

Cyclobutarenes. Part 1. Synthesis of Cyclobutanaphthalene and Phenanthrene Derivatives

Michael K. Shepherd

Department of Pharmacology, University of Bristol, Bristol BS8 1TD

Preparations of 1,2-bis(dibromomethyl)naphthalene (**7**) and 9,10-bis(dibromomethyl)phenanthrene (**8**) are described; reaction of these compounds with sodium iodide at 60 °C gives 1,2-dibromo-1,2-dihydrocyclobuta[*a*]naphthalene (**3**) and 1,2-dibromo-1,2-dihydrocyclobuta[*l*]phenanthrene (**4**). 2,3-Bis(dibromomethyl)naphthalene (**5**) cyclises at 120 °C to give 1,2-dibromo-1,2-dihydrocyclobuta[*b*]naphthalene (**2**) and 6,13-dihydro-6,13-ethenopentacene (**10**).

The most convenient route to 1,2-dihydrobenzocyclobutenes probably remains that discovered by Finkelstein,¹ and subsequently developed by Cava and co-workers.^{2,3} 1,2-Bis(dibromomethyl)benzene is treated with sodium iodide at 60–70 °C to generate the quinomethane 5,6-bis(bromomethylene)cyclohexa-1,3-diene, which then undergoes a concerted cyclisation to 1,2-dibromo-1,2-dihydrobenzocyclobutene (**1**). The dibromide (**1**) is readily reduced to the hydrocarbon,⁴ or debrominated to the reactive intermediate, benzocyclobutene.^{2,3}

This method has not been extended to the synthesis of the naphthalene and phenanthrene analogues (**2**)–(**4**); derivatives of these systems have been prepared by a variety of more laborious routes.^{3,5} 2,3-Bis(dibromomethyl)naphthalene (**5**) is decomposed by sodium iodide at 60–70 °C, although the quinomethane (**15**) has recently been trapped at 90 °C with 1,4-naphthoquinone.⁶ The tetrabromo precursors to (**3**), (**4**) are not described in the literature; prolonged reaction of 1,2-dimethylnaphthalene with *N*-bromosuccinimide gave 1-bromomethyl-2-dibromomethylnaphthalene, and not the tetrabromide (**7**).⁷

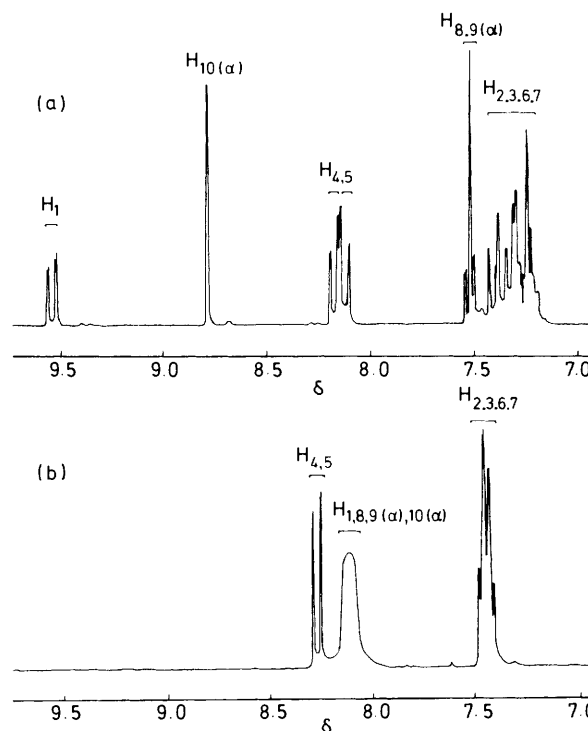
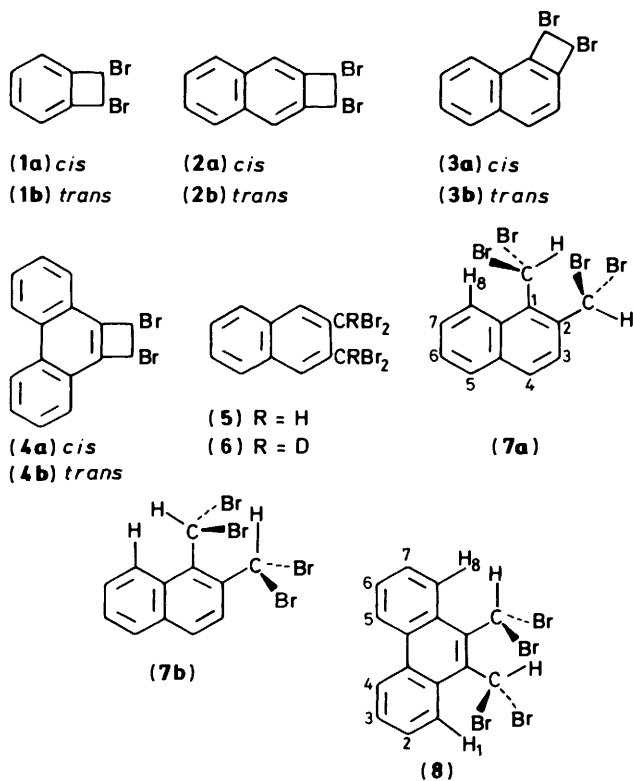


Figure 1. ¹H N.m.r. spectrum of (**8**) in [10-²H]-*o*-xylene (a) at 25 °C, (b) at 135 °C

Results and Discussion

Photobromination of 1,2-dimethylnaphthalene for 24 h gave 1,2-bis(dibromomethyl)naphthalene (**7**). Formation of 1-bromomethyl-2-dibromomethylnaphthalene under these conditions is rapid (< 1 h), but introduction of the fourth bromine atom is retarded by steric hindrance from 8-H and the 2-dibromomethyl group. Similarly, photobromination of 9,10-dimethylphenanthrene for 36 h gave the tetrabromide (**8**). The steric congestion in these compounds becomes obvious upon examination of their ¹H n.m.r. spectra. Thus, the spectrum of phenanthrene (**8**) in CDCl₃ shows signals at δ 7.75 (m, 2-, 3-, 6-, 7-H), 8.00 (s, 9 α -H), 8.07 (dd, 8-H), 8.55 (s, 10 α -H), 8.74 (m, 4-, 5-H), and 9.31 (dd, 1-H) due to restricted rotation of the adjacent dibromomethyl groups. Both 1-H and 10 α -H are shifted to lowfield by the through-space deshielding influence of the 'enveloping' bromine atoms. The temperature dependence of this effect was monitored in 10-²H *o*-xylene (Figure 1). The spectrum at 25 °C shows slight differences to that in CDCl₃,

Table. ^1H and ^{13}C N.m.r. spectra

	Compd.					
	(2a)	(2b)	(3b) ^a	(4b)	(9a)	(9b) ^b
1-H (δ)	5.99 (s)	5.59 (s)	5.71 (s)	5.76 (s)	7.35 (m)	8.15 (m)
2						
3	7.67 (s)	7.69 (s)	7.29 (d)	7.91 (m)	7.35 (m)	7.35 (m)
4	7.85 (m)	7.85 (m)	7.93 (d)	7.64 (m)		
5	7.48 (m)	7.50 (m)	7.61 (m)	8.61 (m)	7.79 (m)	7.79 (m)
6						
7	7.85 (m)	7.85 (m)	7.95 (m)	7.64 (m)	7.35 (m)	7.35 (m)
8	7.67 (s)	7.69 (s)	7.61 (m)		8.15 (m)	8.15 (m)
9				7.91 (m)		
10						
9 (α)					6.61 (s)	6.48 (s)
10 (α)					6.85 (s)	
C-1 (δ')	51.0	49.4	49.5	49.9	127.2	129.1
2						
3	122.1	122.0	119.8	124.0	128.2	
4	128.8	128.8	129.9	128.0	123.9	b
5	126.4	126.4	133.1	127.4		
6						
7	128.8	128.8	127.9	123.0	128.2	
8	122.1	122.0	122.2	127.4	129.1	
9				127.4	124.1	
10				128.0		
10 α				124.0		
					103.5	102.7
					107.0	

^a ^{13}C Signals assigned by comparison with 1,2-dimethylnaphthalene: D. K. Dalling, K. H. Ladner, D. M. Grant, and W. R. Woolfenden, *J. Am. Chem. Soc.*, 1977, **99**, 7142. ^b Signal obscured by isomer (9a).

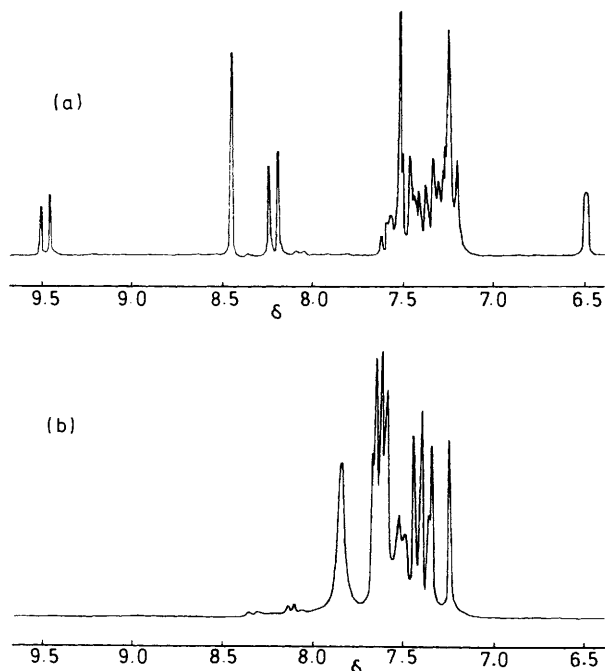


Figure 2. ^1H N.m.r. spectrum of (7) in $[8\text{-}^2\text{H}]\text{toluene}$ (a) at 25 °C, (b) at 100 °C

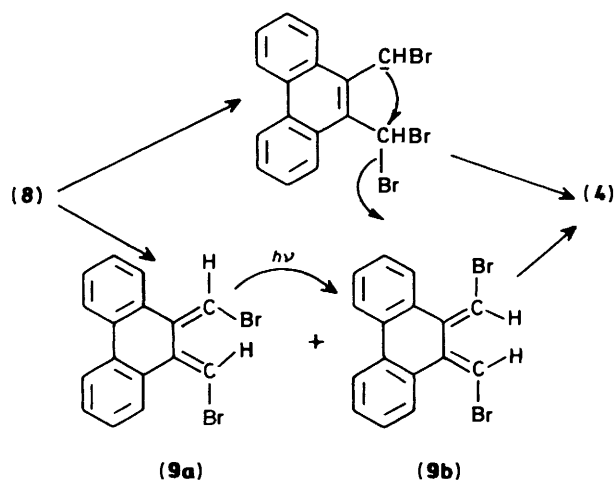
notably the lowfield shift of the 10 α -H singlet, and the highfield shift of the phenanthrene protons 2—8-H. Coalescence occurs at 105 °C ($\Delta G^\ddagger = 73.5 \text{ kJ mol}^{-1}$),⁸ and free rotation is observed at 135 °C.

The spectrum of 1,2-bis(dibromomethyl)naphthalene (7) is more complex (Figure 2), and at least two isomers [*i.e.* (7a) and

(7b)] appear to be present. These could not be separated, but by comparison with (8), signals at δ 8.46 and 9.47 are assigned to 1 α -H and 8-H (7a), respectively. The temperatures required for coalescence (t_c ca. 80 °C, ΔG^\ddagger ca. 70 kJ mol^{-1}) and free rotation (100 °C) reflect the lower degree of hindrance in this molecule.

Reaction of the phenanthrene (8) with sodium iodide in DMF at 55—60 °C gave, after removal of iodine-containing impurities,⁹ *trans*-1,2-dibromo-1,2-dihydrocyclobuta[*l*]phenanthrene [CBP, (4b)] in 62% yield. The *cis*-isomer (4a) was not found. In some experiments the *EZ*-quinomethane (9a), distinguished by singlets in the ^1H n.m.r. spectrum at δ 6.61 and 6.85, could also be detected. Debromination of (8) with zinc in THF gave a 2:1 mixture of the *EZ* and *EE*-quinomethanes (9a,b) in quantitative yield. N.m.r. data for these, and cyclised products, are listed in the Table. The *EE*-isomer (9b) undergoes conrotatory cyclisation to *trans*-CBP (4b) fairly rapidly at 25 °C ($t_{1/2}$ ca. 3 h in CDCl_3), and this may be further indication of the steric constraints imposed by the 1,8-hydrogens. The *EZ*-isomer (9a) did not cyclise thermally, even on prolonged heating, and polymerised above 120 °C. It therefore appears that the predominant pathway to (4b) is not concerted, and may instead involve the participation of a carbanionoid intermediate (Scheme 1). Photoirradiation of the *EZ*-quinomethane (9a) in CCl_4 gave (4b), probably *via* isomerisation to (9b) rather than by an excited state disrotatory ring closure; this readily affords (4b) from (8) in >95% yield. Investigations into this and related cyclisations are continuing.

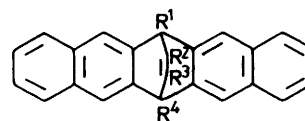
Cyclisation of 1,2-bis(dibromomethyl)naphthalene (7) at 60—65 °C gave a mixture of bromo- and iodo-dihydrocyclobuta[*a*]naphthalenes in 60—70% yield. Attempts to remove the iodo compounds by treatment with $\text{Br}_2\text{-CCl}_4$ ⁹ resulted in decomposition. The major dibromo component is probably the *trans*-isomer (3b), the n.m.r. spectrum showing no discernible coupling between 1-H and 2-H. Quinomethane intermediates could not be isolated.



Scheme 1.

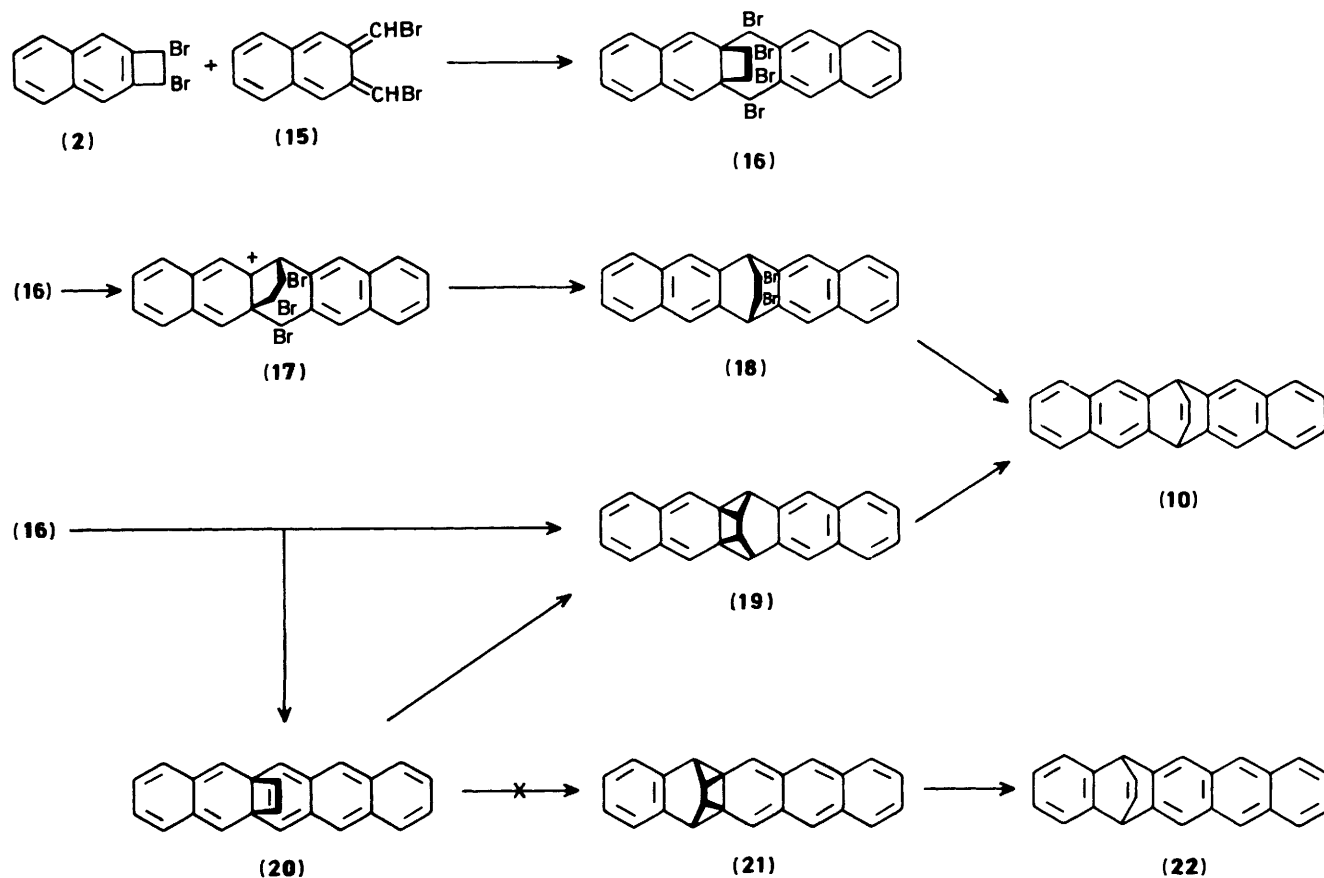
All attempts to cyclise 2,3-bis(dibromomethyl)naphthalene (5) at 60–70 °C were unsuccessful, giving polymeric products. Traces of *cis*- and *trans*-1,2-dibromo-1,2-dihydrocyclobuta[*b*]naphthalenes (CBN, 2a and b) formed at 90 °C, and an optimum yield (*ca.* 20%) was obtained at 120 °C. A third product, 6,13-dihydro-6,13-ethenopentacene (10) (dinaphthobarrelene) was also formed at the higher temperature—apparently by a novel dimerisation and dehalogenation of the quinomethane (15). The barrelene (10) was identified by its n.m.r. spectra: δ_{H} 5.30 (m, 6-, 13-H), 7.02 (m, 15-, 16-H), 7.36 (m, 2-, 3-, 9-, 10-H), 7.70 (m, 1-, 4-, 8-, 11-H), and 7.71 (s, 5-, 7-, 12-,

14-H); δ_{C} 50.1 (C-6, -13), 121.2 (C-5, -7, -12, -14), 125.5 (C-2, -3, -9, -10), 127.4 (C-1, -4, -8, -11), 138.2 (C-15, -16), 131.8 and 142.1 (quaternary carbons). The proton spectrum closely resembles that published for dibenzobarrelene.¹⁰ The mass spectrum shows peaks at 304 (M^+ , 100%) and 152 (M^{2+} , 7%). This rearrangement has been investigated in detail.



- (10) $R^1, R^2, R^3, R^4 = \text{H}$
 (11) $R^1, R^4 = \text{H}, R^2, R^3 = \text{D}$
 (12) $R^2, R^3 = \text{H}, R^1, R^4 = \text{D}$
 (13) $R^1, R^2, R^3, R^4 = \text{D}$
 (14) $R^1, R^2 = \text{H}, R^3, R^4 = \text{D}$

Reduction of dimethylnaphthalene-2,3-dicarboxylate with LiAlD_4 , followed by treatment with PBr_3 , and then *N*-bromosuccinimide, gave 2,3-bis(dibromodeuteriomethyl)naphthalene (6) in 55% overall yield. A 'crossed' reaction between (5) and (6) gave the barrelenes (10–13). ^1H N.m.r. showed that the AA'XX' multiplets due to 6- and 13-H and 15- and 16-H (10) were enhanced by singlets for 6- and 13-H (11) and 15- and 16-H (12). An AX system, indicative of the isomer (14), was not observed. In a second experiment, reaction between (6) and CBN (2) gave 6,13-dideuterio-6,13-ethenopentacene (12) as the only detectable product, the absence of the tetradeuterio isomer (13) showing that reaction between the quinomethane (15) and

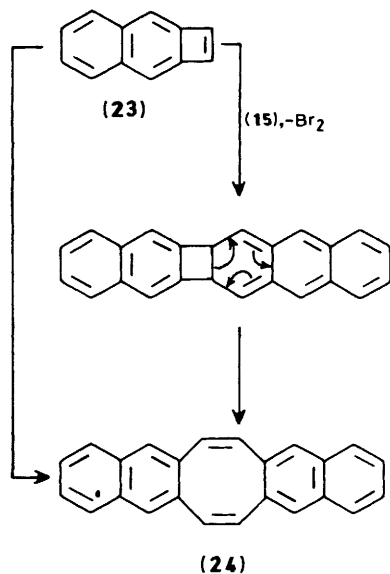


Scheme 2.

CBN (2) is more rapid than cyclisation of (15) to (2). The initial step appears to involve attack of the quinomethane (15) at the 2a(8a)-CBN double bond. This is unexpected, on account of the low bond-order predicted for this position,¹¹ and is attributed to the strain release on conversion of the cyclobutene ring to the propellane intermediate (16). Two mechanisms can be proposed for the subsequent rearrangement of (16) to the barrelene (10) (Scheme 2). The first involves a series of 1,2-shifts *via* cationic intermediates, driven by the combined benefits of ring expansion and rearomatisation, leading to the formation of the dibromide (18). Cava *et al.* have proposed a similar mechanism for the rearrangement of 1,4,9,10-tetrahydro-4a,9a-ethanoanthracene-9,10-diol to 9,10-dihydro-9,10-ethanoanthracene.¹² The second possibility requires formation of the hydrocarbon (19), either directly from (16) or *via* (20). 5,14-Dihydro-5,14-ethenopentacene (22) was not detected amongst the reaction products, but this does not necessarily preclude participation of (20); the naphthoquinomethane (21) would be a higher energy species than the quinomethane (19).

Note that cyclobuta[*b*]naphthalene (23) does not appear to be an intermediate in this process: debromination of a mixture of (5) and CBN (2), under the conditions described by Barton *et al.*,¹³ gave cyclo-octa[1,2-*b*:5,6-*b'*]dinaphthalene (24) (Scheme 3). Treatment of CBN (2) with sodium iodide at 140 °C also gave the cyclo-octene (24)—either *via* dimerisation of (23),¹⁴ or by a two-step coupling; this reaction is too slow at 120 °C to compete with the formation of the barrelene (10).

No barrelene derivatives were formed on treating (7), (8), or 1,2-bis(dibromomethyl)benzene with sodium iodide at 120 °C, possibly owing to the lower reactivity of the respective quinomethanes.



Scheme 3.

Experimental

I.r. spectra were run as Nujol mulls. ¹H N.m.r. spectra were recorded on a JEOL JNM FX200 spectrometer, and ¹³C n.m.r. spectra on a JEOL JNM FX90Q spectrometer, as solutions in deuteriochloroform containing 1% tetramethylsilane as an internal standard. Mass spectra were obtained on an AEI MS902 instrument. T.l.c. was performed using Kieselgel HF₂₅₄₊₃₅₄ (Merck), and column chromatography using silica gel M.F.C. (Hopkin and Williams). 9,10-Dimethylphenanthrene¹⁵ and 2,3-bis(dibromomethyl)naphthalene⁷ were prepared by literature routes.

1,2-Bis(dibromomethyl)naphthalene (7).—A solution of 1,2-dimethylnaphthalene (2.0 g) and bromine (9.2 g) in carbon tetrachloride (125 ml) was refluxed over a 200 W light bulb for 24 h. The solution was cooled, washed with aqueous sodium hydrogen carbonate, dried, and evaporated to give the crude tetrabromide (7) 2.45 g, 40%, m.p. 152–153 °C (after 3 recrystallisations from CHCl₃-EtOH) (Found: C, 30.3; H, 1.7; Br, 68.0. C₁₂H₈Br₄ requires C, 30.5; H, 1.7; Br, 67.8%); ν_{\max} . 1132 and 741 cm⁻¹; m/z 472 (M^+ , 5%), 393,391 (8), 312 (15), 233,231 (60), and 152 (100); n.m.r. spectra, see text. *N*-Bromosuccinimide can be used in place of bromine, this gave a higher yield (52%). Use of a less powerful light source necessitates longer reaction times.

9,10-Bis(dibromomethyl)phenanthrene (8).—Photobromination of 9,10-dimethylphenanthrene (1.0 g) with bromine (3.2 g) in carbon tetrachloride (125 ml) for 36 h gave, after working up as described for (7), the tetrabromide (8) (2.2 g, 87%), m.p. 233–234 °C (from CHCl₃) (Found: C, 36.7; H, 1.9; Br, 61.3. C₁₆H₁₀Br₄ requires C, 36.8; H, 1.9; Br, 61.3%); ν_{\max} . 1130, 745, and 706 cm⁻¹; m/z 522 (M^+ , 1%), 443,441 (6), 362 (17), 283,281 (55), and 202 (100).

1,2-Dibromo-1,2-dihydrocyclobuta[1]phenanthrene (4).—A solution of the tetrabromide (8) (1.0 g) and sodium iodide (2.0 g) in DMF (20 ml) was stirred at 55–60 °C for 8 h. The black solution was cooled, extracted into ether, and washed with 10% aqueous sodium metabisulphate, followed by water. The solution was dried and evaporated to give a solid mixture of bromo and iodo compounds (0.65 g), m.p. 140–160 °C. This crude product was dissolved in carbon tetrachloride (50 ml) containing bromine (1.0 g), and kept at room temperature (preferably in sunlight) for 48 h. The solution was washed as above, dried, and evaporated to give the *trans*-dibromide (4b) (0.43 g, 62%), m.p. 156–157 °C (from CHCl₃-EtOH) (Found: C, 52.8; H, 2.7; Br, 44.5. C₁₆H₁₀Br₂ requires C, 53.0; H, 2.8; Br, 44.2%); ν_{\max} . 1204, 1191, 777, and 742 cm⁻¹; m/z 362 (M^+ , 43%), 283,281 (62), and 202 (100).

EE- and EZ-9,10-Bis(bromomethylene)phenanthrenes (9a,b).—A solution of the tetrabromide (8) (0.5 g) in THF (15 ml) was shaken with activated zinc² (*ca.* 2 g) until reaction ceased (1–2 min). The solution was decanted into ether, washed with water (\times 5), dried, and evaporated to give a 2:1 mixture of the quinomethanes (9a,b) (0.34 g, 98%) as a colourless oil. These could not be separated. A solution of (9a,b) in ethanol deposited, over a period of several days, *trans*-CBP (4b). Evaporation of the filtrate gave the pure *EZ*-isomer (9a) as a glassy oil (Found: C, 53.0; H, 2.7; Br, 44.2. C₁₆H₁₀Br₂ requires C, 53.0; H, 2.8; Br, 44.2%); m/z 362 (M^+ , 14%), 283,281 (48), and 202 (100).

Photocyclisation of (9a,b).—A solution of the quinomethanes (9a,b) (0.2 g) in carbon tetrachloride (50 ml) was refluxed over a 100 W light bulb for 5 h. Evaporation of the solvent gave *trans*-CBP (4b) (0.2 g, 100%), identical with the material prepared above.

1,2-Dibromo-1,2-dihydrocyclobuta[*a*]naphthalene (3).—Reaction of the tetrabromide (7) (1.5 g) and sodium iodide (3.0 g) in DMF (25 ml) at 60–65 °C for 10 h, followed by work-up as described for (4), gave a mixture of bromo and iodo compounds (0.7 g, *ca.* 70%), m.p. 65–90 °C. Recrystallisation from ethanol gave the dibromide, probably the *trans*-isomer (3b) (0.35 g, 35%), m.p. 97–98 °C (Found: C, 46.1; H, 2.6; Br, 51.6. C₁₂H₈Br₂ requires C, 46.2; H, 2.6; Br, 51.3%); ν_{\max} . 1198, 1176, 821, and 759 cm⁻¹; m/z 312 (M^+ , 35%), 233,231 (47), and 152 (100).

Reaction of 2,3-Bis(dibromomethyl)naphthalene (5) with Sodium Iodide.—Sodium iodide (30 g) was added over a period of 1 min to a stirred solution of the tetrabromide (5) (10 g) in DMF (50 ml) at 120 °C. The mixture was stirred for a further 2 min after which it was worked up, as described for (4), to give a brownish gum (3.25 g). Chromatography on a silica column, using 3% chloroform in light petroleum (b.p. 40–60 °C) as eluant, gave a mixture of bromo- and iodo-dihydrocyclobuta[*b*]naphthalenes (1.62 g, see below). Further elution gave 6,13-dihydro-6,13-ethenopentacene (10) (0.35 g, 11%), m.p. 267–268 °C (from CHCl₃–EtOH) (Found: C, 94.7; H, 5.3. C₂₄H₁₆ requires C, 94.7; H, 5.3%); ν_{\max} 881, 750, and 685 cm⁻¹; n.m.r. and mass spectra, see text. Purification of the dibromo product in carbon tetrachloride with bromine, as described for (4), gave after chromatography on silica in light petroleum, *trans*-1,2-dibromo-1,2-dihydrocyclobuta[*b*]naphthalene (2b) (1.23 g, 19%), m.p. 128–130 °C (from EtOH) (lit.,¹⁶ 130–131 °C); followed by the *cis*-isomer (2a) (0.19 g, 3%), m.p. 162–163 °C (from CHCl₃–EtOH) (Found: C, 45.9; H, 2.4; Br, 51.6%; M^+ , 311.8972. C₁₂H₈Br₂ requires C, 46.2; H, 2.6; Br, 51.3%; M , 311.8972); ν_{\max} 902 and 764 cm⁻¹; m/z 312 (M^+ , 7%), 233, 231 (39), and 152 (100).

2,3-Bis(dibromodeuteriomethyl)naphthalene (6).—Reduction of dimethylnaphthalene-2,3-dicarboxylate (4.1 g) with LiAlD₄ (1.0 g) in ether (100 ml), followed by acidification, washing, and evaporation of the organic phase, gave naphthalene-2,3-[$\alpha,\alpha,\alpha',\alpha'$ -²H₄]dimethanol (2.23 g, 73%), m.p. 159–160 °C (from CHCl₃).¹⁷ The diol (1.0 g) in ether (50 ml) was treated with PBr₃ (3.5 g) at 0 °C, stirred for 15 min, and poured onto ice. The organic phase was washed with aqueous sodium hydrogen carbonate, dried, and evaporated to give 2,3-bis-(bromodideuteriomethyl)naphthalene (1.7 g, 96%), m.p. 164–165 °C (from heptane) (Found: C, 45.5; H, 4.3; Br, 50.5. C₁₂D₄H₆Br₂ requires C, 45.3; H, 4.4; Br, 50.3%). The dibromide (1.0 g), *N*-bromosuccinimide (1.15 g), and benzoyl peroxide (10 mg) were refluxed in carbon tetrachloride (50 ml) for 6 h. The mixture was cooled, succinimide was filtered off, and the mixture was evaporated to give the tetrabromide (6) (1.17 g, 78%), m.p. 158–160 °C (from CHCl₃–EtOH) (Found: C, 30.4; H, 1.9; Br, 67.4. C₁₂D₂H₆Br₄ requires C, 30.4; H, 2.1; Br, 67.5%); δ 7.53 (m, 6-, 7-H), 7.85 (m, 5-, 8-H), and 8.17 (s, 1-, 4-H).

Reaction of Compounds (5) and (6) with Sodium Iodide.—Treatment of a solution of the tetrabromides (5) (0.5 g) and (6) (0.5 g) in DMF (15 ml) at 120 °C with sodium iodide (2.0 g), as described above, gave a yellow gum (0.2 g). Preparative t.l.c. with light petroleum (b.p. 40–60 °C) gave a mixture of cyclised products (85 mg), followed by a mixture of the *barrelenes* (10)—(13) (9 mg, ca. 3%), m/z 308 (48%), 307 (46), 306 (100), 305 (67), 304 (71), and 303 (30).

6,13-Dideuterio-6,13-ethenopentacene (12).—Treatment of a solution of the tetrabromide (6) (0.5 g) and CBN (2) (0.5 g) in DMF (10 ml) at 120 °C with sodium iodide (2.0 g), followed by

work-up and preparative t.l.c. as described above, gave a mixture of bromo- and iodo-cyclobuta[*b*]naphthalenes (0.35 g). This was followed by the *barrelene* (12) (27 mg, 8%), m.p. 265–267 °C (Found: M^+ , 306.1374. C₂₄D₂H₁₄ requires M , 306.1378); δ 7.02 (2 H, m, 15-, 16-H), 7.36 (4 H, m, 2-, 3-, 9-, 10-H), 7.70 (4 H, m, 1-, 4-, 8-, 11-H), and 7.71 (4 H, s, 5-, 7-, 12-, 14-H); δ_c 121.2 (C-5, -7, -12, -14), 125.5 (C-2, -3, -9, -10), 127.4 (C-1, -4, -8, -11), 138.2 (C-15, -16), 131.8, and 142.1 (quaternary carbons); m/z 306 (M^+ , 100%) and 153 (10).

Cyclo-octa[1,2-b:5,6-b']dinaphthalene (24).—(a) Zinc (2 g) was added to a well-stirred solution of the tetrabromide (5) (1.0 g) and CBN (2) (0.65 g) in DMF (15 ml) at 100 °C. When the exothermic reaction subsided the mixture was cooled, extracted into ether, and the extract washed, dried, and evaporated to give a gummy solid. Recrystallisation gave the cyclo-octene (24) (0.37 g, 58%), m.p. 249–250 °C (from CHCl₃–heptane) (lit.,¹⁴ 244–244.5 °C).

(b) A solution of CBN (2) (0.25 g) and sodium iodide (1.0 g) in DMF (5 ml) was heated at 140 °C for 6 h. Work-up in the usual manner gave the cyclo-octene (24) (95 mg, 78%), identical with the sample obtained above.

Acknowledgements

The author thanks the referees for helpful comments.

References

- H. Finkelstein, Ph.D thesis, Strasbourg, 1909; *Chem. Ber.*, 1959, **92**, xxxvii.
- M. P. Cava and D. R. Napier, *J. Am. Chem. Soc.*, 1957, **79**, 1701.
- M. P. Cava and M. J. Mitchell, 'Cyclobutadiene and Related Compounds,' Academic Press, New York and London, 1967, and references therein.
- M. P. Cava and D. R. Napier, *J. Am. Chem. Soc.*, 1958, **80**, 2255.
- Rodd's 'Chemistry of Carbon Compounds,' Supplement III F and G, Elsevier Science Publishers B.V., Amsterdam, 1984, and references therein.
- J. Laduranty, L. Lepage, and Y. Lepage, *Can. J. Chem.*, 1980, **58**, 1161.
- W. Ried and H. Bodem, *Chem. Ber.*, 1956, **89**, 708.
- R. K. Harris, 'N.M.R. Spectroscopy,' Pitman Books Ltd, London, 1983.
- M. E. Cracknell, M. C. Goodland, and J. F. W. McOmie, *Bull. Chem. Soc. Jpn.*, 1983, **56**, 965.
- J. C. Muller and J. Vergne, *C.R. Acad. Sci. Paris*, 1966, **263C**, 1452.
- J. L. Crawford and R. E. Marsh, *Acta. Crystallogr., Sect. B*, 1973, **29**, 1238.
- M. P. Cava and R. L. Shirley, *J. Org. Chem.*, 1961, **26**, 2212.
- J. W. Barton, D. V. Lee, and M. K. Shepherd, *J. Chem. Soc., Perkin Trans. 1*, 1985, 1407.
- M. P. Cava and An-Fei C. Hsu, *J. Am. Chem. Soc.*, 1972, **94**, 6441.
- R. DeRidder and R. H. Martin, *Bull. Soc. Chim. Belg.*, 1960, **69**, 534.
- J. Rigaudy and D. Sparfel, *Tetrahedron*, 1978, **34**, 113.
- P. Dizabo, M. F. Mouneyrac, and B. Pasquier-Chenon, *J. Labelled Compd.*, 1966, **2**, 272.

Received 18th April 1985; Paper 5/641