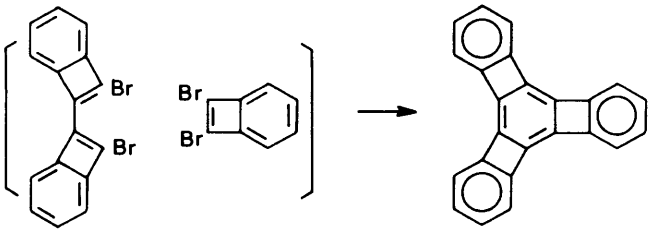
Synthesis and Rearrangements of 1,1′-Bi(benzocyclobutylidene) and its Derivatives

John W. Barton* and Michael K. Shepherd
School of Chemistry, University of Bristol, Cantock's Close, Bristol BS8 1TS

Convenient new preparations of 1-halogeno-1,2-dihydrobenzocyclobutenes (**5**) and (**6**) and 1,1′-bi(benzocyclobutylidene) (**4**) are described. The hydrocarbon (**4**) is susceptible to cationic rearrangements: it forms 5,10-dihydroindeno[2,1-*a*]indene (**16**) on protonation in acetic anhydride, and is oxidised by selenium(IV) oxide to a mixture of the spiroketone (**17**) and 5*H*-indeno[1,2-*c*]-[2]benzopyran-2-one (**18**). The mechanisms of these and other rearrangements are discussed.

A recent communication by Diercks and Vollhardt describes the synthesis of dibenzo[3,4:3′,4′]dicyclobuta[1,2-*a*:1′,2′-*c*]-biphenylene (**3**), a molecule containing a central bond-localised 'cyclohexatriene' ring.[1] Our earlier attempts to prepare this system by flash vacuum thermolysis of benzo[1,2-*c*:3,4-*c*′:5,6-*c*″]-tricinnoline were unsuccessful, the central ring undergoes a [2 + 2 + 2] retrocyclisation at the high temperatures required to effect nitrogen extrusion.[2]

1,2,3,4,5,6-Hexahydrobenzo[*a*,*c*,*e*]tricyclobutene has been prepared independently by the research groups of Thummel[3] and Garratt,[4] the key steps utilising cycloaddition reactions of the diene 1,1′-bi(cyclobutenyl). This prompted us to reason that it might be possible to extend our approach to polycyclic biphenylenes, *via* cycloaddition of 1,2-dibromobenzocyclobutene (**1**) with *o*-quinodimethane and other dienes,[5] to the synthesis of the biphenylene (**3**) by reaction of (**1**) with 2,2′-dibromo-1,1′-bi(benzocyclobutenyl) (**2**) (Scheme 1). A potential precursor to the diene (**2**), 1,1′-bi(benzocyclobutylidene) (**4**), has been prepared by Dürr *et al.*[6] Pyrolysis of the sodium or lithium salts of the tosylhydrazone of benzocyclobuten-1(2*H*)-one gave a low yield of the *E*- and *Z*-isomers of (**4**). Dimethyl[7] and tetramethyl[8] derivatives of (**4**) have been prepared by a similar method. Our ultimate goal—the synthesis of the biphenylene (**3**)—has not been achieved, but in this paper we describe a facile route to (**4**), and some novel rearrangements of this compound.



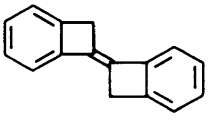
(2) (1) (3)

Scheme 1.

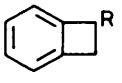
Results and Discussion

In order to prepare 1,1′-bi(benzocyclobutylidene) (**4**) on a multi-gram scale we decided to investigate the Wittig reaction between the triphenylphosphine salt of 1-bromo-1,2-dihydrobenzocyclobutene (**7**) and benzocyclobuten-1(2*H*)-one. The triphenylphosphine salt (**7**) has been reported,[9] but no reactions were described. 1-Halogeno-1,2-dihydrobenzocyclobutenes have been prepared by halogenation of 1,2-dihydrobenzocyclobutene,[10,11] by pyrolytic methods,[12,13] and by reaction of dihalogenocarbenes with cycloheptatriene;[9,14] these reactions either give low yields or require special techniques. Several groups have described the preparation of 1,2-dihydrobenzocyclobutene derivatives by cycloaddition of benzyne to substituted alkenes,[15–21] and we find that this is the method of choice for the preparation of 1-chloro- and 1-bromo-1,2-dihydrobenzocyclobutenes (**5**) and (**6**). Decomposition of benzenediazonium-2-carboxylate in a 1,2-dichloroethane solution of vinyl bromide gave compound (**6**) in 40% yield [the bromide (**6**) can readily be prepared on a 20 g scale by this procedure]. A similar reaction using vinyl chloride gave the chloride (**5**) in 24% yield, the lower yield can probably be attributed to the low boiling point of the alkene component.

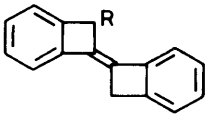
A reaction of the bromide (**6**) with triphenylphosphine in dry toluene gave the phosphonium salt (**7**) in 90% yield. A Wittig reaction of salt (**7**) with benzocyclobuten-1(2*H*)-one in THF gave a 1:1 mixture of the hydrocarbons (**4a**) and (**4b**) in quantitative yield. These compounds could not be separated by chromatography or fractional crystallisation [Dürr *et al.* have separated (**4a**) and (**4b**) by preparative g.l.c.];[6] unless stated otherwise all reactions described below were performed on the isomeric mixture. Pure samples were obtained by manual separation of crystals, giving the *E*-isomer (**4a**), m.p. 178—181 °C, and the *Z*-isomer (**4b**), m.p. 124—126 °C. The spectra of (**4a**) and (**4b**) were virtually indistinguishable, the assignment proposed being on the basis that the *trans*-isomer should have the higher melting point.



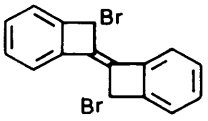
(4a) *E*-isomer
(4b) *Z*-isomer



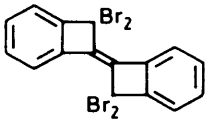
(5) R = Cl
(6) R = Br
(7) R = $\overset{+}{P}Ph_3Br$



(8a) R = Br, *E*-isomer
(8b) *Z*-isomer
(12a) R = Bu^{t}O, *E*-isomer
(12b) *Z*-isomer

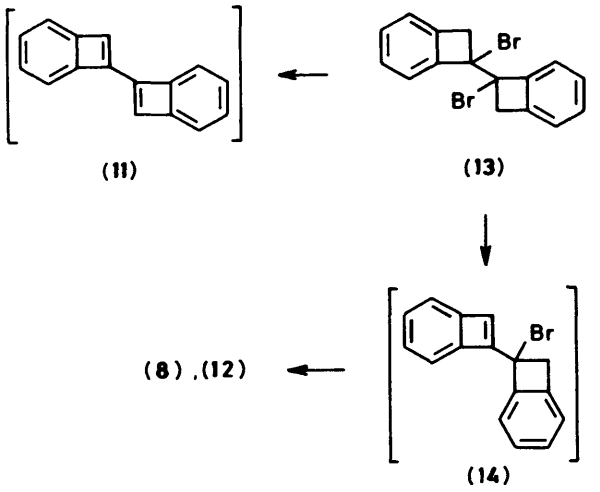


(9)



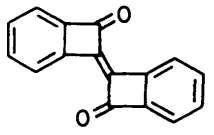
(10)

The reaction of (**4**) in benzene with 2 equiv. of *N*-bromosuccinimide gave a mixture of *E*- and *Z*-monobromides (**8a**) and (**8b**) (49%) and a highly insoluble 2,2′-dibromide (**9**) (6%). The stereochemistry of these compounds has not been established, and attempts to improve the yield of (**9**) were unsuccessful. The monobromides (**8a**) and (**8b**) can be separated by fractional crystallisation. Bromination of (**4**) in CCl_4 or C_6H_6 with 4 equiv. of *N*-bromosuccinimide proved unexpectedly difficult, and was accompanied by polymerisation (Cava has suggested that polymer formation during 1,2-dihydrobenzocyclobutene bromination may be due to generation of benzocyclobutene).[10] No tetrabromide (**10**) could be detected. Attempts to generate the reactive bi(benzocyclobutenyl) intermediate (**11**) from the bromides (**8**) and (**9**) failed: treatment of



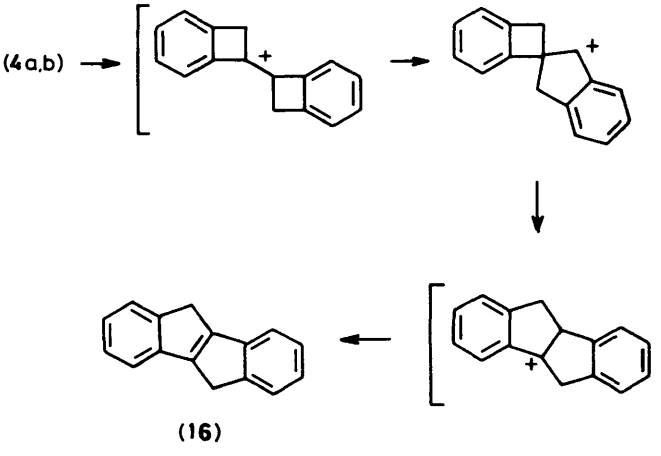
Scheme 2.

the monobromides with potassium t-butoxide in a range of solvents gave the corresponding t-butyl ethers (**12**), *via* S_N2 displacement, in high yield. The bromide (**6**) is dehydrobrominated to benzocyclobutene under these conditions;[10] our failure to observe (**11**) presumably reflects the higher energy of this species. The dibromide (**9**) is debrominated by zinc, but adducts were not formed with dienophiles such as *N*-phenylmaleimide or maleic anhydride. A reaction of 1,1′-dibromo-1,1′,2,2′-tetrahydro-1,1′-bi(benzocyclobutenyl) (**13**), prepared by bromination of (**4**) in CCl_4, with potassium t-butoxide gave a mixture of the bromides (**8a**) and (**8b**) and ethers (**12a**) and (**12b**), rather than the diene (**11**). Use of 1,8-diazabicyclo[5.4.0]undec-7-ene as the base gave (**8a**) and (**8b**) in quantitative yield, this provides a much more convenient route to the monobromides than that described above. The mechanism of this rearrangement is unclear. A possible pathway involves formation of the monobenzocyclobutene (**14**), followed by an unusual [1,3]-intramolecular bromine migration (Scheme 2). However (**14**), if formed, could not be trapped with dienes.



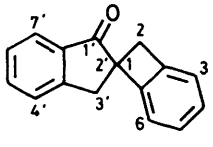
(**15a**) *E*-isomer
(**15b**) *Z*-isomer

1,1′-Bi(benzocyclobutylidene) (**4**) undergoes a rapid rearrangement in acetic anhydride containing sulphuric acid to 5,10-dihydroindeno[2,1-*a*]indene (**16**), the reaction proceeding by a sequence of 1,2-carbonium ion shifts (Scheme 3). Oxidation of (**4**) with selenium(IV) oxide in acetic acid or ethanol failed to give either of the diketones (**15a**) or (**15b**). Instead two

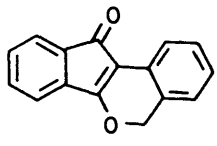


Scheme 3.

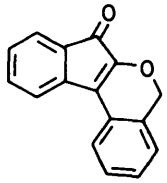
rearranged products were isolated, the colourless spiroketone (**17**) (30%), and a red crystalline compound $C_{16}H_{10}O_2$ (26%). Further oxidation of the ketone (**17**) did not give this second product, and a reaction using a pure sample of the *E*-isomer (**4a**) gave the same ratio of products. We propose the structure (**18**) for the red crystalline product on the basis of spectroscopic evidence. The i.r. spectrum shows carbonyl absorption at 1 719 cm^{-1}, typical for indenones,[22] and a strong C–O stretching vibration at 1 139 cm^{-1}. The ^1H n.m.r. spectrum shows only aromatic protons (8 H, m) at δ7.01—7.68, and a singlet (2 H) typical of cyclic benzyl ethers at δ5.2.[23] The ^{13}C n.m.r. spectrum shows eight tertiary aromatic carbons, one carbonyl carbon at δ188.9, and one secondary carbon (CH_2O) at δ70.4. Furthermore, the colour of compound (**18**) implies the presence of a chromophore such as indenone—the indenoisocoumarin (**20**) has been isolated as orange crystals.[24] Formation of the isomer (**19**) appears less likely on mechanistic grounds, and this isomer can also be excluded by the absence of the lowfield signals characteristic of the 'bay' protons in the ^1H n.m.r. spectrum. The



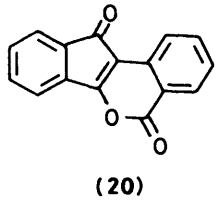
(**17**)



(**18**)

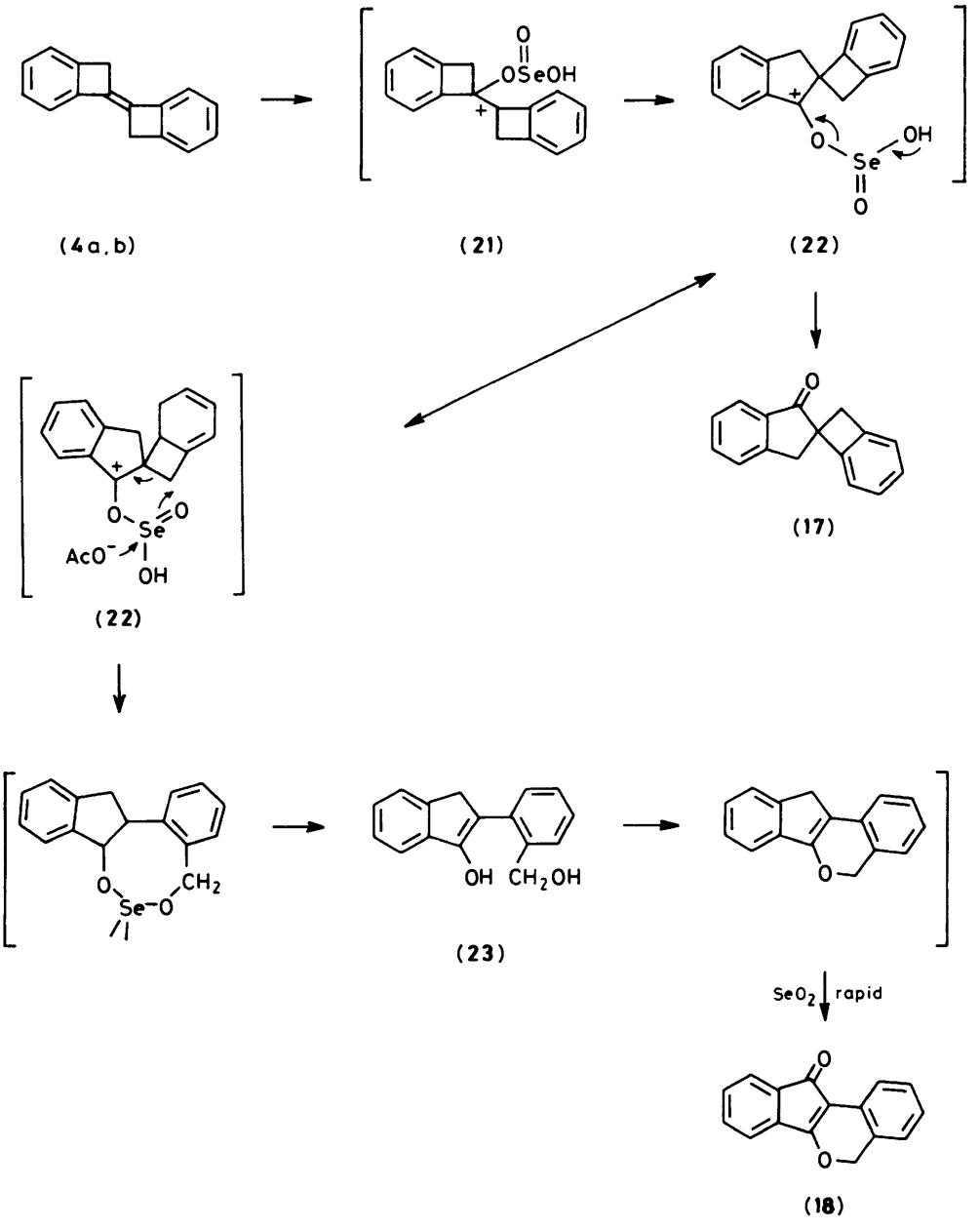


(**19**)



(**20**)

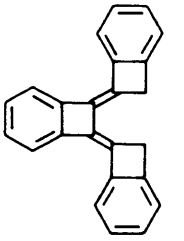
'bay' protons 1-H and 10-H in 7*H*-benzo[*c*]fluorene resonate at δ8.6 and 8.2 respectively, whereas the corresponding 6-H and 7-H in 11*H*-benzo[*a*]fluorene give signals at δ7.7 and 7.6.[25] A possible mechanism for this rearrangement is illustrated in Scheme 4. Both compounds (**17**) and (**18**) probably form *via* carbonium ion rearrangements following initial formation of the selenite(IV) ester (**21**) [a selenium(II) ester is also possible].



Scheme 4.

The rearrangement of intermediate (**22**) is speculative—a second molecule of SeO_2 may be involved—but it seems likely that the diol (**23**) (or a derivative) is a precursor to (**18**). 1*H*-2-Benzopyran has been prepared by cyclisation of a similar intermediate.[26] Attempts to oxidise the ketone (**18**) to the diketone (**20**) using selenium(IV) oxide or ruthenium(VIII) oxide[27] resulted in decomposition.

A Wittig reaction between the salt (**7**) and benzocyclobutene-1,2-dione gave a 1:1 mixture of the *Z,Z* and *E,Z* isomers of bis(benzocyclobutylidene)benzocyclobutene (**24a**) and (**24b**); these could not be separated by fractional crystallisation or by chromatography under the conditions tried. This ratio of products, and the absence of the hindered *E,E*-isomer, reflects the observations of structural isomerism in 1,2-bis(benzylidene)benzocyclobutene and its derivatives by Blomquist and Hruby.[28] The methylene protons in the *Z,Z*-isomer (**24a**) resonate as a singlet at δ3.80, whereas those in the *E,Z*-isomer



(**24a**) *Z,Z*-isomer

(**24b**) *E,Z*-isomer

(**24b**) show singlets of equal intensity at δ3.85 and 4.09. The signals due to the aromatic protons in both isomers coincide as a complex multiplet in the range δ7.13—7.40. This compound decomposes slowly in solution, forming a fluorescent polymer.

Experimental

Unless otherwise stated the following conditions apply. Organic extracts were dried over sodium sulphate or magnesium sulphate. ^{1}H N.m.r. spectra were recorded on a JEOL JNM FX200 spectrometer as Nujol mulls, and ^{13}C n.m.r. spectra on a JEOL JNM FX90Q spectrometer, as solutions in deuteriochloroform containing 1% tetramethylsilane as internal standard. Mass spectra were obtained on an AEI MS902 instrument. Benzocyclobuten-1(2*H*)-one[21] and benzocyclobutene-1,2-dione[29] were prepared by literature methods.

1-*Chloro*-1,2-*dihydrobenzocyclobutene* (**5**).—A suspension of benzenediazonium-2-carboxylate (prepared from 7.0 g of anthranilic acid)[30] in 1,2-dichloroethane (200 ml) containing vinyl chloride (12.5 g) was stirred and heated to reflux. A solid CO_2 trap was necessary to prevent loss of vinyl chloride. Gas evolution commenced at *ca.* 45 °C. When this had ceased, the dark solution was refluxed for 10 min. and the solvent distilled off, leaving a pungent brown oil. This was chromatographed on alumina, using light petroleum (b.p. 40—60 °C) as eluant, to give 1-chloro-1,2-dihydrobenzocyclobutene (**5**) (3.2 g, contaminated with biphenylene). Distillation (65 °C at 3 Torr) gave a pure sample (1.7 g, 24%).

1-*Bromo*-1,2-*dihydrobenzocyclobutene* (**6**).—A suspension of benzenediazonium-2-carboxylate (prepared from 35 g of anthranilic acid)[30] in 1,2-dichloroethane (500 ml) containing vinyl bromide (100 mg) was stirred and heated to reflux. An ice–ethanol trap was necessary to prevent loss of vinyl bromide. When gas evolution ceased the solution was refluxed for 30 min., and then worked up as described for (**5**) above, to give 1-bromo-1,2-dihydrobenzocyclobutene (**6**) as a colourless aromatic liquid (19.1 g, 40%).

1,1′-*Bi*(*benzocyclobutylidene*) (**4**).—Butyl-lithium in hexane (1.45M; 7.8 ml) was added under nitrogen to a stirred suspension of the phosphonium salt (**7**) (5.0 g) in dry tetrahydrofuran (THF) (125 ml) at 25 °C, forming a deep red solution. After 5 min benzocyclobuten-1(2*H*)-one (1.33 g) in dry THF (10 ml) was added dropwise, and the resulting pale yellow solution refluxed for 15 min. The solvent was removed under reduced pressure, and the pink residue extracted with hot light petroleum (b.p. 60—80 °C) (3 × 100 ml). The combined extracts were evaporated to *ca.* 50 ml, cooled, and the crystalline mixture of isomers (**4a**) and (**4b**) filtered off (2.30 g, 100%), m.p. 120—160 °C (from EtOH) (Found: C, 94.3; H, 5.9. $C_{16}H_{12}$ requires C, 94.1; H, 5.9%). Manual separation of crystals gave the individual isomers (**4a**), m.p. 178—181 °C; δ3.80 (4 H, s, 2,2,2′,2′-H) and 7.19 (8 H, s, 3—6, 3′—6′-H); δ_C 37.6 (2,2′-CH_2), 118.8, 122.7, 127.5, 128.1 (CH, ArH), and 127.4, 144.9, and 145.0 (quaternary carbons); $\nu_{max.}$ 1 350, 1 000, 759, and 719 cm^{-1}; *m/z* (%) 204 (M^+, 96), 203 (100), and 202 (89); and (**4b**), m.p. 124—126 °C; δ3.70 (4 H, s, 2,2,2′,2′-H) and 7.26 (8 H, s, 3—6, 3′—6′-H); δ_C 36.6 (2,2′-CH_2), 119.2, 122.6, 127.5, 127.9 (CH, ArH), and 144.6 and 144.8 (quaternary carbons); $\nu_{max.}$ 1 000 and 750 cm^{-1}; *m/z* (%) 204 (M^+, 100), 203 (92), and 202 (92).

Reaction of Compound (**4**) *with* N-*Bromosuccinimide*.—(i) A solution of compound (**4**) (1.0 g) and *N*-bromosuccinimide (1.75 g) in benzene (100 ml) was refluxed over a 100 W light bulb for 45 min. The resulting brown solution was passed down a short silica column to remove succinimide and *N*-bromosuccinimide residues, and evaporated to *ca.* 25 ml. Filtration gave 2,2′-*dibromo*-1,1′-*bi*(*benzocyclobutylidene*) (**9**) (100 mg, 6%), m.p. 269—270 °C (sublimes >180 °C) (stereochemistry not established) (Found: M^+, 361.9117. $C_{16}H_{10}Br_2$ requires *M*, 361.9129); δ($^2H_8$ toluene) 5.51 (2 H, s, 2,2′-H) and 7.01—7.28 (8 H, m, 3—6, 3′—6′-H); *m/z* (%) 362 (M^+, 14), 283, 281 (16), and 202 (100). Evaporation of the filtrate followed by crystallisation of the residue (from EtOH, 25 ml) gave a mixture of the *monobromides* (**8a**) and (**8b**) (0.69 g, 50%), m.p. 80—95 °C (Found: C, 67.8; H, 3.9; Br, 28.2. $C_{16}H_{11}Br$ requires C, 67.8; H, 3.9; Br, 28.3%). Fractional crystallisation from ethanol gave samples of the pure isomers (stereochemistry not established): m.p. 99—100 °C; δ 3.85 (2 H, dd, 2′,2′-H), 5.89 (1 H, s, 2-H), and 7.17—7.46 (8 H, m, ArH); δ_C 36.2 (C-2′), 45.5 (C-2), 119.6, 119.8, 122.4, 122.8, 127.8, 128.9, 129.0, 130.7 (CH, ArH), and 129.7, 143.0, 143.8, 145.3, and 146.2 (quaternary carbons); $\nu_{max.}$ 1 350, 1 139, 791, and 746 cm^{-1}; *m/z* (%) 284, 282 (M^+, 23), 203 (96), and 202 (100); and m.p. 117—120 °C; δ 3.86 (2 H, s, 2,2′-H), 5.85 (1 H, s, 2-H), and 7.20—7.42 (8 H, m, ArH); δ_C 37.4 (C-2′), 45.9 (C-2), 119.5, 121.4, 122.6, 127.9, 128.9, 129.1, and 130.7 (CH, ArH); $\nu_{max.}$ 1 496, 1 361, 1 159, 803, and 760 cm^{-1}; *m/z* (%) 284, 282 (M^+, 31), 203 (94), and 202 (100). Carbon tetrachloride can be used instead of benzene as a solvent for this reaction, this gives a lower yield (35%) of the monobromides (**8a**) and (**8b**).

(ii) A suspension of compound (**4**) (100 mg) and *N*-bromosuccinimide (365 mg) in carbon tetrachloride or benzene (50 ml) was refluxed as above for 48 h. Decomposition occurred, but no tetrabromide (**10**) could be detected.

1,1′-*Dibromo*-1,1′,2,2′-*tetrahydro*-1,1′-*bi*(*benzocyclobutenyl*).—A solution of compound (**4**) (0.5 g) in carbon tetrachloride (30 ml) was treated with bromine (0.4 g) and the solvent removed under reduced pressure. Crystallisation of the oil so obtained gave the *title compound* (**13**) (0.88 g, 99%), as a mixture of two isomers, m.p. 80—90 °C (Found: C, 53.0; H, 3.5; Br, 43.8. $C_{16}H_{12}Br_2$ requires C, 52.8; H, 3.3; Br, 44.0%); δ 3.74 (4 H, m, 2,2,2′,2′-H) and 7.04—7.37 (8 H, m, ArH); $\nu_{max.}$ 990, 761, 741, and 715 cm^{-1}; *m/z* (%) 364 (M^+, 2), 285, 283 (3), and 202 (100).

Reaction of Compound (**13**) *with Base*.—(i) A solution of compound (**13**) (2.0 g) in t-butyl alcohol (50 ml) containing potassium t-butoxide (2.0 g) was refluxed for 12 h. The suspension was cooled, poured onto ether, and washed with 10% aqueous hydrochloric acid. It was then dried and evaporated to give a gum which was chromatographed on alumina using 1% EtOAc in light petroleum (b.p. 40—60 °C) as eluant. This gave 2-bromo-1,1′-bi(benzocyclobutylidene) (**8a**) and (**8b**) (350 mg, 23%) (both isomers, properties as described above), followed by 2-*t-butoxy*-1,1′-*bi*(*benzocyclobutylidene*) (**12a**) and (**12b**) (530 mg, 40%) (both isomers), m.p. 120—130 °C (Found: C, 86.9; H, 7.2%; M^+, 276.1517. $C_{20}H_{20}O$ requires C, 87.0; H, 7.2%; M^+, 276.1514). Fractional crystallisation (from EtOH–H_2O) gave the individual isomers (stereochemistry not established), m.p. 133—134.5 °C; δ 1.38 (9 H, s, Bu^t), 3.77 (2 H, dd, 2′,2′-H), 5.53 (1 H, s, 2-H), and 7.19—7.39 (8 H, m, ArH); $\nu_{max.}$ 1 200, 1 168, 1 070, 1 055, and 761 cm^{-1}; *m/z* (%) 276 (M^+, 9), 220 (75), 219 (100), 191 (78), 84 (63), and 57 (40); and m.p. 140—141 °C; δ 1.45 (9 H, s, Bu^t), 3.80 (2 H, s, 2′,2′-H), 5.48 (1 H, s, 2-H), and 7.19—7.25 (8 H, m, ArH); $\nu_{max.}$ 1 171, 1 074, and 778 cm^{-1}; *m/z* (%) 276 (M^+, 14), 220 (90), 219 (100), and 191 (72).

(ii) A solution of compound (**13**) (100 mg) and 1,8-diazabicyclo[5.4.0]undec-7-ene (30 mg) in propan-2-ol (10 ml) were refluxed for 6 h. The solution was cooled and worked up as described above to give a mixture of the monobromides (**8a**) and (**8b**) (75 mg, 97%), identical with the sample prepared above. A reaction in the presence of 1,3-diphenylisobenzofuran gave only the monobromides (**8a**) and (**8b**), no adducts being detected.

5,10-*Dihydroindeno*[2,1-a]*indene* (**16**).—Sulphuric acid (1 drop) was added to a stirred solution of the hydrocarbon (**4**)

(100 mg) in acetic anhydride (10 ml). After being stirred for several min. the mixture was poured onto ether, and neutralised with aqueous sodium hydrogen carbonate. The solution was dried and evaporated to give the title compound (**16**) (63 mg, 63%), m.p. 200—201 °C (from EtOH) (lit.,[31] 204—208 °C); δ 3.57 (4 H, s, 5,5,10,10-H) and 7.15—7.76 (8 H, m, ArH).

Reaction of Compound (**4**) *with Selenium*(IV) *Oxide*.—A solution of (**4a**) and (**4b**) (1.0 g) and selenium(IV) oxide (1.0 g) in acetic acid was refluxed for 40 min., cooled, filtered, and the solvent removed under reduced pressure. The residue was dissolved in ether, and the solution washed with 5% aqueous sodium hydrogen carbonate. The organic phase was dried, evaporated, and chromatographed on alumina, using 10% ethyl acetate in light petroleum (b.p. 40—60 °C) as the eluant. This gave *spiro*[*benzocyclobutene*-1(2H),2′-*inden*]-1′(3′H)-*one* (**17**) (320 mg, 30%), m.p. 84—86 °C [from light petroleum (b.p. 80—100 °C)] (Found: C, 87.1; H, 5.3. $C_{16}H_{12}O$ requires C, 87.3; H, 5.5%); δ 3.44 (2 H, dd, 3′-CH_2), 3.61 (2 H, s, 2-CH_2), and 6.84—7.85 (8 H, m, ArH); δ_C 38.0 (3′-CH_2), 41.8 (2-CH_2), 120.4—135.0 (CH, ArH), and 58.6, 136.1—152.3, 205.7 (quaternary carbons); $\nu_{max.}$ 1 720, 1 615, 922, 781, 742, and 720 cm^{-1}; *m/z* (%) 220 (M^+, 100), 191 (57), and 189 (26); 2,4-*dinitrophenylhydrazone* derivative: orange crystals, m.p. 195—197 °C; *m/z* (%) 400 (M^+, 30). Further elution gave 5H-*indeno*[1,2-c][2]*benzopyran*-11-*one* (**18**) (300 mg, 26%) as deep red crystals, m.p. 144—146 °C (from EtOH–H_2O) (Found: C, 81.9; H, 4.1. $C_{16}H_{10}O_2$ requires C, 82.0; H, 4.3%); ^{1}H n.m.r., see text; δ_C 70.4 (CH_2O), 120.2—133.9 (CH, ArH), and 140.8, 149.5, and 188.9 (quaternary carbons); $\nu_{max.}$($CHBr_3$) 1 720, 1 620, 1 446, 1 139, 1 032, 1 000, and 765 cm^{-1}; *m/z* (%) 234 (M^+, 100), 205 (17), and 178 (70); 2,4-*dinitrophenylhydrazone* derivative: black rods, m.p. 270—272 °C (sublimes >250 °C); *m/z* (%) 414 (M^+, 11). Ethanol can also be used as the solvent for this reaction, this gives only traces of (**18**).

1,2-*Bis*(1,2-*dihydrobenzocyclobut*-1-*ylidene*)-1,2-*dihydrobenzocyclobutene* (**24**).—A Wittig reaction between the salt (**7**) (5.0 g) and benzocyclobutene-1,2-dione (0.75 g) as described for (**4**) gave, after chromatography on silica using dichloromethane–light petroleum (b.p. 40—60 °C) (1:1) as eluant, the *title compound* (**24**) (0.45 g, 26%), m.p. 155—165 °C, as a mixture of isomers which could not be separated (Found: C, 94.6; H, 5.3. $C_{24}H_{16}$ requires C, 94.7; H, 5.3%); ^{1}H n.m.r., see text; $\nu_{max.}$ 1 145, 985, 722, and 671 cm^{-1}; *m/z* (%) 304 (M^+, 33), 303 (28), and 100 (100).

References

1 R. Diercks and K. P. C. Vollhardt, *J. Am. Chem. Soc.*, 1986, **108**, 3150.
2 J. W. Barton and M. K. Shepherd, *Tetrahedron Lett.*, 1984, **25**, 4967.
3 W. Nutakul, R. P. Thummel, and A. D. Taggart, *J. Am. Chem. Soc.*, 1979, **101**, 770.
4 C. W. Doecke, P. J. Garratt, Hooshang Shahriari-Zavareh, and R. Zahler, *J. Org. Chem.*, 1984, **49**, 1412.
5 J. W. Barton, M. K. Shepherd, and R. J. Willis, *J. Chem. Soc., Perkin Trans. 1*, 1986, 967.
6 H. Dürr, H. Nickels, L. A. Pacala, and M. Jones, *J. Org. Chem.*, 1980, **45**, 973.
7 M. A. O'Leary and D. Wege, *Tetrahedron Lett.*, 1978, 2811.
8 H. Durr, H. Nickels, and W. Philippi, *Tetrahedron Lett.*, 1978, 4387.
9 M. R. DeCamp and L. A. Viscogliosi, *J. Org. Chem.*, 1981, **46**, 3918.
10 M. P. Cava and D. R. Napier, *J. Am. Chem. Soc.*, 1958, **80**, 2255.
11 L. Horner, W. Kirmse, and K. Muth, *Chem. Ber.*, 1958, **91**, 430.
12 P. Schiess, M. Heitzmann, S. Rutschmann, and R. Stäheli, *Tetrahedron Lett.*, 1978, 4569.
13 P. Schiess, S. Rutschmann, and A. Vien Toan, *Tetrahedron Lett.*, 1982, 3665.
14 A. P. Ter Borg and A. F. Bickel, *Recl. Trav. Chim. Pays-Bas*, 1961, **80**, 1217.
15 H. H. Wasserman and J. Solodar, *J. Am. Chem. Soc.*, 1965, **87**, 4002.
16 T. Matsuda and T. Mitsuyasu, *Bull. Soc. Chem. Jpn.*, 1966, **39**, 1342.
17 T. V. Senchenko, V. E. Platonov, and G. G. Takobson, *J. Org. Chem. U.S.S.R.*, 1977, **13**, 1765.
18 M. Jones and R. H. Levin, *Tetrahedron Lett.*, 1968, 5593.
19 M. Jones and R. H. Levin, *J. Am. Chem. Soc.*, 1969, **91**, 6411.
20 M. A. O'Leary, M. B. Stringer, and D. Wege, *Aust. J. Chem.*, 1978, **38**, 2003.
21 O. Abou-Teim, M. C. Goodland, and J. F. W. McOmie, *J. Chem. Soc., Perkin Trans. 1*, 1983, 2659.
22 C. S. Marvel and C. W. Hinman, *J. Am. Chem. Soc.*, 1954, **76**, 5435.
23 C. Normant-Chefnay, *Bull. Soc. Chim. Fr.*, 1971, 1362.
24 P. Yates and E. Lewars, *J. Chem. Soc., Chem. Commun.*, 1967, 622.
25 D. W. Jones, R. S. Matthews, and K. D. Bartle, *Spectrochim. Acta, Part A*, 1972, **28**, 2053.
26 J. N. Chatterjea, *Chem. Ber.*, 1958, **91**, 2636.
27 B. T. Lawton, W. A. Szarek, and J. K. N. Jones, *Carbohydr. Res.*, 1969, **10**, 456.
28 A. T. Blomquist and V. J. Hruby, *J. Am. Chem. Soc.*, 1967, **89**, 4996.
29 M. E. Cracknell, M. C. Goodland, and J. F. W. McOmie, *Bull. Chem. Soc. Jpn.*, 1983, **56**, 965.
30 F. M. Logullo, A. H. Seitz, and L. Friedman, *Org. Synth.*, Coll. Vol. 5, 54.
31 S. Wawzonek, *J. Am. Chem. Soc.*, 1940, **62**, 745.

Received 4th August 1986; *Paper* 6/1583