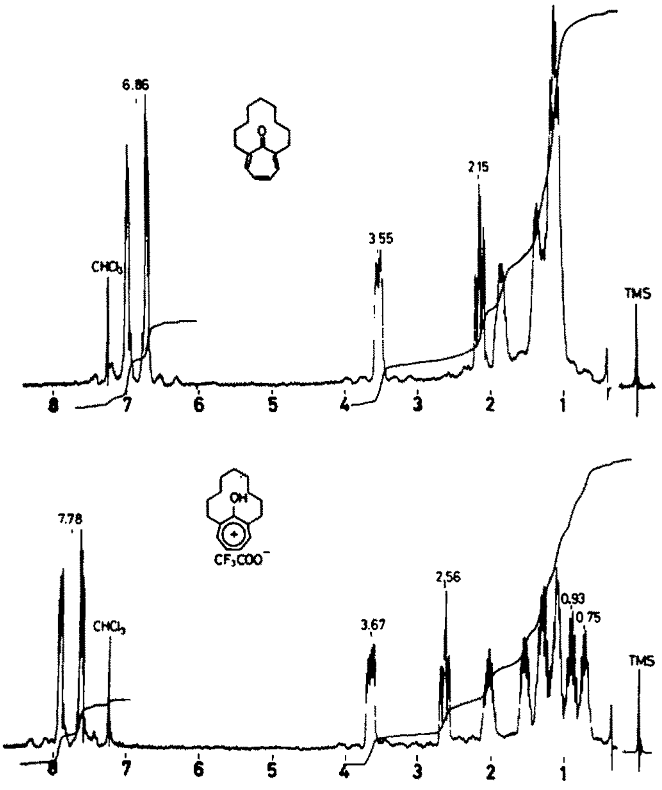
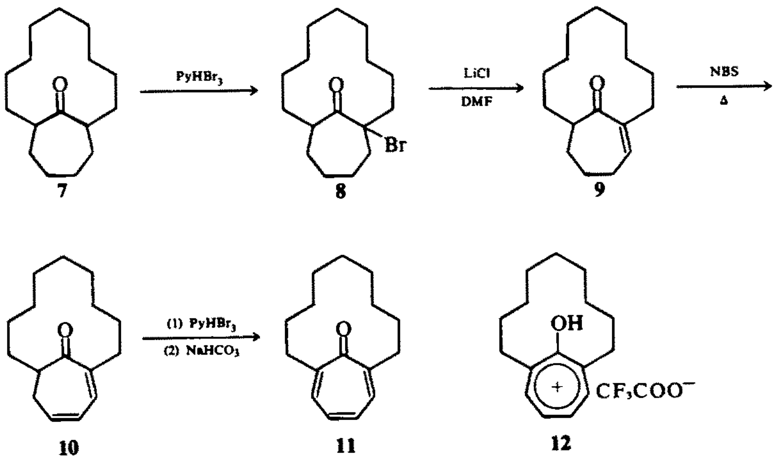


Fig 4. PMR of **11** (upper) and **12** (below) (220 MHz, CDCl₃, TMS, r.t.).



Mesylation of **6** by means of sodium hydride and methane-sulfonyl chloride, followed by reduction of the resulting sulfonate with sodium metal in liquid ammonia, yielded 12-methyl[9]metacyclophane (**15**) along with the recovered phenol **6**. The PMR spectrum (Experimental) clearly shows that the nonamethylene chain is swinging up and down the aromatic ring. The motion of the chain does not seem to be frozen even at −112°.*

*Reaction of **6** with halocarbenes*

Reactivity of the bridged phenol in the Reimer–Tiemann reaction deserves to be examined because the bridging effect and the accompanying

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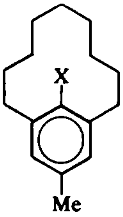
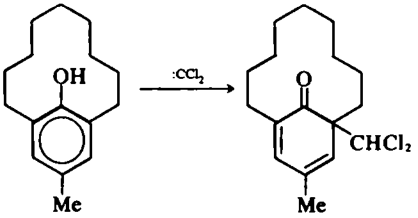
*[9]Metacyclophane has been obtained by G. Pagani (see Ref 18).

Table 1. CMR of **11** ($CDCl_3$, TMS standard, taken by Mr. Hirose, JEOL Co.)

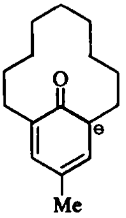
Peak No.	Chemical shift (ppm)	Height	Chemical shift (ppm)(CF_3COOH)	Height
1	23·297	3764	23·479	3543
2	23·600	6268	23·661	5621
3	26·452	6867	26·331	10576
4	26·634	8307		
5	36·705	6578	37·252	4275
6	130·746	7164	134·143	5237
7	132·809	6210	138·269	4027
8	150·100	2535	151·192	2149
9	188·808	1189	189·233	788



13: X = OMe
14: X = OAc
15: X = H



6 **16**



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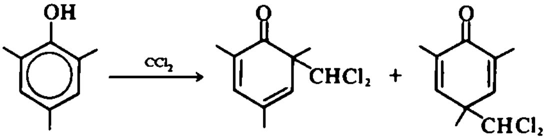
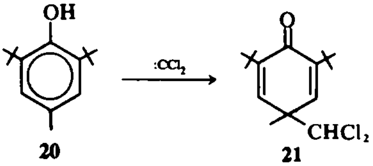
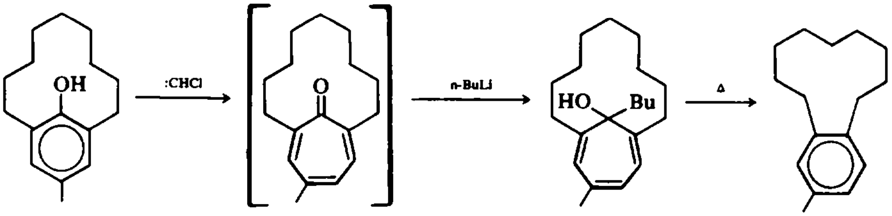
strain should affect the reaction course. Dichlorocarbene generated by use of the phase-transfer technique[19] reacted with **6** to yield the dienone **16**, whereas the less hindered phenol **17** gave a mixture (4:1) of **18** and **19**. The more hindered phenol **20** afforded cross-conjugated cyclohexadienone **21** exclusively, probably because the *ortho* positions are sterically hindered by two Bu groups. The fact that the bridged phenol **6** yielded only **16** may be ascribed to the constraint by the nonamethylene chain. The strained system* prefers sp^3 bridgehead



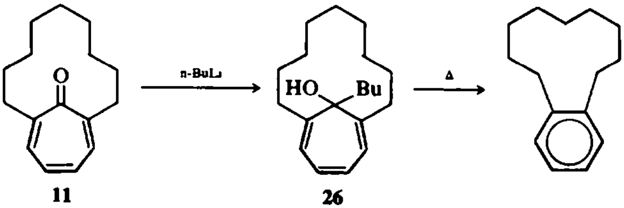
17 **18** **19**



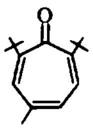
20 **21**



6 **23** **24** **25**



11 **26** **27**



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*The constraint is directed to the one side of the aromatic ring. The effect is also observed in the UV spectrum of **6** as a bathochromic shift (vide supra).

carbon rather than the planar sp^2 carbon. Thus the reaction proceeded between **22** and dichlorocarbene to yield only **16**.

The reaction of monochlorocarbene with the bridged phenol was studied to obtain the ring-expanded bridged tropone **23**. The phenol **6** in dichloromethane was treated with three equivalents of n-butyllithium, giving hydroxytropylidene (**24**). Gas-chromatographic separation (190–200°) of crude **24** caused the decomposition of the compound and the isolated product proved to be ortho–bridged toluene **25**. Supposedly the thermal fragmentation[21] is especially facilitated by the constraint of the nonamethylene chain. The reaction path was attested by the reaction of the bridged tropone **11** with n-butyllithium, followed by the thermolysis, affording benzocycloundecene (**27**), whereas the more hindered phenol **20** gave the ring-expanded tropone **28**. The subsequent nucleophilic addition of n-butyllithium to the CO group of **28** is possibly prevented by the neighbouring Bu groups.*

EXPERIMENTAL

PMR spectra were obtained on a JEOL C-60-H spectrometer (60 MHz), a Varian HA-100D spectrometer (100 MHz) or on a Varian HR-220 spectrometer (220 MHz) in CCl_4 or $CDCl_3$ soln. IR spectra were recorded on a Shimadzu IR-27-G spectrometer, mass spectra on a Hitachi RMU-6L machine and UV spectra on a Shimadzu MPS-50L. All temps are uncorrected.

Bicyclo[9.3.1]*pentadecan*-15-*one* (**2**). A mixture of xylene (28 ml) and **1** (12·7 g, 50 mmol) was added dropwise to the suspension of sodium hydride (2·40 g, 100 mmol) in xylene mixture (10 ml) at room temp (*ca* 45 min). After stirring was continued for 1 h trimethylene dibromide (10·0 g, 50 mmol) was added rapidly and the mixture was heated at 85–92° for 22 h. Work-up gave a viscous oil (9·10 g), which was dissolved in a mixture of AcOH (100 ml), water (40 ml) and conc H_2SO_4 (30 ml). Heating the solvent to reflux for 15 h, the subsequent work-up and fractional distillation at 103–105°/0·1 mm gave *cis* and *trans* mixture of **2** (3·76 g, 34%), which solidified on standing, m.p. 58–60° (MeOH). IR (Nujol): 1710, 1122, 1060, 740, 725 cm^{-1}; PMR (CCl_4): δ 0·5–3·1 (m); ms: *m/e* 222 (M^+). (Found: C, 81·1; H, 12·0%. $C_{15}H_{26}O$ requires: C, 81·0; H, 11·8%).

Bicyclo[9.3.1]-$\Delta^{1(14)}$-*pentadecen*-15-*one* (**3**). Pyridinium hydrobromide perbromide (775 mg, 2·4 mmol) was added to **2** (538 mg, 2·4 mmol) in AcOH (4 ml) at 50° under N_2. The mixture was heated at 70° for 20 h. Another crop of $PyHBr_3$ (500 mg) was added and the heating was continued for 2 days. Water was then added and the mixture was extracted with n-hexane. Evaporation of the solvent gave crystallines (710 mg). Recrystallization from MeOH gave 1-bromobicyclo[9.3.1]pentadecan-15-one (340 mg, 47%).

This compound was obtained by an alternative method. Br_2 (2·1 g, 0·7 ml, 13 mmol) was added to the soln of **2** (2·22 g, 10 mmol) in AcOH (6 ml) at room temp. After the addition was complete the mixture was heated at 70° for 24 h. Work-up gave a pale yellow oil (*ca* 2·8 g) which solidified. Recrystallization from MeOH afforded pale yellow needles (1·01 g, 34% yield), m.p. 84·0–84·5°. IR (Nujol): 1725 cm^{-1}; PMR ($CDCl_3$): δ 0·5–3·1 (m); ms: *m/e* 300 (M^+), 302 ($M^+ + 2$). (Found: C, 59·6; H, 8·5%. $C_{15}H_{25}BrO$ requires: C, 59·8; H, 8·4%).

The crystalline bicylic bromoketone (1·00 g, 3·3 mmol) was heated with LiCl (200 mg, 4·7 mmol) in DMF (12 ml) for 4·5 h at 93°. Work-up afforded an oil (660 mg, 88%) which was practically pure by GLC assay. Distillation at 120–125° (bath temp)/0·1 mm, followed by recrystallization from EtOH, gave an analytical sample, m.p. 67–68°. IR (neat): 1674, 783, 734 cm^{-1}; PMR (CCl_4): δ 1·0–3·0 (m, 23 H, methylenes and methine), 6·2–6·4 (m, 1 H, –CH=); ms: *m/e* 220 (M^+). (Found: C, 81·6; H, 10·8%. $C_{15}H_{24}O$ requires: C, 81·8; H, 11·0%).

15-*Hydroxy*[9]*metacyclophane* (**4**). The enone **3** (186 mg, 0·85 mmol) was heated under N_2 with S (28·6 mg, 0·89 mmol) at 160–200° for 30 min. Extraction with ether and the subsequent purification by preparative TLC (PLC) (silica gel, n-hexane elution, R_f 0·1–0·2) afforded the bridged phenol **4** (91 mg, 49% yield), b.p. 130–140° (bath temp)/0·07 mm. IR (CCl_4): 3650, 3040, 1588, 1190 cm^{-1}; IR (neat): 3570, 3040, 1590, 1190, 770, 745 cm^{-1}; ms: *m/e* (relative abundance) 218 (M^+, 82), 161 (28), 147 (33), 121 (61), 120 (100), 107 (53), 91 (46). (Found: *m/e* 218·1664 (M^+). $C_{15}H_{22}O$ requires: *m/e* 218·1671).

The exo-methylene ketone **5**. To a mixture of cyclododecanone (18·2 g, 0·1 mol) and sodium hydride (2·4 g, 0·1 mol) suspended in benzene (30 ml) 3-chloro-2-chloromethylpropene (12·5 g, 0·1 mol) was added all at once and the mixture was heated to boil for 3 days. Addition of water (100 ml), followed by extraction with n-hexane and subsequent work-up, gave **5** (8·2 g, 34%), b.p. 125–130°/2 mm, m.p. 53–58° (MeOH) (perhaps a mixture of *cis* and *trans* isomers). IR (Nujol): 3080, 1710, 1652, 890, 740 cm^{-1}; NMR (CCl_4): δ 0·6–2·9 (m, 24 H, methylenes and methines), 4·7–4·9 (m, 2 H, $=CH_2$); ms: *m/e* 234 (M^+). (Found: C, 81·9; H, 11·2%. $C_{16}H_{26}O$ requires: C, 82·0; 11·2%).

15-*Hydroxy*-12-*methyl*[9]*metacyclophane* (**6**). The ketone **5** (2·75 g, 11·8 mmol) was heated under N_2 with S (0·400 g, 12·5 mmol) at 200–220° for 4·5 h. The organic substances were taken into ether and distilled at 145–149°/0·5 mm, affording the crystalline bridged *p*-cresol **6** (1·39 g, 51%), m.p. 82–83° (n-hexane). IR (KBr): 3495, 3005, 1605, 1193, 836, 752, 722 cm^{-1}; IR (Nujol): 3475, 1191, 760 cm^{-1}; ms: *m/e* (relative abundance) 232 (M^+, 100), 161 (20), 147 (16), 135 (44), 134 (63), 121 (53), 91 (45). (Found: C, 82·6; H, 10·4%. $C_{16}H_{24}O$ requires: C, 82·7; H, 10·4%).

1-*Bromobicyclo*[9.4.1]*hexadecan*-16-*one* (**8**). The ketone **7** (664 mg, 2·81 mmol) was admixed with AcOH (7 ml) and $PyHBr_3$(1·02 g, 3·20 mmol) and the mixture was heated under N_2 at 60° for 44 h. When the mixture was cooled in an ice bath, white needles (715 mg, 81%) of **8** were obtained, m.p. 156–157° (acetic acid). IR (Nujol): 1710 cm^{-1}; PMR ($CDCl_3$): δ 0·7–3·3 (m); ms: *m/e* 314 (M^+), 316 ($M^+ + 2$). (Found: C, 60·9; H, 8·7%. $C_{16}H_{27}BrO$ requires: C, 61·0; H, 8·6%).

Bicyclo[9.4.1]-$\Delta^{1(15)}$-*hexadecen*-16-*one* (**9**). A mixture of **8** (823 mg, 2·61 mmol), LiCl (150 mg, 3·53 mmol), and DMF (11 ml) was heated at 130–140° for 13 h. Work-up yielded an oil (571 mg, 94%), b.p. 120–130° (bath temp)/0·08 mm. IR (neat): 1683, 1632 cm^{-1}; PMR (CCl_4): δ

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*Less hindered phenol, meisitol **17**, was recovered unchanged upon attempted reaction with monochlorocarbene under similar conditions. Steric hindrance to some extent appears prerequisite to this kind of ring-expansion.

0·8–3·2 (m, 25 H, methylenes and methines), 6·0–6·4 (AB quartet, J = 4·8, 9·0 Hz, 1 H, –CH=); ms: *m/e* 234 (M$^+$). (Found: C, 81·9; H, 11·2%. $C_{16}H_{26}O$ requires: C, 82·0; H, 11·2%).

2,7-*Nonamethylenetropone* (**11**). A soln of **9** (1·55 g, 6·64 mmol), NBS (1·55 g, 8·71 mmol), and a small amount (*ca* 10 mg) of benzoyl peroxide in CCl_4 (20 ml) was heated under N_2 at 85° for 6 h. After cooling in an ice bath the ppts were filtered off, and the soln was concentrated *in vacuo* by warming at 40° for 20 min. The residue was mixed with $PyHBr_3$ (2·30 g, 7·19 mmol) in AcOH (30 ml) and heated under N_2 for 1 h at 90–95°. Neutralization of the mixture with $NaHCO_3$aq, followed by extraction with benzene and the subsequent PLC purification (silica gel, benzene/n-hexane = 1/1 elution, R_f 0·4–0·6), afforded an oily **11** (535 mg, 35%). Distillation at 150–180°/0·2 mm, followed by recrystallization from n-hexane, yielded an analytical sample, m.p. 60–64·5°. IR (KBr): 1620, 1575, 1515, 1070, 790, 730 cm^{-1}; IR (neat): 1675, 1624, 1588, 1515, 1075, 795, 738 cm^{-1}; ms: *m/e* (relative abundance) 230 (M$^+$, 85), 173 (48), 159 (86), 147 (100), 145 (81), 134 (96), 120 (79), 107 (86), 105 (61), 91 (83); UV (EtOH): λ_{max} ($\log \epsilon$) 239 (4·31), 314 (3·78). (Found: C, 83·3; H, 9·8%. $C_{16}H_{22}O$ requires: C, 83·4; H, 9·6%).

Methyl ether of the bridged phenol **6**. To a suspension of sodium hydride (25 mg, 1·0 mmol) in THF the phenol **6** (232 mg, 1·0 mmol) in THF was added drop by drop. After 1 h MeI (0·2 ml) was added at room temp and the mixture was heated at 76° for 4 h. Usual work-up and distillation at 120–125° (bath temp)/2 mm gave **13** (212 mg, 86%), which solidified on standing, m.p. 61–62° (n-hexane). IR (neat): 1218, 1022 cm^{-1}; PMR (CCl_4): δ 0·2–3·4 (m + s (δ 2·23), 21 H, methylenes and methyl), 3·63 (s, 3 H, MeO-), 6·70 (s, 2 H, aromatic); ms: *m/e* 246 (M$^+$). (Found: C, 82·9; H, 10·5%. $C_{17}H_{26}O$ requires: C, 82·9; H, 10·6%).

Acetate of **6**. A mixture of **6** (260 mg, 1·14 mmol) and pyridine (3·5 ml) was added to sodium hydride (55 mg, 2·3 mmol). The resulting soln was stirred for 1 h, treated with Ac_2O (0·2 ml) and then heated to reflux for 2 h. Usual work-up yielded a solid **14** (213 mg, 71%), m.p. 85·5–86·5° (methanol). IR (Nujol): 1763, 1220, 1185, 905 cm^{-1}; PMR (CCl_4): δ 0·2–3·0 (m + two s (δ 2·20, 2·26), 24 H, methylenes and methyls), 6·71 (s, 2 H, aromatic); ms: *m/e* 274 (M$^+$). (Found: C, 79·0; H, 9·6%. $C_{18}H_{26}O_2$ requires: C, 78·8; H, 9·6%).

12-*Methyl*[9]*metacyclophane* (**15**). The phenol **6** (232 mg, 1·0 mmol) in THF (1 ml) was treated with sodium hydride (50 mg, 2·0 mmol) suspended in THF (1 ml). Methanesulfonyl chloride (150 mg, 1·3 mmol) was then added at room temp and the mixture was worked up after 13 h. The crude sulfonate (380 mg) was dissolved in THF (5 ml) and liq ammonia (50 ml), and Na metal (100 mg, 4·0 g-atom) was added at −78°. The soln was gradually warmed up to room temp until most of ammonia was evaporated. Usual work-up and the subsequent purification of the product on PLC (silica gel, n-hexane elution, R_f 0·45) gave **15** (90 mg, 75% yield based on the consumed **6**) along with the recovered phenol (R_f 0·15, 103 mg, 44%). The physical properties of **15** are as follows: b.p. 115–120°/0·06 mm; IR (neat): 3030, 1606, 838, 705 cm^{-1}; PMR (CCl_4): δ 0·5–2·3 (m, 14 H, methylenes), 2·30 (s, 3 H, Me), 2·65 (t, 4 H, benzylic methylenes), 6·68 (s, 2 H, C_{11}-H, C_{13}-H), 6·94 (s, 1 H, C_{15}-H); ms: *m/e* (relative abundance) 216 (M$^+$, 95), 201 (15), 173 (24), 159 (34), 145 (100), 131 (47), 120 (59), 119 (58), 118 (57), 105 (99), 91 (46). (Found: C, 88·8; H, 11·1%. $C_{16}H_{24}$ requires: C, 88·8; H, 11·2%).

Reaction of **6** *with dichlorocarbene*. To a mixture of **6** (223 mg, 1 mmol), Cetrimide (36 mg, 0·1 mmol) and chloroform (0·40 ml, 5 mmol) 50% NaOH aq (200 mg of NaOH and 0·2 ml water) was added dropwise (*ca* 13 min) under N_2 and vigorous stirring at 50°. Stirring was continued for 4 h (50–55°). The mixture was neutralized with dil HCl and extracted with ether. Work-up afforded **16** (240 mg, 76%), which was gas-chromatographically pure. Analytical sample was obtained by PLC (alumina, n-hexane elution, R_f 0·45–0·5) followed by recrystallization from EtOH, m.p. 127–129°. IR (KBr): 3040, 1655 (sh), 1646, 1228, 814, 770, 748, 720 cm^{-1}; PMR (CCl_4): δ 0·8–3·3 (m + d (δ 1·98, J = 1·2 Hz), 21 H, methylenes and methyl), 6·07 (s, 1 H, $-CHCl_2$), 6·37 (m, 1 H, –CH=), 6·69 (m, 1 H, –CH=); ms: *m/e* 314 (M$^+$), 316 (M$^+$ + 2), 318 (M$^+$ + 4); UV (EtOH): λ_{max} ($\log \epsilon$) 317 (3·35). (Found: C, 64·7; H, 7·6%. $C_{17}H_{24}Cl_2O$ requires: C, 64·8; H, 7·7%).

Reaction of the hindered phenol **20** *with dichlorocarbene*. The phenol **20** (220 mg, 1 mmol) was treated with $CHCl_3$ (0·4 ml, 5 mmol), 50% NaOH aq (0·25 ml, 5 mmol) and Cetrimide (4 mg, 0·01 mmol) as described above. Work-up, followed by PLC purification (silica gel, n-hexane elution, R_f 0·35–0·55), afforded white needles (235 mg, 78%) of **21**, m.p. 83–84° (EtOH). IR (Nujol): 1665, 1646, 1249, 928, 902, 880, 769, 731 cm^{-1}; PMR (CCl_4): δ 1·24 (s, 18 H, t-Bu), 1·40 (s, 3 H, Me), 5·54 (s, 1 H, $CHCl_2$), 6·44 (s, 2 H, –CH=); ms: *m/e* 302 (M$^+$), 304 (M$^+$ + 2), 306 (M$^+$ + 4). (Found: C, 63·4; H, 8·0%. $C_{16}H_{24}Cl_2O$ requires: C, 63·4: H, 8·0%).

Reaction of mesitol (**17**) *with dichlorocarbene*. Mesitol (545 mg, 4 mmol) was subjected to the dichlorocarbene reaction described as above. Work-up and the separation of the products by PLC (silica gel, n-hexane elution) gave **18** (236 mg, 59%, R_f 0·4–0·55) and the cross-conjugated cyclohexadienone **19** (67 mg, 17%, R_f 0·15–0·25).[22] IR (neat) of **18**: 1670 (sh), 1650, 1234, 889, 829, 786, 742 cm^{-1}; PMR (CCl_4) of **18**: δ 1·24 (s, 3 H, Me), 1·87 (s, 3 H, Me), 2·02 (d, J = 2·1 Hz), 3 H, Me), 5·94 (s, 1 H, $CHCl_2$), 6·14 (s, 1 H, –CH=), 6·65 (s, 1 H, –CH=). IR (neat) of **19**: 1670, 1638, 1210, 905, 778, 757 cm^{-1}; PMR (CCl_4) of **19**: δ 1·38 (s, 3 H, Me), 1·92 (s, 6 H, Me), 5·58 (s, 1 H, $CHCl_2$), 6·58 (s, 2 H, –CH=).

Reaction of **6** *with monochlorocarbene*. n-BuLi (3 mmol) in n-hexane was added dropwise (10 min) to the dichloromethane (4 ml) soln of **6** (232 mg, 1·0 mmol) at room temp under N_2. Stirring was continued for 5 h. Work-up followed by PLC purification (silica gel, benzene/n-hexane = 1/1 elution) yielded the recovered **6** (91 mg, 39%, R_f 0·50–0·65) and the bridged **24** (100 mg, 55% based on the consumed phenol, R_f 0·70–0·85), b.p. 145–150° (bath temp)/0·1 mm. IR (neat): 3640, 1684, 1630, 1210, 1128, 850, 810 cm^{-1}; PMR (CCl_4): δ 0·5–3·0 (m + s (δ 1·96), 31 H, methylenes, methyl and OH), 5·4–5·8 (ABM pattern, J_{AB} = 6·9 Hz, 3 H, –CH=); ms: *m/e* (relative abundance) 302 (M$^+$, trace), 245 (M$^+$-Bu, 57), 105 (100). Since the isolation of **24** in completely pure state failed due to instability to heat or to a trace of acid, satisfactory elemental analysis of the compound was not obtained.

Thermolysis of **24**. This was performed on a JEOL JGC 1100 (He gas, 0·55 kg/cm^2, injection temp 290°, detector temp 145°, column (SE 30, 25%, 1 m) temp 190°) gas-chromatograph, and the product **25** was collected, b.p. 110–115° (bath temp)/2 mm. IR (neat): 3050, 3010, 1611, 1500, 1348, 878, 810 cm^{-1}; PMR (CCl_4): δ 0·7–2·2 (m, 14 H, methylenes), 1·35 (s, 3 H, Me), 2·66 (t, J = 6·4 Hz, 4 H, benzylic), 6·7–7·0 (m, ABM pattern, J_{AB} = 7·9 Hz, 3 H, aromatic); ms: *m/e* (relative abundance) 216 (M$^+$, 63), 145

(52), 119 (100), 118 (53), 105 (40). Found: C, 89·1; H, 11·4%. $C_{16}H_{24}$ requires: C, 88·8; H, 11·2%.

The collection of the more volatile component (C_5) was futile.

Benzocycloundecene (**27**). The bridged tropone **11** (230 mg, 1 mmol) was treated with n-BuLi (1·5 mmol). Work-up gave a bridged **26**. IR (neat): 3640, 3550, 3040, 1645, 1130, 748 cm^{-1}; PMR (CCl_4): δ 0·6–3·2 (m, 18 H, methylenes and OH), 5·7–6·3 (m, A_2B_2 pattern, 4 H, –CH=); ms: *m/e* 288 (M^+). (Found: *m/e* 288·2457 (M^+). $C_{20}H_{32}O$ requires: *m/e* 288·2453.)

The hydroxytropylidene **26** was thermolyzed as above. An oily product **27** (26%) was obtained, b.p. 115–120° (bath temp)/3 mm. IR (neat): 3070, 3020, 1493, 750 cm^{-1}; PMR (CCl_4): δ 0·6–1·9 (m, 14 H, methylenes), 2·56 (t, J = 6·0 Hz, 4 H, benzylic), 6·72 (br s, 4 H, aromatic); ms: *m/e* (relative abundance) 202 (M^+, 72), 131 (63), 118 (54), 105 (100), 104 (91), 91 (49). (Found: *m/e* 202·1737 (M^+). $C_{15}H_{22}$ requires: *m/e* 202·1722.)

2,7-Di-t-butyl-4-methyltropone (**28**). This was obtained by the reaction of 2,6-di-t-butyl-4-methylphenol (110 mg, 0·5 mmol), n-BuLi (1·5 mmol) and dichloromethane (2 ml) at −78°. Work-up and the subsequent PLC purification yielded **28** (45 mg, 39% yield) along with an unidentified product (39 mg). IR (neat) of **28**: 3010, 1635, 1615, 1483, 1377, 1363, 1261, 872, 839, 820 cm^{-1}; PMR (CCl_4): δ 1·31 (s, 18 H, tBu), 2·18 (s, 3 H, Me), 4·2–4·8 (m, ABM pattern, J_{AB} = 6·4 Hz, 3 H, =CH–); ms: *m/e* 232 (M^+). (Found: C, 82·5; H, 10·5%. $C_{16}H_{24}O$ requires: C, 82·7; H, 10·4%).

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