I (X = Br, Y = CN), 623-00-7; I (X = Br, Y = COOEt), 5798-75-4; I (X = Br, Y = COMe), 99-90-1; I (X = Br, Y = NO_2), 586-78-7; I (X = Br, Y = CHO), 1122-91-4; I (X = Y = Me), 106-42-3; I (X = Me, Y = H), 108-88-3; I (X = Me, Y = CF_3), 6140-17-6; I (X = Me, Y = CN), 104-85-8; I (X = Me, Y = COOEt), 94-08-6; I (X = Me, Y = COMe), 122-00-9; I (X = Me, Y = NO_2), 99-99-0; I (X = Me, Y = CHO), 104-87-0; I (X = Y = H), 71-43-2; I (X = H, Y = CF_3), 98-08-8; I (X = H, Y = CN), 100-47-0; I (X = H, Y = COOEt), 93-89-0; I (X = H, Y = COMe), 98-86-2; I (X = H, Y = NO_2), 98-95-3; I (X = H, Y = CHO), 100-52-7; I (X = Y = CF_3), 433-19-2; I (X = CF_3, Y = CN), 455-18-5; I (X = CF_3, Y = COOEt), 583-02-8; I (X = CF_3, Y = COMe), 709-63-7; I (X = CF_3, Y = NO_2), 402-54-0; I (X = CF_3, Y = CHO), 455-19-6; I (X = Y = CN), 623-26-7; I (X = CN, Y = COOEt), 7153-22-2; I (X = CN, Y = COMe), 1443-80-7; I (X = CN, Y = NO_2), 619-72-7; I (X = CN, Y = CHO), 105-07-7; I (X, Y = COOEt), 636-09-9; I (X = COOEt, Y = COMe), 38430-55-6; I (X = COOEt, Y = NO_2), 99-77-4; I (X = COOEt, Y = CHO), 6287-86-1; I (X = Y = COMe), 1009-61-6; I (X = COMe, Y = NO_2), 100-19-6; I (X = COMe, Y = CHO), 3457-45-2; I (X = Y = NO_2), 100-25-4; I (X = NO_2, X = CHO), 555-16-8; I (X = Y = CHO), 623-27-8; I (X = OH, Y = NO_2), 100-02-7; I (X = OH, Y = CN), 767-00-0; I (X = OH, Y = CHO), 123-08-0; I (X = OH, Y = H), 108-95-2; I (X = OH, Y = F), 371-41-5; I (X = Y = OH), 123-31-9; I (X = OH, Y = NH_2), 123-30-8; I (X = CH_3, Y = OH), 106-44-5; I (X = CF_3, Y = OH), 402-45-9.

5,6-Didehydro-7-bromodibenzo[*a*,*c*]cyclooctene and 5,6-Didehydro-8-*tert*-butoxydibenzo[*a*,*c*]cyclooctene as Reactive Intermediates.[1] A Convenient Synthesis of Dibenzo[*a*,*c*]cyclooctene

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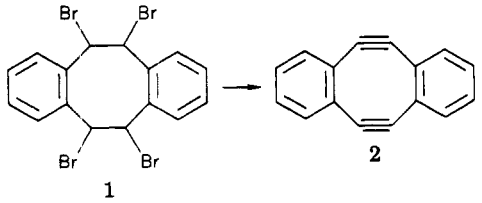
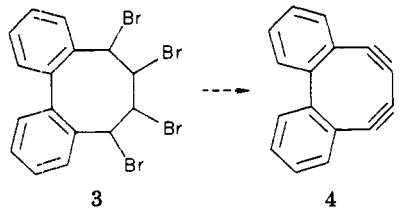
Received January 17, 1980

A convenient synthesis of dibenzo[*a*,*c*]cyclooctene (**8**) is described, which on bromination yielded 5,6,7,8-tetrabromo-5,6,7,8-tetrahydrodibenzo[*a*,*c*]cyclooctene (**3**). Dehydrobromination of **3** led to 6,7-dibromodibenzo[*a*,*c*]cyclooctene (**9**), 5-*tert*-butoxy-7-bromodibenzo[*a*,*c*]cyclooctene (**11**), and 5,7-di-*tert*-butoxydibenzo[*a*,*c*]cyclooctene (**13**) via the presumed reactive intermediates 5,6-didehydro-7-bromodibenzo[*a*,*c*]cyclooctene (**10**) and 5,6-didehydro-8-*tert*-butoxydibenzo[*a*,*c*]cyclooctene (**12**). This reaction path is compatible with the observed formation of 1,4:5,8-diepoxy-1,4,5,8-tetrahydro-1,4,5,8-tetraphenyl-2,3:6,7-dibenzotetraphenylene (**14**) by dehydrobromination of the tetrabromide **3** or the dibromide **9** with potassium *tert*-butoxide in the presence of 1,3-diphenylisobenzofuran.

We have reported previously that dehydrobromination of 5,6,11,12-tetrabromo-5,6,11,12-tetrahydrodibenzo[*a*,*e*]cyclooctene (**1**) with potassium *tert*-butoxide leads to



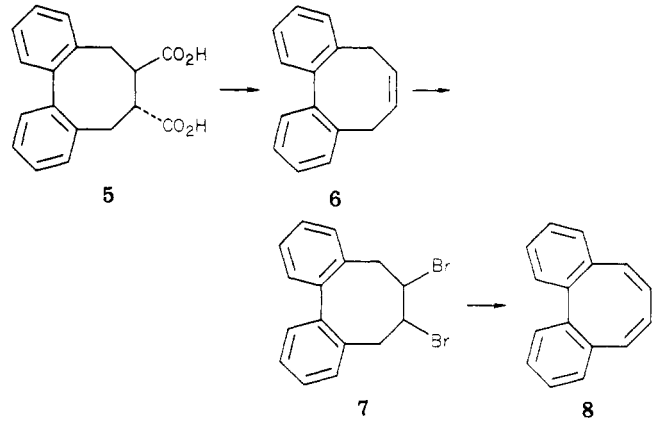
1 **2**



3 **4**

5,6,11,12-tetradehydrodibenzo[*a*,*e*]cyclooctene (**2**) as a relatively stable crystalline compound.[3] It was of interest to investigate whether the analogous dehydrobromination of 5,6,7,8-tetrabromo-5,6,7,8-tetrahydrodibenzo[*a*,*c*]cyclooctene (**3**)[4] would yield 5,6,7,8-tetradehydrodibenzo[*a*,*c*]cyclooctene (**4**), although the presence of a 1,3-diyne unit in **4** would make it very unlikely that such a compound could be isolated. We now report the results of the dehydrobromination of the tetrabromide **3**. Although there was no indication of the formation of the diacetylene **4**, evidence was obtained that 5,6-didehydro-7-bromodibenzo[*a*,*c*]cyclooctene (**10**) and 5,6-didehydro-8-*tert*-butoxydibenzo[*a*,*c*]cyclooctene (**12**) were formed as reactive intermediates.

The starting material, dibenzo[*a*,*c*]cyclooctene (**8**), has



5 **6** **7** **8**

been synthesized previously in ~30% yield from 5,8-dihydrodibenzo[*a*,*c*]cyclooctene (**6**) by a method involving a low-pressure pyrolysis step.[4,5] Since this is rather inconvenient experimentally, we have developed the following superior method. Decarboxylation of *trans*-5,6,7,8-tetrahydrodibenzo[*a*,*c*]cyclooctene-6,7-dicarboxylic acid

(1) Unsaturated Eight-Membered Ring Compounds. 15. For part 14, see H. N. C. Wong, T. L. Chan, and F. Sondheimer, *Tetrahedron Lett.*, 667 (1978).

(2) Shanghai Institute of Organic Chemistry, Academia Sinica, Shanghai, China.

(3) H. N. C. Wong, P. J. Garratt, and F. Sondheimer, *J. Am. Chem. Soc.*, **96**, 5604 (1974).

(4) J. Wolpers, Ph.D. Thesis, University of Cologne, 1964.

(5) E. Vogel, W. Frass, and J. Wolpers, *Angew. Chem.*, **75**, 979 (1963); *Angew. Chem., Int. Ed. Engl.*, **2**, 625 (1963).

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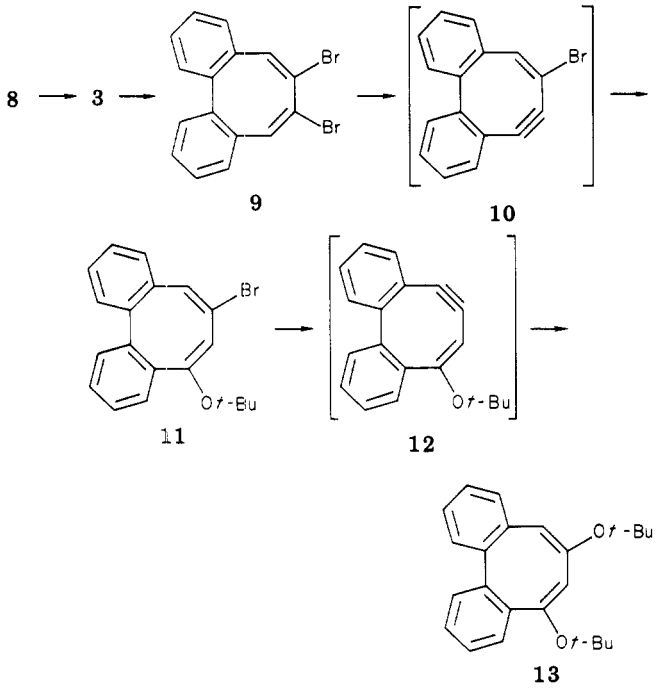
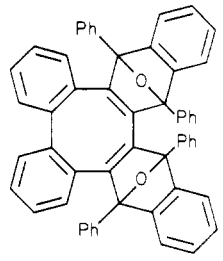
(5)[6] with lead tetraacetate and pyridine in benzene at 80 °C, according to Vogel et al.[5] and Wolpers,[4] gave 5,8-dihydrodibenzo[a,c]cyclooctene (6) in 44% yield. Addition of bromine in carbon tetrachloride furnished the dibromide 7 (stereochemistry not determined), which was dehydrobrominated directly with 1,5-diazabicyclo[4.3.0]non-5-ene (DBN) in boiling benzene. This procedure led to 37% (based on 6) of dibenzo[a,c]cyclooctene (8), with physical properties essentially identical with those reported by Vogel et al.[5] and Wolpers.[4]

Bromination of 8 with 2 molar equiv of bromine in carbon tetrachloride yielded 53% of the tetrabromide 3[4] (stereochemistry not determined). Dehydrobromination of 3 with ~5 molar equiv of potassium *tert*-butoxide in tetrahydrofuran gave rise to three new products. Their spectral properties (see Experimental Section) showed these to be 6,7-dibromodibenzo[a,c]cyclooctene (9) (8.7% yield), 5-*tert*-butoxy-7-bromodibenzo[a,c]cyclooctene (11) (8.9% yield), and 5,7-di-*tert*-butoxydibenzo[a,c]cyclooctene (13) (32% yield). Dehydrobromination of 3 with only ~2 molar equiv of potassium *tert*-butoxide gave a 60% yield of 6,7-dibromodibenzo[a,c]cyclooctene (9) as sole product, which could then be converted to 5,7-di-*tert*-butoxydibenzo[a,c]cyclooctene (13) in 50% yield by further treatment with an excess of potassium *tert*-butoxide.



The most likely explanation for the above-described results is that the tetrabromide 3 first suffers loss of two molecules of hydrogen bromide to give the dibromide 9. Further dehydrobromination of 9 leads to the reactive 5,6-didehydro-7-bromodibenzo[a,c]cyclooctene (10), which on addition of a *tert*-butoxy anion and protonation yields the *tert*-butoxy bromo compound 11. Further loss of hydrogen bromide from 11 gives the reactive 5,6-didehydro-8-*tert*-butoxydibenzo[a,c]cyclooctene (12), which finally on further addition of a *tert*-butoxy anion and protonation leads to the di-*tert*-butoxy compound 13. It is of interest that the first addition of the *tert*-butoxy anion to 10 results in attack at the 5-position, while the second addition of the *tert*-butoxy anion to 12 results in attack at the 6-position. This presumably is due to steric reasons.

Treatment of either the tetrabromide 3 or the dibromide 9 with an excess of potassium *tert*-butoxide in the presence of diphenylisobenzofuran (DIB) gave the bis-DIB adduct 14 (stereochemistry not determined) in 19% yield. This

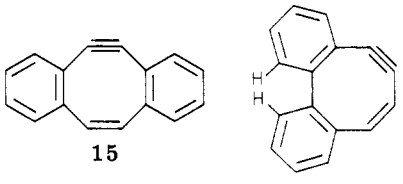


14

reaction presumably involves addition of 1 molecule of DIB to 10 followed by dehydrobromination and addition of a second molecule of DIB to the resulting acetylene.

Formation of the di-*tert*-butoxy compound 13 as well as the bis-DIB adduct 14 from the bromides 3 and 9 could conceivably involve the 1,3-diacetylene 4 as a transient intermediate. However, there is no reason to postulate such a strained species, and we much prefer our proposed routes to the observed products.

We have shown previously[3] that 5,6-didehydrodibenzo[a,e]cyclooctene (15), presumably containing a planar



15 16

conjugated eight-membered ring, is sufficiently stable that it can be isolated.[7] By contrast, compounds 10 and 12, containing the isomeric 5,6-didehydrodibenzo[a,c]cyclooctene system 16, appear to be insufficiently stable for isolation to be possible. A possible reason for this instability is that there would be considerable nonbonded interaction of the two benzenoid protons indicated in formula 16 in a planar molecule, resulting in severe strain.

Experimental Section

Melting points were determined on a hot-stage microscope and are uncorrected. ^{1}H NMR spectra were recorded on a Varian T-60 (60 MHz) spectrometer with $CDCl_3$ solutions, Me_4Si being used as an internal standard. Mass spectra were recorded on either an AEI MS-9 or MS-12 spectrometer. Preparative thick-layer chromatography was carried out on Merck Kieselgel 60 PF_{254}. Potassium *tert*-butoxide was purified by sublimation under reduced pressure. Solvents were purified and dried by standard methods. All evaporations of solvents were carried out under reduced pressure.

5,8-Dihydrodibenzo[a,c]cyclooctene (6).[4] *trans*-5,6,7,8-Tetrahydrodibenzo[a,c]cyclooctene-6,7-dicarboxylic acid (5)[6] (11.34 g, 0.0429 mol), lead tetraacetate (25.5 g), and pyridine (7 g) in anhydrous benzene (75 mL) were stirred at 80 °C (external temperature) for 6 h. The mixture was filtered, and the insoluble material was washed with benzene. The combined benzene solutions were washed successively with 10% aqueous HCl (250 mL), water (250 mL), saturated aqueous Na_2CO_3 (250 mL), and water (2 × 250 mL). The solution was dried (Na_2SO_4) and evaporated, and the residue was chromatographed on a column of alumina (40 g, grade I). Elution with benzene–petroleum ether (2:3), bp 60–80 °C, and crystallization from MeOH yielded 6 (3.93 g, 44%), mp 106–107 °C (lit.[4] mp 107 °C).

(6) L. V. Dvorken, R. B. Smyth, and K. Mislow, *J. Am. Chem. Soc.*, 80, 486 (1958).

(7) See also M.-K. Au, T.-W. Siu, T. C. W. Mak, and T. L. Chan, *Tetrahedron Lett.*, 4269 (1978).

Dibenzo[*a*,*c*]cyclooctene (8). A solution of bromine (2.9 g, 0.018 mol) in CCl_4 (30 mL) was added during 15 min to a stirred solution of **6** (3.715 g, 0.018 mol) in CCl_4 (70 mL), and stirring was continued for a further 15 min. Evaporation of the solvent gave crude crystalline **7**, which was boiled under reflux at 90 °C (external temperature) with DBN (8.4 g) in anhydrous benzene (70 mL) for 12 h. The mixture was allowed to cool and was washed successively with 10% aqueous H_2SO_4 (2 × 100 mL) and water (2 × 100 mL). The solution was dried ($MgSO_4$) and evaporated. Crystallization of the residue from EtOH yielded **8** (1.37 g, 37%): mp 122–124 °C (lit.[4,5] mp 124 °C); ^1H NMR δ 6.00 (d, 2 H, J = 11.8 Hz), 6.62 (d, 2 H, J = 11.8 Hz), 7.00–7.40 (m, 8 H); mass spectrum, m/e 204 (M^+), 178 ($M^+ - C_2H_2$).

Anal. Calcd for $C_{16}H_{12}$: C, 94.08; H, 5.92. Found: C, 93.88; H, 6.11.

5,6,7,8-Tetrabromo-5,6,7,8-tetrahydrodibenzo[*a*,*c*]cyclooctene (3).[4] A solution of bromine (0.78 g, 4.88 mmol) in CCl_4 (3 mL) was added dropwise to a solution of **8** (0.5 g, 2.45 mmol) in CCl_4 (6 mL). The solution was then stirred for 1 h at room temperature and for 1 h at 60 °C. Evaporation and crystallization from CS_2–petroleum ether, bp 60–80 °C, yielded **3** (0.69 g, 53%), mp 170–171 °C (lit.[4] mp 175–176 °C).

6,7-Dibromodibenzo[*a*,*c*]cyclooctene (9), 5-*tert*-Butoxy-7-bromodibenzo[*a*,*c*]cyclooctene (11), and 5,7-Di-*tert*-butoxydibenzo[*a*,*c*]cyclooctene (13) from 5,6,7,8-Tetrabromo-5,6,7,8-tetrahydrodibenzo[*a*,*c*]cyclooctene (3). A solution of **3** (50 mg, 0.0954 mmol) in anhydrous THF (2 mL) was added dropwise to a stirred solution of potassium *tert*-butoxide (55 mg, 0.49 mmol) in anhydrous THF (2 mL) under N_2. The solution was then stirred for a further 5 min, 5% aqueous HCl (10 mL) was added, and the organic materials were extracted with ether (25 mL). The ethereal solution was washed with water (2 × 25 mL) and dried (Na_2SO_4). The residue obtained by evaporation was chromatographed on a preparative SiO_2 plate (pentane–ether 12:1).

The more polar fraction contained **13** (10.5 mg, 32%): mp 65–66 °C by crystallization from MeOH; ^1H NMR δ 0.95 (s, 9 H), 1.09 (s, 9 H), 5.43 (s, 1 H), 6.14 (s, 1 H), 7.00–7.35 (M, 8 H); mass spectrum, m/e 348 (M^+), 292 ($M^+ - C_4H_8$), 236 ($M^+ - 2\ C_4H_8$); exact mass calcd for $C_{24}H_{28}O_2$ 348.209, found 348.221.

The less polar fraction contained two compounds and was rechromatographed on a preparative SiO_2 plate (pentane). The less polar compound was **9** (3.0 mg, 9.7%): mp 183–183.5 °C by crystallization from EtOH; ^1H NMR δ 7.07 (s, 2 H), 7.13–7.51 (m, 8 H); mass spectrum, m/e 360 (M^+), 281 ($M^+ - {}^{79}Br$), 202 ($M^+ - {}^{79}Br_2$); exact mass calcd for $C_{16}H_{10}Br_2$ 359.915, found 359.924. The more polar compound was **11** (3.0 mg, 8.9%): mp 85–86.5 °C by crystallization from MeOH; ^1H NMR δ 1.05 (s, 9 H), 5.69 (s, 1 H), 6.96 (s, 1 H), 7.20–7.50 (m, 8 H); mass spectrum, m/e 354 (M^+), 298 ($M^+ - C_4H_8$), 219 ($M^+ - C_4H_8 - {}^{79}Br$); exact mass calcd for $C_{20}H_{19}BrO$ 354.062, found 354.058.

6,7-Dibromodibenzo[*a*,*c*]cyclooctene (9) from 5,6,7,8-Tetrabromo-5,6,7,8-tetrahydrodibenzo[*a*,*c*]cyclooctene (3). A solution of potassium *tert*-butoxide (240 mg, 2.138 mmol) in anhydrous THF (10 mL) was added dropwise to a stirred solution of **3** (507.2 mg, 0.968 mmol) in anhydrous THF (10 mL) at room temperature under N_2. After the addition, the mixture was stirred for 2 h, 5% aqueous HCl (20 mL) was added, and the organic materials were extracted with ether (30 mL). The ethereal solution was washed with water (3 × 20 mL) and dried ($MgSO_4$). The residue obtained by evaporation was chromatographed on two preparative SiO_2 plates (pentane) to yield **9** (209.5 mg, 60%); the physical data were identical with an authentic sample.

5,7-Di-*tert*-butoxydibenzo[*a*,*c*]cyclooctene (13). A solution of the dibromide **9** (51 mg, 0.141 mmol) in anhydrous THF (2 mL) was added dropwise to a solution of potassium *tert*-butoxide (62 mg, 0.552 mmol) in anhydrous THF (2 mL). The mixture was stirred for 1 h, 2.5% aqueous HCl (10 mL) was added, and the organic materials were extracted with ether (20 mL). The ethereal solution was washed with water (2 × 20 mL) and dried ($MgSO_4$). The residue, after evaporation, was chromatographed on a preparative SiO_2 plate (pentane–ether 12:1) to yield **13** (24.8 mg, 50%); the physical data were identical with an authentic sample.

1,4:5,8-Diepoxy-1,4,5,8-tetrahydro-1,4,5,8-tetraphenyl-2,3:6,7-dibenzotetraphenylene (14) from 5,6,7,8-Tetrabromo-5,6,7,8-tetrahydrodibenzo[*a*,*c*]cyclooctene (3). A solution of **3** (50.7 mg, 0.0967 mmol) in anhydrous THF (2 mL) was added dropwise to a stirred solution of potassium *tert*-butoxide (120 mg, 1.069 mmol) and diphenylisobenzofuran (52.5 mg, 0.194 mmol) in anhydrous THF (5 mL) at room temperature under N_2. The mixture was stirred for 72 h, 5% aqueous HCl (100 mL) was added, and the resulting solution was extracted with ether (60 mL). The ether solution was washed with water (3 × 100 mL) and dried ($MgSO_4$). The residue after evaporation was chromatographed on a preparative SiO_2 plate (pentane–ether 12:1) to yield the bis-DIB adduct **14** (13.65 mg, 19%): mp 213–216 °C dec by recrystallization from EtOH; ^1H NMR δ 6.17–8.00 (m); mass spectrum, m/e 740 (M^+), 470 (M^+ – DIB); exact mass calcd for $C_{56}H_{36}O_2$ 740.272, found 740.272.

1,4:5,8-Diepoxy-1,4,5,8-tetrahydro-1,4,5,8-tetraphenyl-2,3:6,7-dibenzotetraphenylene (14) from 6,7-Dibromodibenzo[*a*,*c*]cyclooctene (9). A solution of **9** (95.2 mg, 0.263 mmol) in anhydrous THF (5 mL) was added dropwise to a stirred solution of potassium *tert*-butoxide (120 mg, 1.069 mmol) and 1,3-diphenylisobenzofuran (142.9 mg, 0.528 mmol) in anhydrous THF (5 mL) at room temperature under N_2. The mixture was stirred for 72 h, 5% aqueous HCl (50 mL) was added, and the resulting solution was extracted with ether (60 mL). The ethereal solution was washed with water (3 × 30 mL) and dried ($MgSO_4$). The residue after evaporation was chromatographed on a preparative SiO_2 plate (pentane–ether 12:1) to yield the bis-DIB adduct **14** (30.85 mg, 16%); the physical data were identical with those obtained previously.

Acknowledgment. We thank Professor E. Vogel for sending us a copy of the Ph.D. thesis of Dr. J. Wolpers. H.N.C.W. acknowledges with thanks the award of a Ramsay Memorial Fellowship, administered by University College London.

Registry No. 3, 73368-46-4; **5**, 73368-47-5; **6**, 10038-46-7; **7**, 73368-48-6; **8**, 217-22-1; **9**, 73368-49-7; **10**, 73368-50-0; **11**, 73368-51-1; **12**, 73368-52-2; **13**, 73368-53-3; **14**, 73384-31-3; 1,3-diphenylisobenzofuran, 5471-63-6.