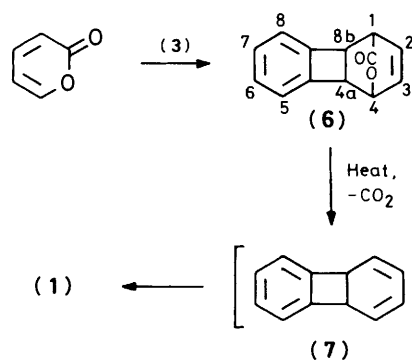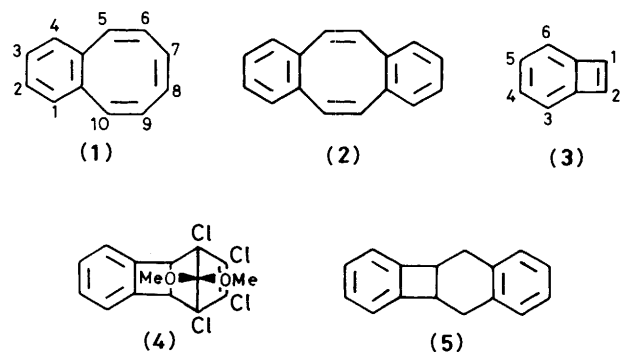# Benzocyclo-octenes. Part 4.[1] Benzo- and Dibenzo[a,e]-cyclo-octene Synthesis via Benzocyclobutene

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The cycloadduct of benzocyclobutene with 2H-pyran-2-one readily undergoes thermal elimination of carbon dioxide and subsequent valence isomerisation to give benzocyclo-octene; analogous reactions of benzocyclobutene with alkyl and aryl derivatives of 2H-pyran-2-one and of thiophene 1,1-dioxide give benzocyclo-octenes directly at temperatures below 100 °C. The corresponding adducts of cyclopenta-2,4-dienones are mostly more stable thermally, but undergo decarbonylation at higher temperatures. Dibenzo[a,e]cyclo-octenes have been obtained directly by reactions of benzocyclobutene with halogenated 1,2-quinodimethanes.

Largely due to the inaccessibility of benzocyclo-octene (1) its chemistry[2] has received little attention by comparison with that of the parent cyclo-octene (cyclo-octatetraene).[3] In connection with studies of benzocyclo-octenes formed in addition reactions of biphenylene[1] we required a more convenient synthesis of (1) and certain of its derivatives. The present paper describes work directed towards a general synthesis of annelated cyclo-octenes utilising cycloadditions of the reactive intermediate, benzocyclobutene (3).

Scheme 1.

95—100 °C gave the lactone (6) in 44% yield. Experiments conducted at lower temperatures (50—80 °C) gave the angular dimer of (3), 6a,10b-dihydrobenzo[a]biphenylene,[10] as the principal product.

The stereochemistry of the adduct (6) has not been established, but is probably endo.[5,11] It melts at 111—13 °C with decarboxylation to give benzocyclo-octene (1) quantitatively, thus the isolation of (6) is unnecessary and reactions carried out at 156 °C gave (1) directly in substantially higher yields. Similar reactions conducted at 95—100 °C with 4,6-dimethyl- and 3,4,5,6-tetraphenyl-2H-pyran-2-ones gave the benzocyclo-octenes (8) and (9), no lactone intermediates being found. Our failure to detect 4a,8b-dihydrobiphenylene intermediates in these reactions is unsurprising in the light of recently published data for (7), which is reported to have a half-life of 1 min at 0 °C.[12] A reaction of (3) with 2H-pyran-2-one in refluxing acetic acid gave, in addition to benzocyclo-octene (1) and benzocyclobutene dimer, a low yield of a compound $C_{13}H_{10}O_2$, isomeric with the adduct (6).[13] While the mass spectrum of (6) shows evidence of cycloreversion to the starting materials, that of the isomer does not, and attempts to decarboxylate it thermally were unsuccessful; its structure is under investigation.

Benzocyclobutene (3) reacted similarly with thiophene 1,1-dioxides at lower temperatures to give the corresponding benzocyclo-octenes in acceptable yields; thus 2,5-dimethyl-, 3,4-dimethyl-, 2,3,4,5-tetramethyl-, and 2,3,4,5-tetraphenyl-thiophene-1,1-dioxides gave respectively (10) (59%), (11) (78%), (12) (38%), and (9) (65%). Elimination of sulphur dioxide took place under the reaction conditions and the initial adducts were not found. The instability of many thiophene dioxides appears to be the main limitation of this as a good general method.

(1)   (2)   (3)

(4)   (5)

Apart from reports of the formation of (1) and (2) in reactions of transition-metal complexes of benzocyclobutene,[4] few relevant studies have appeared. Boulton and McOmie[5] prepared the adduct (4) by generation of (3) in the presence of 1,2,3,4-tetrachloro-5,5-dimethoxycyclopenta-1,3-diene. Hydrolysis of (4) followed by thermal decarbonylation afforded 6,7,8,9-tetrachlorobenzocyclo-octene by valence isomerisation of the 4a,8b-dihydrobiphenylene intermediate; however, attempts to prepare the hydrocarbon (1) by this route were unsuccessful. Nenitzescu et al. have obtained dibenzo[a,e]-cyclo-octene (2) by thermal isomerisation of the linear dimer[6] of (3) and also by benzylic bromination and subsequent debromination of the tetrahydrobenzo[b]biphenylene (5), the adduct formed by generating benzocyclobutene (3) and 1,2-quinodimethane simultaneously.[7] The latter approach has also been used more recently by Vogel et al.[8,9] for syntheses of benzo[c]-and dibenzo[c,j]-octalenes.

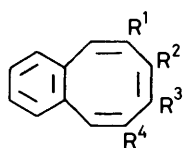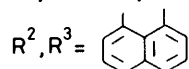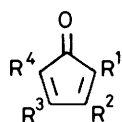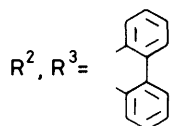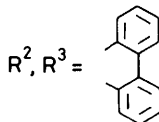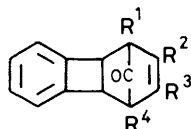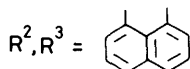## Results and Discussion

Benzocyclo-octenes.—The reaction of benzocyclobutene (3), generated by debromination of 1,2-dibromo-1,2-dihydrobenzocyclobutene with zinc,[10] with 2H-pyran-2-one (Scheme 1) at
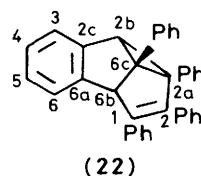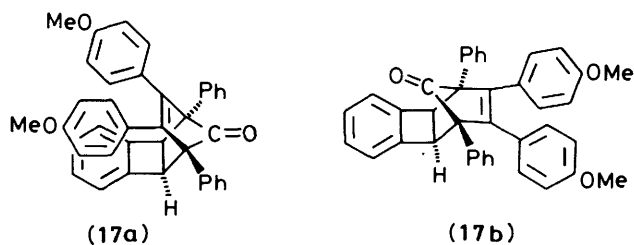
(8) R^1, R^3 = Me; R^2, R^4 = H
(9) R^1, R^2, R^3, R^4 = Ph
(10) R^1, R^4 = Me; R^2, R^3 = H
(11) R^2, R^3 = Me; R^1, R^4 = H
(12) R^1, R^2, R^3, R^4 = Me
(20) R^1, R^4 = Ph;

R^2, R^3 =

(21) R^1, R^4 = Ph;

R^2, R^3 =

(13) R^1, R^2, R^3, R^4 = Ph
(14) R^1, R^4 = Ph;
     R^2, R^3 = C_6H_4OMe-p
(15) R^1, R^4 = Ph;

R^2, R^3 =

(19) R^1, R^4 = Ph;

R^2, R^3 =

(16) R^1, R^2, R^3, R^4 = Ph
(17) R^1, R^4 = Ph;
     R^2, R^3 = C_6H_4OMe-p
(18) R^1, R^4 = Ph;

R^2, R^3 =

(17a)   (17b)

(22)
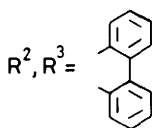
Derivatives of the reactive cyclopentadienone system gave cycloadducts under even milder conditions. Reactions of (3) with tetracyclone (13), with 3,4-di(4-methoxyphenyl)-2,5-diphenylcyclopenta-2,4-dienone (14), and with phencyclone (15) in THF at room temperature gave the bridged ketones (16), (17), and (18), but the adduct from acecyclone (19) was decarbonylated under the reaction conditions to the cyclo-octene (20). The ^{1}H n.m.r. spectra of the adducts (16)—(18) indicate that the expected *endo* isomer is formed in each case. For example, a comparison of models of the *endo* (17a) and *exo* (17b) isomers of the methoxylated adduct (17) shows that in the *endo* isomer the 4-methoxyphenyl rings lie over the periphery of the benzocyclobutane aromatic system, thus these ring protons should experience considerable shielding relative to those of (17b). The first-order ^{1}H n.m.r. spectrum of the adduct is consistent with this, the ring protons of the 4-methoxyphenyl substituents giving rise to a high-field AB system (J 9.0 Hz) centred at δ 6.2 p.p.m. The protons of the phenyl substituents resonate in the normal benzenoid position, merged with the aromatic protons of the benzocyclobutane moiety. The spectrum of the tetracyclone adduct (16) is more complex, the protons of the shielded phenyl substituents (R^2, R^3) resonating in two groups at δ 6.2 (4 H, dd, the 2,6 and 2′,6′ protons) and at δ 6.8 (6 H, m, the 3,4,5 and 3′,4′,5′ protons). Off-resonance decoupling of the highfield signal causes collapse of the multi-

plet at δ 6.8 to the expected A_2B system. In the phencyclone adduct (18) the benzocyclobutane aromatic protons are shifted to higher field (δ 6.6) by the proximity of the phenanthrene nucleus which in turn is subjected to a reciprocal, though less significant, effect from the benzocyclobutane aromatic ring.

Thermal decarbonylation of (18) in diglyme at 160 °C gave the annelated cyclo-octene (21), but the tetracyclone adduct (16) gave another valence isomer, tetrahydrotetraphenylbenzo[*a*]cyclopropa[*cd*]pentalene (22) under these conditions. Further experiments have established that 6,7,8,9-tetraphenylbenzocyclo-octene (9) rearranges rapidly to (22) above 150 °C. This thermal rearrangement will be discussed in detail in a forthcoming paper.

Dibenzo[a,e]*cyclo-octenes.*—We sought to shorten the Merritzescu route[7] (see above) to dibenzo[*a,e*]cyclo-octene (2) by utilising a bromine-containing 1,2-quinodimethane component in the cycloaddition reaction (Scheme 2). This proved

→ (2)

(23)
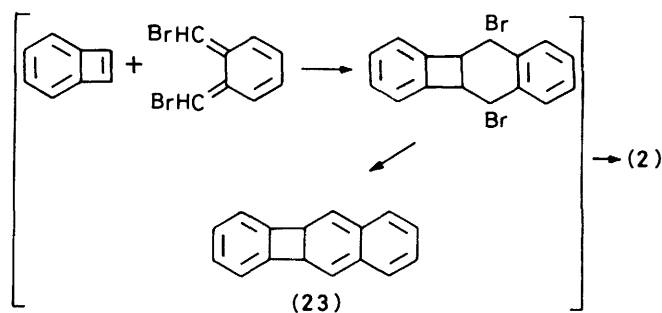
Scheme 2.

successful, the reaction of a concentrated equimolar solution of 1,2-dibromo-1,2-dihydrobenzocyclobutene and 1,2-bis(dibromomethyl)benzene with zinc at 100 °C giving (2) (39%) directly. To test the generality of the method the reaction of benzocyclobutene (3) with the quinodimethane (24), generated from 2,3-bis(dibromomethyl)biphenylene, was investigated (Scheme 3). This reaction gave, in addition to the expected benzocyclo-octabiphenylene (26), a small amount of the bisadduct (27). The cyclo-octene (26) did not react with (3) under similar conditions, thus it appears that (27) is formed by reaction of (3) with the valence isomer (25) before the competing ring opening to (26) occurs, implying that (25) is longer-lived than the quinodimethane intermediate (23), above. The ^{1}H n.m.r. spectrum of (27) shows it to have the predicted *endo,endo*
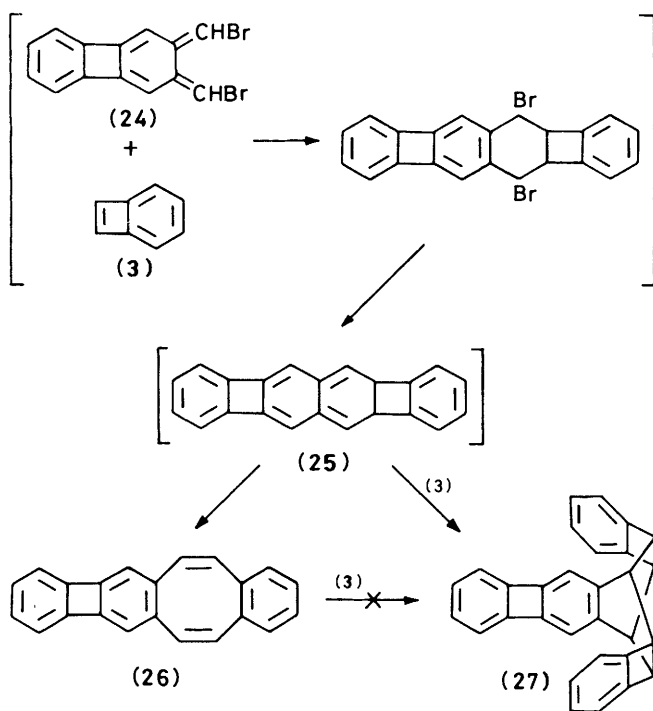
Scheme 3.

geometry, the benzocyclobutane aromatic rings flanking the biphenylene system bringing about a shift of the 'inner' pair of biphenylene protons to high field (δ 6.05).

Experimental

Cycloaddition reactions were run in N,N-dimethylformamide (DMF) or tetrahydrofuran (THF); glyme and diglyme were found to be satisfactory alternatives. Organic extracts were dried over sodium sulphate. ^{1}H N.m.r. spectra were obtained on a JOEL JNM FX200 spectrometer. Samples were run as solutions in $CDCl_3$ at ambient temperature and chemical shifts are recorded as p.p.m. downfield from internal tetramethyl-silane. I.r. spectra were run as Nujol mulls unless otherwise stated. Mass spectra were obtained on an AEI MS902 instrument operated at 70 eV and a source temperature of 200 °C.

The following starting materials were prepared by literature routes: trans-1,2-dibromo-1,2-dihydrobenzocyclobutene,[14] $2H$-pyran-2-one,[15] 4,6-dimethyl-$2H$-pyran-2-one,[16] 3,4,5,6-tetra-phenyl-$2H$-pyran-2-one,[17] 2,5- and 3,4-dimethylthiophene-1,1-dioxides,[18] 2,3,4,5-tetraphenylthiophene-1,1-dioxide,[19] phen-cyclone (15),[20] 3,4-bis(4-methoxyphenyl)-2,5-diphenylcyclo-penta-2,4-dienone,[21] and acecyclone (19).[20]

Reactions of Benzocyclobutene with 2H-Pyran-2-one.—(a). A solution of trans-1,2-dibromo-1,2-dihydrobenzocyclobutene (13.1 g) and $2H$-pyran-2-one (4.8 g) in DMF (100 ml) was added during 1 h to a rapidly-stirred and heated (steam-bath) suspension of zinc dust (20 g) and $2H$-pyran-2-one (4.8 g) in DMF (75 ml). After a further 2 h at 95—100 °C, the solution was filtered through Celite, diluted to 1 l with water, and refrigerated. Next day the crystalline material was collected, dried, and recrystallised from benzene–hexane to give the lactone (6) as prisms (4.4 g, 44%), m.p. 111—113 °C (decomp.) (Found: C, 78.8; H, 5.1. $C_{13}H_{10}O_2$ requires C, 78.8; H, 5.05%); $v_{max.}$ 1 740, 1 610, 1 165, 998, and 962 cm^{-1}; δ_H 3.83 (2 H, m, 1,8a-H), 4.06 (1 H, m, 4a-H), 5.43 (1 H, m, 4-H), 6.02—6.10 (2 H,

m, 2,3-H), and 7.00—7.07 (4 H, m, 5—8-H); m/z (%) 198 (M^+, 3), 154 ($M^+ - CO_2$, 43), 153 (34), and 102 (100).

(b). The reaction was run as in (a), but in refluxing DMF. After dilution of the filtered reaction solution, the products were collected by extraction with dichloromethane. Evaporation of the dried extracts and chromatography of the residue on silica with hexane as eluant gave, after a small fore-run of the angular benzocyclobutene dimer, benzocyclo-octene (1) (4.5 g, 58%), m.p. 49—50 °C (from aqueous EtOH), identical with an authentic sample.[1]

6,7,8,9-Tetraphenylbenzocyclo-octene (9).—(a). trans-1,2,-Di-bromo-1,2-dihydrobenzocyclobutene (1.9 g) was added during 1 h to a stirred suspension of 3,4,5,6-tetraphenyl-$2H$-pyran-2-one (1.5 g) and zinc dust (3.0 g) in DMF (15 ml) at 95—100 °C. The solution was diluted with dichloromethane (100 ml), filtered from zinc residues, and poured into water (250 ml). The organic phase was washed with 10% hydrochloric acid (2 × 50 ml) and water, then dried and evaporated under reduced pressure. Chromatography of the resulting oil on alumina with hexane–ethyl acetate (19:1) as eluant gave, after a fore-run of benzocyclobutene dimer, the *title compound* (9) (0.26 g, 15%), m.p. 151—152 °C (from EtOH) (Found: C, 94.3; H, 5.6. $C_{36}H_{24}$ requires C, 94.3; H, 5.7%); $v_{max.}$ (KCl disc) 1 595, 1 490, 1 440, 1 030, 863, 760, and 690 cm^{-1}; δ_H 6.69—7.76 (m); m/z (%) 458 (M^+, 100), and 280 (50).

(b). Zinc dust (1.6 g) was added in portions to a stirred solution of trans-1,2-dibromo-1,2-dihydrobenzocyclobutene (1.0 g) and 2,3,4,5-tetraphenylthiophene 1,1-dioxide (0.7 g) in DMF (20 ml) at 95—100 °C. After work-up as described in (a), the oil so obtained was crystallised from ethanol to give (9) (0.51 g, 65%), m.p. 151—152 °C.

6,8-Dimethylbenzocyclo-octene (8).—The reaction of trans-1,2-dibromo-1,2-dihydrobenzocyclobutene (2.2 g) and 4,6-di-methyl-$2H$-pyran-2-one (1.0 g) was run as described in method (a) for compound (9). After work-up, the resulting oil was chromatographed on alumina in pentane to give first benzo-cyclobutene dimer (0.5 g) followed by the *title compound* (8) (0.55 g, 37%) as a mobile oil (Found: C, 92.0; H, 7.9. $C_{14}H_{14}$ requires C, 92.3; H, 7.7%); $v_{max.}$(liq.) 3 100—2 900, 1 432, 770, and 735 cm^{-1}; δ_H 1.73 (3 H, d, 8-Me), 1.85 (3 H, d, 6-Me), 5.56 (1 H, br s, 7-H), 5.97 (1 H, d, 9-H), 6.28 (1 H, br s, 5-H), 6.49 (1 H, d, 10-H), and 6.93—7.18 (4 H, m, 1—4-H); m/z (%) 182 (M^+, 74), 167 (100), 165 (40), and 152 (31).

6,9-Dimethylbenzocyclo-octene (10).—A reaction between (3) and 2,5-dimethylthiophene 1,1-dioxide, using method (b) as for compound (9) above, gave, after chromatography on silica in hexane, the *title compound* (10) (59%) as a mobile oil (see ref. 22) (Found: C, 92.3; H, 7.65%); $v_{max.}$ (liq. film) 3 100—2 900, 1 459, 1 445, 850, 757, and 743 cm^{-1}; δ_H 1.87 [6 H, d, $J_{5,Me}$ 1.5 Hz, 6(9)-Me], 5.76 [2 H, s, 7(8)-H], 6.34 [2 H, d, 5(10)-H], and 6.92—7.16 (4 H, m, 1—4-H); m/z (%) 182 (M^+, 100), 167 (100), 165 (57), 152 (69), and 141 (60).

7,8-Dimethylbenzocyclo-octene (11).—In the same way, a reaction using 3,4-dimethylthiophene 1,1-dioxide gave the *title compound* (11) (78%), m.p. 76—77 °C (from aqueous EtOH) (Found: C, 92.25; H, 7.7%); $v_{max.}$ 840 and 765 cm^{-1}; δ_H 1.65 [6 H, s, 7(8)-Me], 6.00 [2 H, d, 6(9)-H], 6.39 [2 H, d, 5(10)-H], and 6.96—7.19 (4 H, m, 1—4-H); m/z (%) 182 (M^+, 80), 167 (100), and 152 (37).

6,7,8,9-Tetramethylbenzocyclo-octene (12).—In the same way, a reaction using 2,3,4,5-tetramethylthiophene 1,1-dioxide gave the *title compound* (12) (38%), m.p. 73—74 °C (from aqueous EtOH) (Found: C, 91.3; H, 8.6. $C_{16}H_{18}$ requires C, 91.4; H,

8.6%); $\nu_{max.}$ 1 501, 850, and 763 cm^{-1}; δ_H 1.62 [6 H, s, 7(8)-Me], 1.90 [6 H, d, $J_{5,Me}$ 1.5 Hz, 6(9)-Me], 6.18 [2 H, d, 5(10)-H], and 6.98—7.13 (4 H, m, 1—4-H); m/z (%) 210 (M^+, 94), 195 (100), and 165 (36).

Reactions of Benzocyclobutene with Cyclopentadienones.—With 2,3,4,5-Tetraphenylcyclopenta-2,4-dienone (**13**). Activated zinc dust[11] (3.0 g) was added in portions to a stirred solution of tetracyclone (2.5 g) and *trans*-1,2-dibromo-1,2-dihydrobenzo-cyclobutene (1.65 g) in THF (15 ml), the exothermic reaction being controlled by means of a cooling (water) bath. When the reaction ceased (discharge of the colour of the cyclone) the pale yellow suspension was diluted with dichloromethane (100 ml), filtered from zinc residues, then washed with 10% hydro-chloric acid and water. Evaporation of the dried solution under reduced pressure gave a viscous gum which on trituration with ether yielded *endo*-1,4,4a,8b-*tetrahydro*-1,2,3,4-*tetraphenyl*-1,4-*methanobiphenylen*-9-*one* (**16**) (2.1 g, 69%). It formed colour-less prisms, m.p. 197.5—198 °C (decomp.) (from benzene) (Found: C, 91.3; H, 5.4. $C_{37}H_{26}O$ requires C, 91.4; H, 5.35%); $\nu_{max.}$ 1 765 cm^{-1} (CO); δ_H 4.51 [2 H, s, 4a(8b)-H], 6.19—6.25 [4 H, dd, 2(3)-Ph], 6.68—6.92 [6 H, m, 2(3)-Ph], 7.19—7.42 [10 H, m, 1(4)-Ph], and 7.30—7.58 (4 H, m, 5—8-H); m/z (%) 458 (M^+ − CO, 100), 381 (26), and 280 (43).

With the 3,4-*Bis*(p-*methoxyphenyl*)-2,5-*diphenylcyclopenta-2,4-dienone* (**14**). A reaction was carried out as in the previous experiment, but using cyclone (**14**), giving *endo*-2,3-bis(*p*-meth-oxyphenyl)-1,4-diphenyl-1,4,4a,8b-tetrahydro-1,4-methano-biphenylen-9-one (**17**) (65%), m.p. 198.5—199.5 °C (decomp.) (from toluene–cyclohexane) (Found: C, 85.5; H, 5.25. $C_{39}H_{30}O_3$ requires C, 85.7; H, 5.5%); $\nu_{max.}$ 1 780 cm^{-1} (CO); δ_H 3.60 (6 H, s, Me), 4.52 [2 H, s, 4a(8b)-H], 6.06—6.38 [8 H, q, 2(3)-Ar], and 7.14—7.62 [14 H, m, 5,8-H and 1(4)-Ph]; m/z (%) 518 (M^+ − CO, 100), 446 (28), and 310 (29).

With 1,3-*diphenyl*-2H-*cyclopenta*[l]*phenanthren*-2-*one* (**15**). A reaction, carried out in the same way using (**15**), gave *endo*-9,14-diphenyl-9,9a,13b,14-tetrahydro-9,14-methanophenan-thro[9,10-*b*]biphenylen-15-one (**18**) (65%), m.p. 254.5—255 °C (decomp.) (from benzene) (Found: C, 91.7; H, 4.9. $C_{37}H_{24}O$ requires C, 91.7; H, 5.0%); $\nu_{max.}$ 1 770 cm^{-1} (CO); δ_H 4.80 [2 H, s, 9a(13b)-H], 6.64 (4 H, m, 10—13-H), 6.97—8.05 [16 H, m, 1—3 and 6—8-H and 9(14)-Ph] and 8.44 [2 H, dd, 4(5)-H]; m/z (%) 456 (M^+ − CO, 66), 384 (68), and 278 (100).

With 7,9-*Diphenyl*-8H-*cyclopenta*[a]*acenaphthylen*-8-*one* (**19**). A reaction, carried out in the same way using (**19**), gave the cyclo-octene (**20**) (77.5%) as yellow crystals, m.p. 235—235.5 °C (from methylcyclohexane) (Found: C, 94.6; H, 5.3. $C_{34}H_{22}$ requires C, 94.85; H, 5.3%); δ_H 6.96 (2 H, d, vinylic) and 7.16—7.68 (20 H, m, ArH); m/z (%) 430 (M^+, 100), 353 (39), 352 (22), 328 (34), and 252 (39).

Decarbonylation of the Adduct (**16**). The adduct (**16**) (1 g) was refluxed in diglyme (20 ml) until the evolution of carbon monoxide ceased (*ca.* 20 min). The solution was diluted with water (100 ml) and the product collected by ether extraction. Evaporation of the dried extract under reduced pressure gave 2a,2b,6b,6c-*tetrahydro* 1,2,2a,6c-*tetraphenylbenzo*[a]*cyclopro-pa*[cd]*pentalene* (**22**) as a colourless glass (0.95 g) which resisted attempts at crystallisation from various solvents. Vacuum sublimation gave finely-divided material of the same type. It slowly softened on heating without showing a definite melting point (Found: C, 94.0; H, 5.4. $C_{36}H_{26}$ requires C, 94.3; H, 5.7%); δ_H 4.20 (1 H, s, 2b-H), 4.86 (1 H, s, 6b-H), and 6.42—7.78 (24 H, m, Ar-H); m/z (%) 458 (M^+, 100).

Decarbonylation of the Adduct (**18**).—A solution of the adduct (480 mg) in triglyme (10 ml) was refluxed for 2 h, cooled, and diluted with water. The solid which separated was crystal-lised from toluene to give the cyclo-octene (**21**) (235 mg, 52%),

m.p. 309—311 °C (Found: C, 94.4; H, 5.1. $C_{36}H_{24}$ requires C, 94.7; H, 5.3%); δ_H 7.10—7.80 (22 H, m) and 8.61 (2 H, dd, phenanthrene bay protons); m/z (%) 456 (M^+, 100), 379 (30), and 278 (78).

Dibenzo[a,e]*cyclo-octene* (**2**).—Activated zinc dust[11] (7.5 g) was added in one portion to a stirred solution of *trans*-1,2-dibromo-1,2-dihydrobenzocyclobutene (1.23 g) and 1,2-bis(di-bromomethyl)benzene (2.0 g) in DMF (20 ml) at 95—100 °C. When the violent exothermic reaction ceased, the solvent was removed under reduced pressure and the residue extracted with dichloromethane (Soxhlet). Evaporation of the extracts and chromatography of the residue on alumina with hexane–ethyl acetate (99:1) as eluant gave dibenzo[a,e]cyclo-octene (315 mg, 39%), m.p. 106—108 °C (lit.,[23] m.p. 106.8—108.1 °C) (from EtOH).

2,3-*Bis*(*dibromomethyl*)*biphenylene.*—2,3-Dimethylbiphenyl-ene was prepared from biphenylene by successive formylation and reduction, using methods similar to those previously described.[24] A solution of the hydrocarbon (2.52 g) and *N*-bromosuccinimide (10 g) in dry carbon tetrachloride (300 ml) was refluxed for 2 h under irradiation from a 150 W tungsten bulb. After filtration from succinimide, the solution was evaporated under reduced pressure and the residue crystallised from chloroform–hexane to give the title compound as a bright yellow solid (5.36 g, 77%), m.p. 174—176 °C (decomp.) It was used immediately without further purification; on keeping it slowly darkened and decomposed.

Reaction of Benzocyclobutene with the Quinodimethane (**24**).—Activated zinc dust (1 g) was added in one portion to a stirred solution of *trans*-1,2-dibromo-1,2-dihydrobenzocyclo-butene (175 mg) and 2,3-bis(dibromomethyl)biphenylene (300 mg) in THF (5 ml) at room temperature with cooling (water-bath) to moderate the initial vigorous reaction. Work-up as for the cyclone adducts and chromatography on alumina in hexane–ethyl acetate (20:1) gave *benzo*[a]*biphenyleno*[2,3-*e*]-*cyclo-octene* (**26**) as lemon-yellow crystals (59 mg, 35%), m.p. 193—195 °C (Found: M^+ 278.1093. $C_{22}H_{14}$ requires M^+ 278.1095); $\nu_{max.}$ (KCl disc) 1 428, 1 280, 890, 755, and 735 cm^{-1}; δ_H 6.33 [2 H, s, 5(14)-H], 6.48 [2 H, d, 6(13)-H], 6.58—6.75 (4 H, m, 1—4-H), 6.66 [2 H, d, 7(12)-H], and 7.00—7.19 (4 H, m, 8—11-H). Further elution gave the *bis-adduct* (**27**) (14 mg, 6%) as pale yellow crystals, m.p. 315—318 °C (Found: M^+ 380.1561. $C_{30}H_{20}$ requires M^+ 380.1565); $\nu_{max.}$ (KCl disc) 1 462, 1 437, 1 270, 1 212, 888, and 738 cm^{-1}; δ_H 3.51 (4 H, m, four-membered ring), 3.72 (2 H, m, bridgehead), 6.05 (2 H, s, 'inner' biphenylene ring), 6.27—6.52 (4 H, m, 'outer' biphenylene ring), and 7.00—7.19 (8 H, m, benzocyclobutane aromatic ring).

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