Synthesis of Benzo[1,2:4,5]dicycloheptene-1,9-dione via 6,7,12,13-Tetrahydro-7,12-methano-3*H*-cycloheptacyclodecene-3,14-dione and Its Protonation Behavior

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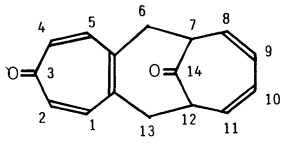
6,7,12,13-Tetrahydro-7,12-methano-3*H*-cycloheptacyclodecene-3,14-dione has been synthesized starting from the [4+6]-cycloaddition product of the reaction of 3,4-bis(methylene)-7,7-dibromobicyclo-[4.1.0]heptane with tropone. The adducts were transformed to their epoxides, which were treated with trifluoroacetic acid to give the 3,14-dione. This was transformed to benzo[1,2:4,5]dicycloheptene-1,9-dione, bis(tropono)benzene, by two different methods: (1) by heating it with trichloroacetic acid and DDQ in toluene or (2) through bromination followed by heating in DMF. The 1,9-dione is protonated in concd sulfuric acid to give bis(hydroxytropylium) dication, while it is protonated mainly (>80%) on the C-9 carbonyl oxygen and less (<40%) on the C-1 carbonyl oxygen in deuteriochloroform containing trifluoroacetic acid.

In a previous paper,[1] we reported the scope and limitations for one pot synthesis of substituted tropones starting from 7,7-dihalo-2,3- (or 3,4-) epoxybicyclo-[4.1.0]heptane derivatives.

Using this procedure with the epoxides obtained from cycloaddition products of 3,4-bis(methylene)-7,7-dibromobicyclo[4.1.0]heptane (**1**)[1] with tropone, we obtained 6,7,12,13-tetrahydro-7,12-methano-3*H*-cycloheptacyclodecene-3,14-dione (**2**).



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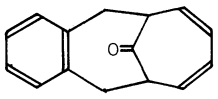

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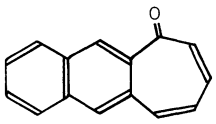

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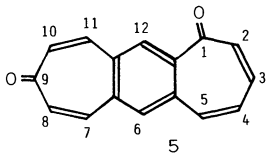

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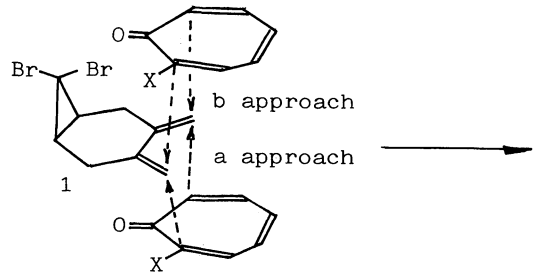
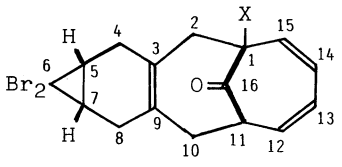
Fujise et al. observed the oxidative rearrangement of 5,6,12,13-tetrahydro-6,11-methanobenzocyclodecen-13-one (**3**) to 6*H*-cyclohepta[*b*]naphthalen-6-one (**4**) by heating with DDQ in DMF or with trityl tetrafluoroborate.[2] If this rearrangement is accomplished in dione **2**, we may obtain a new bis(tropono)benzene (**5**).

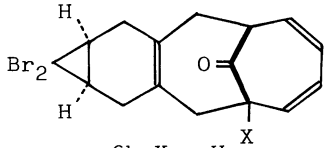
Results and Discussion

Synthesis of Benzo[1,2:4,5]dicycloheptene-1,9-dione (5). 6,7,12,13-Tetrahydro-7,12-methano-3*H*-cycloheptacyclodecene-3,14-dione (2). When 3,4-bis(methylene)-7,7-dibromobicyclo[4.1.0]heptane (**1**) was used as a diene in the [6+4] cycloaddition reaction with tropone in refluxing toluene, tetracyclic compounds **6a** and **6b** were obtained in a ratio of 3.8:1. This reaction proceeded more regioselectively in benzene solution in a sealed tube at 100 °C (yield, 90%; **6a**:**6b**=9:1). Because it is known that tropone adds anti to cyclopentadiene or furan in a sense of $[_6\pi_s+_4\pi_s]$cycloaddition preventing secondary orbital repulsion,[3,4] it seems reasonable to assume that the main product of the cycloaddition to **1** might be **6a**,





6a X = H
6c X = Cl

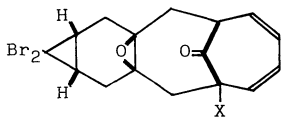


6b X = H

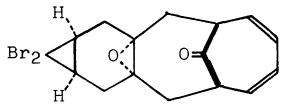
Scheme 1.

formed by the approach from the less hindered side (a) of **1**, and the minor product might be **6b**, formed by the attack from the more hindered side (b) of **1** (Scheme 1).

Though compound **1** did not react with 2-chlorotropone in refluxing toluene, they produced the [6+4] adduct **6c** in benzene solution in a sealed tube at 100 °C (yield 52%; solely *anti*).



7a X = H
7c X = Cl



7b

Epoxidation of a mixture of **6a** and **6b** with *m*-chloroperbenzoic acid (mCPBA) resulted in a mixture of **7a** and **7b** in the same ratio as that of the starting material. We have already seen that the epoxidation is usually prohibited or only proceeds with difficulty from the *syn*-face of the dibromomethylene bridge in the 3,4-annelated 7,7-dibromobicyclo[4.1.0]hept-3-ene moiety,[1,5] therefore, the major product is expected to be *anti*-7 (**7a**) and the minor one to be *syn*-7 (**7b**). Compound **6c** was also converted to an epoxide (**7c**) as a single product.

Treatment of the epoxides, **7a** or a mixture of **7a** and **7b**, with 20 equimolar amounts of trifluoroacetic acid (TFA) either in refluxing chloroform or preferably in toluene at 100 °C, gave tropone **2** in 41—55% yields.[6] On the other hand, when **7a** was treated with 4 equimolar amounts of trichloroacetic acid (TCA) in refluxing toluene for 4 h, it gave benzo[1,2:4,5]dicycloheptene-1,9-dione (**5**) in a 27% yield. As it is reasonable to assume that compound **5** might be formed via tropone **2**, this was treated with TCA in toluene at 100 °C in the presence or absence of 2,3-dichloro-4,5-dicyano-*p*-benzoquinone (DDQ) (Table 1). From Table 1, it is clear that the presence of DDQ did not much improve the yield of bistropone **5** and, on the other hand, in the presence of 1 or 2 equimolar amounts of TCA and DDQ, a new rearranged product, benzoheptalene derivative **8**, was isolated in a 10% yield in addition to **5**.

Structures of Tropones 2, 5, and 8. 6,7,12,13-Tetrahydro-7,12-methano-3*H*-cycloheptacyclodecene-3,14-dione (2). From ^{1}H and ^{13}C NMR spectra, it is clear that compound **2** has a plane of symmetry. Thus, it shows seven kinds of proton signals and nine kinds of carbon signals. The IR spectrum shows two strong absorptions at 1631 and 1595 cm^{-1} characteristic of tropone[7] in addition to a normal carbonyl absorption at 1703 cm^{-1}. These spectral data are compatible with structure **2** resulting from the normal ring opening of **7a** and **7b**.

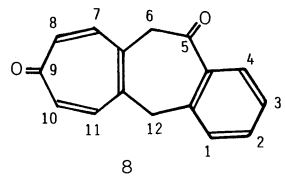
Benzo[1,2:4,5]dicycloheptene-1,9-dione (5). In the ^{13}C NMR spectrum, two carbonyl carbon signals are seen at 187.9 and 187.2 ppm attributed to the tropone carbonyl,[8] in addition to twelve olefinic carbon signals in which four are assigned to quaternary carbons. Signals attributed to C_8/C_{10} or C_7/C_{11} are unresolved. In ^{1}H NMR spectra, all ten kinds of protons are detected, in which two singlets (8.75 and 7.94 ppm) are assigned to the aromatic protons on the benzene ring, and one in the lowest field is assigned to a proton on C_{12} as it is expected to be deshielded by the ortho carbonyl group. A series of signals, 6.99(bd), 7.13(ddd), 6.82(ddd), and 7.38 (bd) ppm are assigned to H_2, H_3, H_4, and H_5, respectively, and are coupled vicinally to each other with bond order alteration as shown by the coupling constants: $J_{2,3}$=12.2, $J_{3,4}$=7.8, $J_{4,5}$=11.6 Hz. Two pairs of signals coupled to each other (6.83(d), 7.63(d) and 6.86(dd), 7.52(d)) are assigned to H_8, H_7 and H_{10}, H_{11}. In the IR spectrum, two sets of characteristic tropone absorption are seen at 1634, 1610, 1594, and 1584 cm^{-1}.[7] In the mass spectrum, in addition to the molecular ion peak (m/z=234), peaks due to M^+—CO and M^+—2CO were observed, in which the latter constitutes the base peak. These spectral data support a structure in which the benzene ring is fused at its 1,2 and 4,5 positions with two tropone rings, one symmetrically (at the 4,5 position of the tropone ring) and the other unsymmetrically (at the 2,3 position) as in **5**.

6,12-Dihydrobenzo[*b*]heptalene-5,9-dione (8). In the ^{13}C NMR spectrum, in addition to two carbonyl carbon signals (204.0(ketone) and 186.2 ppm (tropone)), twelve aromatic and two aliphatic carbon signals were observed. In the ^{1}H NMR spectrum, characteristic AA'BB' proton signals for 4,5-annelated tropones were seen at δ=7.02 (1H, dd, J=12.7, 2.7 Hz), 7.05 (1H, dd, J=12.7, 2.7 Hz), and 7.21 (2H, bd, J=12.7 Hz). The

Table 1. Oxidative Rearrangement of **2**

Entry	Acid[a] equiv	DDQ[a] equiv	Solvent	Temperature/°C	Time h	Yield/%[b] 5	8
1	TCA/5	Nil	Toluene	100	50	21	0
2	TCA/1	2	Toluene	100	30	18	10
3	TCA/2	2	Toluene	100	30	19	10
4	TCA/1	6	Toluene	100	30	23	0
5	AcOH/1	4	Toluene	100	50	17	0
6	Nil	5	CH_3CN	Reflux	30	7	0

a) Quantities of acid and 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) used are shown in equivalet(s) per mole of **2**. b) Isolated yields are shown.



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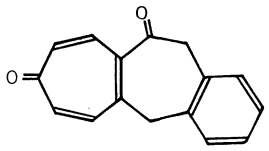

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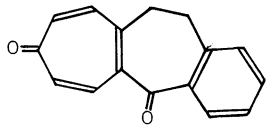

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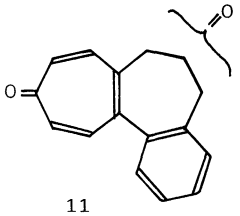
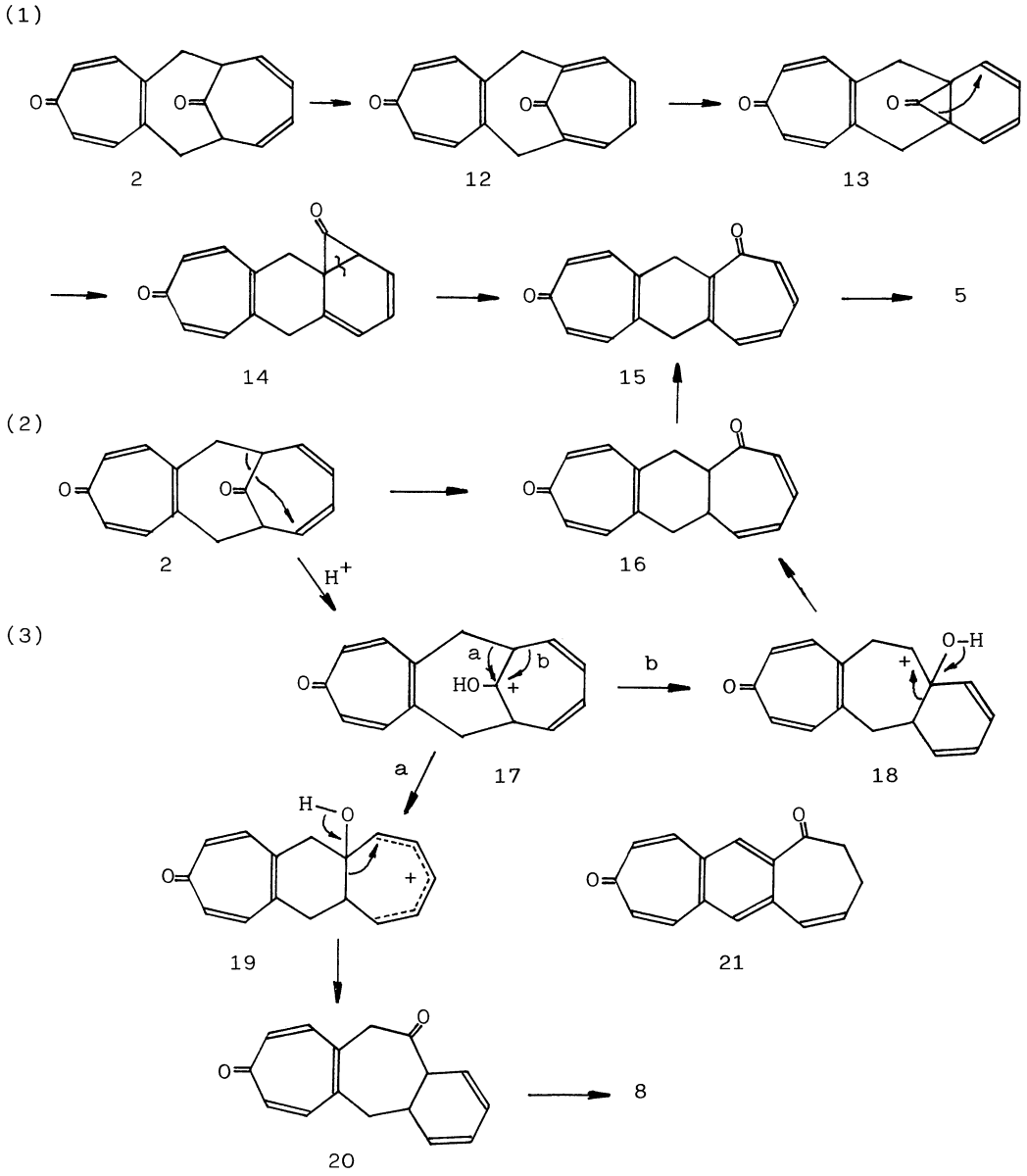


11

aromatic signals at 7.39, 7.65, 7.51, and 7.60 ppm in this order showed similar vicinal coupling constants, $J_{1,2}=J_{2,3}=J_{3,4}=7.8$ Hz, and meta coupling, $J_{1,3}=J_{2,4}=$ 1.0—1.5 Hz, which predicted a complete double bond delocalization. This supports the presence of an *o*-annelated benzene ring. Aliphatic proton signals were also seen as a broad singlet at 2.90—3.10 ppm (4H). Among four possible structures, (**8**)—(**11**), structure **8** may well predict the identical chemical shifts of H_7 and H_{11} (both are not adjacent to a carbonyl group or an aromatic ring), and the relatively low chemical shift of H_4.

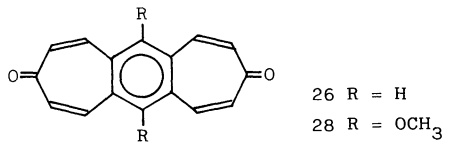
The Reaction Mechanism for Formation of 5. Formation of **5** (and **8**) from **2** may be explained by the three mechanisms shown in Scheme 2: (1) Initial dehydrogenation of **2** to bistropone (**12**), followed by a 6π-electrocyclic reaction to **13**, then a [1,5]sigmatropic



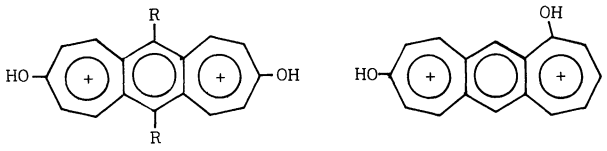
Scheme 2.

shift of the carbonyl carbon[2] results in a norcaradienone derivative (**14**), which undergoes 6π-retrocyclization to a 6,12-dihydro compound of **5** (**15**). (2) A thermal [1,5]-sigmatropic shift of **2** controlled by orbital symmetry gives a tetrahydro compound of **5** (**16**). Dehydrogenation of **16** may give **5** via **15**. (3) The protonated form (**17**) of **2** may undergo two successive 1,2-cationic rearrangements[9,10] to **16** via **18**. The last mechanism can only explain the formation of **8** through **19**. The NMR spectra of **2** in DMSO-d_6 revealed that compound **5** and its dihydro derivative (**21**) were formed at elevated temperatures (>155 °C), but these products were not detected below 145 °C.

Another Route to 5 Starting from 2. Next, the bromination/dehydrobromination procedure of **2** was studied. We found that this procedure gave an improved yield (56%) of **5**. Thus, tropone **2** was treated with 1 equimolar amount of bromine to give a dibromide (**22**), which was transformed to **5** by heating at 100 °C in *N*,*N*-dimethylformamide (DMF). This reaction can be predicted by the following two mechanisms as shown in Scheme 3: (1) two successive dehydrobrominations of **22** may give bis(tropono)phane **12**, which follows the sequence (1) in Scheme 2 leading to **5**. (2) If deprotonation occurs on the brominated carbon of allylic cation **23** formed from **22** by Br^-- elimination in DMF, diene **24** may be formed. This can then undergo a [1,5]sigmatropic shift assisted by bromine to give **25**, which may be transformed to **5** via **15**. At present, it is left to be discovered which mechanism is involved.



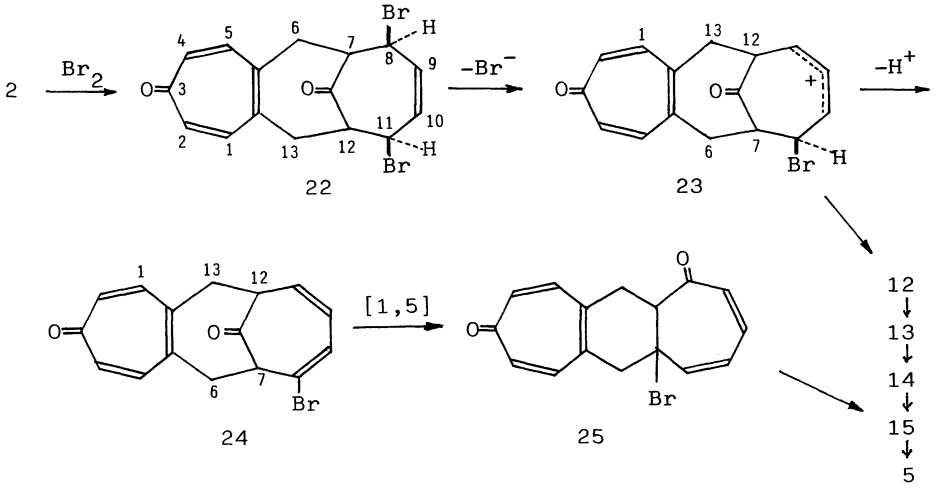
26 R = H
28 R = OCH_3



27 R = H
29 R = OCH_3

30

Protonation of Benzo[1,2:4,5]dicycloheptene-1,9-dione (5). In 1969, Föhlisch et al. synthesized benzo-[1,2:4,5]dicycloheptene-3,9-dione (**26**) and suggested the formation of the corresponding bis(hydroxytropylium) dication (**27**) in concentrated sulfuric acid on the basis of a bathochromic shift (Δ+30 nm) of the absorption maximum compared with that in methanol (λ_{max} 296 nm).[11] We also compared the spectrum of the 6,12-dimethoxy derivative (**28**)[12] in ethanol (λ_{max} 313 nm) with the one in concd sulfuric acid (λ_{max} 347 nm) and found a similar bathochromic shift (Δ+34 nm), suggesting the formation of dication **29**. The same tendency (Δ+36 nm) was observed in the electronic spectra for **5** in ethanol (λ_{max} 284 nm) and in concd sulfuric acid (λ_{max} 320 nm). This fact supports the existence of dication (**30**) in concd



Scheme 3.

Table 2. ^{1}H NMR Chemical Shifts (δ in ppm) of Compounds **5** and **28** in the Presence or Absence of TFA[a]

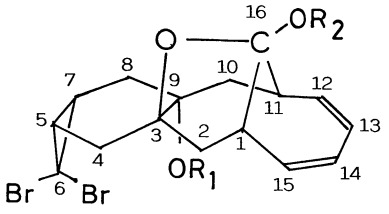
Solvent	Compound **28**		Compound **5**							
	H_2, H_4, H_8, H_{10}	H_1, H_5, H_7, H_{11}	H_8 and H_{10}		H_7 and H_{11}		H_2	H_3	H_4	H_5
$CDCl_3$	6.92	8.08	6.83	6.86	7.52	7.63	6.99	7.13	6.82	7.38
$CDCl_3$ (TFA)	8.12	9.60	7.80	7.95	8.75	8.83	7.54	7.34	7.39	7.98
	−1.29	−1.52	−0.97	−1.09	−1.23	−1.20	−0.55	−0.21	−0.57	−0.60

a) 5 Drops of TFA and 1 drop of trifluoroacetic anhydride were added to a 5% solution of the sample in $CDCl_3$.

sulfuric acid.

Additionally, the ^{1}H NMR spectra of **5** and **28** in $CDCl_3$ in the presence of a large excess of TFA containing one drop of trifluoroacetic anhydride were examined. From Table 2, though the deshielding shifts of the signals due to protons H_7, H_8, H_{10}, and H_{11} of **5** are 80% of those due to the respective protons in **28**, signals due to protons H_2, H_3, H_4, and H_5 in **5** showed only a moderate deshielding shift, which means protonation occured mostly (>80%) on the C_9 carbonyl oxygen and less on the C_1 carbonyl oxygen (<40%) in **5** under the same conditions.

The reduction potential of **5** was examined by a cyclic voltammograph. An irreversible reduction curve was obtained. The reduction started at −1.03 V and the first peak was observed at −1.2 V, but the second peak varied considerably in the second and the later cycles. We have observed the corresponding peaks of the reduction wave for benzo- or naphtho-annelated tropones to range from −1.6 to −1.8 V.[13] Enhancement of the electron affinity of compound **5** is clearly recognized. The systematic study of the electron affinities of various troponobenzenes and bis(tropono)benzenes is now under investigation and will be reported in a separate paper.



31 a R_1= $COCF_3$, R_2= H

b R_1= H, R_2= $COCF_3$

Experimental

General Procedure. The NMR spectra were taken on JEOL Models GX400 (^{1}H; 400 MHz, ^{13}C; 100 MHz) and FX100 (1H; 100 MHz, ^{13}C; 25 MHz), or a Hitachi Model R90H (1H; 90 MHz) FT-NMR spectrometer. Deuteriochloroform was used as solvent in every case unless otherwise specified. The existence of spin–spin coupling was confirmed by double irradiation experiments. The IR spectra were recorded on a JASCO Model A-102 spectrometer and the UV spectra on a Hitachi Recording spectrometer Model 323. The reduction potential of **5** was recorded on a BAS voltammetry control unit Model CV-1B in acetonitrile containing tetrabutylammonium perchlorate (10^{-1} mol dm^{-3}) as the supporting electrolyte. Ferrocene was used as an internal standard (+0.40 V).

[4+6]Cycloaddition of Diene 1 to Tropone. Method A. A solution of diene **1** (550 mg, 2.0 mmol) and tropone (284 mg, 2.7 mmol) dissolved in toluene was refluxed for 17 h. The residue, obtained after evaporation of the solvent under reduced pressure, was purified by chromatography on silica gel to give products **6a** and **6b** (591 mg, 77%; 3.8:1). The main product **6a**; mp 166—168 °C. ^{1}H NMR (400 MHz): See Table 3. ^{13}C NMR (100 MHz) δ=26.2 (C5, C7), 28.7 and 34.7 (C2, C10 and C4, C8), 38.3 (C6), 55.1 (C1, C11), 127.4 (C3, C9), 125.2 and 127.6 (C12, C15 and C13, C14), 207.4 (C16). IR (nujol mull) ν_{max} 1695, 1680 cm^{-1}. Found: C, 50.01; H, 4.24%. Calcd for $C_{16}H_{16}OBr_2$: C, 50.03; H, 4.20%. Compound **6b** was not obtained in a pure state. The content of **6b** in a mixture was estimated by ^{1}H NMR spectra. **6b**: ^{1}H NMR (400 MHz): See Table 3. ^{13}C NMR (100 MHz) δ=26.1 (C_5, C_7), 29.1 and 34.4 (C_2, C_{10} and C_4, C_8), 36.7 (C_6), 55.7 (C_1, C_{11}), 127.4 (C_3, C_9), 124.9 and 126.7 (C_{12}, C_{15} and C_{13}, C_{14}), 207.4 (C_{16}).

Method B. A mixture of diene **1** (0.90 g, 3.24 mmol) and tropone (519 mg, 4.89 mmol) dissolved in benzene (2.7 mL) was sealed in a glass tube and heated at 100 °C for 16 h. The mixture was then concentrated in vacuo and chromatographed on silica gel to give a mixture of **6a** and **6b** (9:1)(1.13 g, 90%).

[6+4]Cycloaddition of 1 to 2-Chlorotropone. A mixture of diene **1** (992 mg, 3.57 mmol) and 2-chlorotropone (600 mg, 4.27 mmol) dissolved in benzene (6 mL) was heated in a sealed tube at 100 °C for 37 h. The usual workup as above gave

Table 3. ^{1}H NMR Chemical Shifts (δ in ppm) and Their Coupling Constants (J in Hz) of Compounds **6a**, **6b**, **7a**, and **7b** in Deuteriochloroform (400 MHz)

Proton	6a	6b	7a	7b
H_{13} H_{14}	5.83 (A_2) of $A_2B_2X_2$	5.813 (A_2) of $A_2B_2X_2$	5.962 (d)	5.88 (m)
H_{12} H_{15}	5.51 (B_2) of $A_2B_2X_2$	5.470 (B_2) of $A_2B_2X_2$	5.605 (t)	5.60 (m)
H_1 H_{11}	3.43 (m)	3.5—3.42 (m)	3.391 (dd)	3.48 (m)
H_2 H_{10}	2.445 (dd)	2.49—2.38	2.453 (dd)	2.42 (dd)
$H_{2'}$ $H_{10'}$	2.352 (dd)	2.25 (dd)	2.215 (dd)	2.24 (dd)
H_4 H_8	2.450 (dd)	2.49—2.38	2.357 (ddm)	2.43 (d)
$H_{4'}$ $H_{8'}$	2.01 (d)	2.09 (d)	1.778 (d)	1.81 (dm)
H_5 H_7	1.94—1.86	1.94—1.86	1.68—1.73	1.70 (m)
$J_{12,13}$	11.8 (Hz)	11.9 (Hz)	11.5 (Hz)	—
$J_{11,12}$	6.0	—	—	6.6 Hz
$J_{1,2}$	6.0	—	6.8	8.1
$J_{1,2'}$	6.0	6.4	7.8	10.3
$J_{2,2'}$	14.5	14.4	15.6	14.7
$J_{4,4'}$	16.8	16.4	16.8	15.4
$J_{4,5}$	5.0	—	6.6	—
$J_{4',5}$	0.0	0.0	0.0	—

Table 4. The Chemical Shifts (δ in ppm) and the Coupling Constants (J in Hz) of Compounds **6c** and **7c**

Protons	6c	7c
H_{13}	5.915 (ddd) (ppm)	5.974 (ddd) (ppm)
H_{14}	5.865 (dd)	5.898 (dd)
H_{12}	5.573 (dd)	5.620 (dd)
H_{15}	5.778 (d)	5.798 (d)
H_{11}	3.762 (m)	3.50—3.57 (m)
H_2	3.372 (d)	3.290 (d)
H_{10}	2.550 (dd)	2.630 (dd)
$H_{2'}$	2.425 (d)	2.327 (d)
$H_{10'}$	2.3—2.43 (b)	2.271 (dd)
H_4	2.764 (bd)	2.45—2.54
H_8	2.3—2.43 (b)	2.28—2.38
$H_{4'}$ $H_{8'}$	1.97—2.11	1.72—1.8
H_5 H_7	1.87—1.97 (m)	
$J_{13,14}$	6.6 (Hz)	6.4 (Hz)
$J_{14,15}$	11.5	11.2
$J_{12,13}$	11.5	11.1
$J_{11,13}$	1.7	1.8
$J_{11,12}$	5.0	4.8
$J_{2,2'}$	15.4	16.1
$J_{10,11}$	9.0	9.9
$J_{10,10'}$	15.8	15.6
$J_{10',11}$	0.0	4.2

colorless crystals of **6c** (755 mg, 52%), mp 176—177.5 °C. ^{1}H NMR (400 MHz): See Table 4. ^{13}C NMR (100 MHz) δ=197.4 (s), 132.4 (d), 131.1 (s), 128.2 (d), 126.1 (s), 124.8 (d), 123.4 (d), 81.4 (s), 53.0 (d), 41.7 (t), 37.7 (s), 36.4 (t), 29.7 (t), 28.6 (t), 26.2 (d), 26.1 (d). IR (nujol mull) ν_{max} 1716, 1420, 1320, 1200, 1125, 1155 cm^{-1}. Found: C, 45.95; H, 3.59%. Calcd for $C_{16}H_{15}OBr_2Cl$: C, 45.91; H, 3.61%.

Epoxidation of Adduct 6. A solution of *m*-CPBA (779 mg, 4.51 mmol) in dichloromethane (11 mL) was added dropwise at −10 °C to a mixture (3:1) of adducts **6a** and **6b** (1.17 g, 3.05 mmol) dissolved in dichloromethane (10 mL) and stirred for 4 h below 0 °C. More dichloromethane was added in order to dissolve precipitated *m*-chlorobenzoic acid and the solution was washed successively with 10% aq sodium hydrogensulfite (twice), 5% aq sodium hydrogencarbonate (twice), and saturated brine, and then dried. After concentration, the residue was chromatographed on silica gel to give epoxides **7a** (715 mg, 59%) and **7b** (202 mg, 17%). **7a**: Mp 97.5—101 °C (CH_2Cl_2–hexane). ^{1}H NMR (400 MHz): See Table 3. ^{13}C NMR (100 MHz) δ=191.1 (s), 129.1 (d), 126.0 (d), 61.6 (s), 51.9 (d), 38.5 (s), 34.1 (t), 28.7 (t), 24.6 (d). IR ($CHCl_3$) ν_{max} 3000, 2910, 1700, 995, 840 cm^{-1}. Found: C, 48.03; H, 4.05%. Calcd for $C_{16}H_{16}O_2Br_2$: C, 48.03; H, 4.03%. **7b**: Mp 101—104 °C. ^{1}H NMR (400 MHz): See Table 3. IR ($CHCl_3$) ν_{max} 3000, 2930, 1700, 1080, 860 cm^{-1}. Found: C, 48.06; H, 4.05%. Calcd for $C_{16}H_{16}O_2Br_2$: C, 48.03; H, 4.03%.

Tropone 2 from Epoxide 7a. TFA (1.67 mL, 5 molar equiv) was added to a solution of **7a** (1.74 g, 4.34 mmol) in toluene (17 mL) and heated at 80 °C for 1.5 h. At this point, an additional TFA (6.69 mL, 20 molar equiv) was introduced and the mixture was refluxed for an additional 27 h. After cooling, it was diluted with chloroform and washed successively with water, 5% aq sodium hydrogencarbonate, and saturated brine, and then dried. After concentration to dryness, the residue was triturated with ethyl acetate to give pale yellow crystals (509 mg) of **2**. The filtrate of the crystals gave a 2nd crop (58 mg) of **2** after chromatographic separation (total yield, 55%). **2**: Mp 226—231 °C (CH_2Cl_2–AcOEt). ^{1}H NMR (400 MHz) δ=3.00 (2H, dd, J=14.4, 7.2 Hz; H_6, H_{13}), 3.14 (2H, dd, J=14.4, 4.2 Hz; $H_{6'}$, $H_{13'}$), 3.68 (2H, m; H_7, H_{12}), 5.57 (2H, m; H_8, H_{11}), 5.78 (2H, m; H_9, H_{10}), 6.89 (2H, dm, J=12.5 Hz; H_2, H_4), 6.98 (2H, dm, J=12.5 Hz; H_5, H_1). ^{13}C NMR (100 MHz) δ=205.8 (s), 186.3 (s), 145.1 (s), 141.3 (d), 139.6 (d), 126.6 (d), 125.5 (d), 56.0 (d), 39.7 (t). IR ($CHCl_3$) ν_{max} 1703, 1631, 1595 cm^{-1}. Found: C, 80.48; H, 5.90%. Calcd for $C_{16}H_{14}O_2$: C, 80.65; H, 5.92%.

Direct Formation of Bis(tropono)benzene 5 from Tropone 2 (Table 1; Entry 3). DDQ (294 mg, 1.27 mmol) in toluene (7.5 mL) was added to a solution of tropone **2** (150 mg, 0.630 mmol) and TCA (208 mg, 1.27 mmol) in toluene (2.5 mL) and the resulting solution was stirred for 30 h at 100 °C. After cooling, the mixture was diluted with chloroform and then washed successively with water, 5% aq sodium hydrogencarbonate, and saturated brine, and then dried. After concentration, the residue was separated by chromatography to give **5** (27.5 mg, 19%) and **8** (15.5 mg, 10%). The procedures for other entries in Table 1 are similar to this one. **5**: Mp 206.5—209.0 °C. ^{1}H NMR (400 MHz) δ=6.82 (1H, ddd, J=11.6, 7.8, 1.0 Hz; H_4), 6.83 (1H, d, J=12.7 Hz) and 6.86 (1H, dd, J=12.9, 2.6 Hz)(H_8, H_{10}), 6.99 (1H, d, J=12.2 Hz; H_2), 7.13 (1H, ddd, J=12.2, 7.8 Hz; H_3), 7.38 (1H, bd, J=11.6 Hz; H_5), 7.52 (1H, d, J=12.9 Hz) and 7.63 (1H, d, J=12.7 Hz)(H_7, H_{11}), 7.94 (1H, s; H_6), 8.75 (1H, s; H_{12}). ^{13}C NMR (100 MHz) δ=187.9 (s), 187.2 (s), 140.7 (d), 139.6 (d), 139.5 (d), 138.8 (s), 138.2 (d), 138.0 (s), 137.6 (s), 136.8 (d), 136.7 (d), 136.5 (s), 135.8 (d), 135.7 (d), 128.6 (d, 2C). IR ($CHCl_3$) ν_{max} 3040, 1634, 1610, 1594, 1584, 1338 cm^{-1}. MS m/z (%) 234 (47, M^+), 206 (15, M^+—CO), 178 (100, M^+—2CO), 152 (10). UV λ_{max} (log ε) 237 (4.31), 284 (4.68), 351 (4.07). **8**: ^{1}H NMR (400 MHz); see in the text. ^{13}C NMR (100 MHz) δ=204.1, 186.2, 145.6, 143.5, 141.6, 140.5, 140.1, 139.8, 139.4, 138.6, 132.2, 129.4, 129.2, 127.9, 47.2, 33.9. IR ($CHCl_3$) ν_{max} 1680, 1624, 1594, 1570, 900 cm^{-1}.

Bis(tropono)benzene 5 from Epoxide 7a. A solution of **7a** (143 mg, 0.356 mmol) and TCA (140 mg, 0.51 mmol) in toluene (5.0 mL) was refluxed for 28 h. After cooling, the mixture was diluted with chloroform and washed successively with water, 5% aq sodium hydrogencarbonate, and saturated brine, and then dried. After concentration, the residue was chromatographed on silica gel to give **5** (27.4 mg, 27%).

Bis(tropono)benzene 5 from 2 via Bromination and Dehydrobromination. Bromination of 2. A solution of bromine (0.77 molar solution, 8.6 mL) in chloroform was added dropwise to a solution of **2** (158 mg, 0.66 mmol) in chloroform (6.0 mL) on ice in a period of 20 min. Stirring was continued for 30 min at the same temperature and the precipitates formed (**22**; 134 mg, 77%) were collected by filtration. This compound was used directly without further purification. The symmetrical nature of the ^{1}H NMR spectrum suggests that two bromine atoms add to **2** symmetrically from less-hindered *exo*-directions. **22**: ^{1}H NMR (90 MHz, DMSO-d_6 δ=2.8—3.1 (4H, m; $2H_6$, $2H_{13}$), 3.21—3.5 (2H, m; H_7, H_{12}), 5.0 (2H, bs; H_8, H_{11}), 6.1 (2H, bs; H_9, H_{10}), 6.7 (2H, d, J=12.0 Hz; H_2, H_4), 7.13 (2H, d, J=12.0 Hz; H_1, H_5). IR (nujol mull) ν_{max} 1710, 1600 cm^{-1}.

Bis(tropono)benzene 5 from Dibromide 22. A solution of dibromide **22** (151 mg, 0.38 mmol) in DMF (7.5 mL) was heated at 100 °C for 3 h with stirring. After cooling, the

solvent was evaporated under aspirator vacuum and the residue was purified with silica-gel chromatography to give **5** (65 mg, 73%).

Thermal Rearrangement of Epoxide 2 to Bis(tropono)benzene 5 via 6,12-Dihydro Compound of 5 (15). A 10% solution of **2** in DMSO-d_6 was heated to the appropriate temperature and the reaction was monitored by ^{1}H NMR measurement (90 MHz). Below 145 °C for 2 h, no change in the ^{1}H NMR spectrum of the starting material was observed. However, after 2 h at 155 °C, compound **2** was transformed to a product believed to be **21** in a 40% yield. This was isolated using chromatography and its NMR spectrum was taken. ^{1}H NMR (400 MHz) of the product, δ=2.56—2.64 ($2H_3$, m), 2.99—3.31 ($2H_2$, m), 6.35 (H_4, dt, J=11.8, 5.5 Hz), 6.58 (H_5, d, J=11.8 Hz), 6.78 (H_8 or H_{10}, dd, J=12.3, 2.6 Hz), 6.83 (H_{10} or H_8, dd, J=12.3, 2.6 Hz), 7.36 (H_{11} or H_7, d, J=12.3 Hz), 7.49 (H_7 or H_{11}, d, J=12.3 Hz), 7.54 (H_6, s), 8.18 (H_{12}, s). This compound does not seem to be the primary product resulting from a simple [1,5]shift but the product formed by dehydrogenation and migration of double bonds. It was observed that compound **2** was partially transformed to **5** concomitant with some decomposition by heating at 170 °C for 2 h.

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6) When a solution of epoxide **7a** (32.2 mg, 0.083 mmol) dissolved in chloroform (1.0 mL) was heated at 65 °C with TFA (0.13 mL, 1.66 mmol) for 2 h, a single product (R_f=0.18) different from the starting compound **7a** (R_f=0.34) on TLC (silica gel/benzene–ethyl acetate (9:1)) was observed. The product was isolated by column chromatography as an oil (21 mg; 60%). ^{1}H NMR (400 MHz) δ=5.919 (H_{14}, dd), 5.849 (H_{13}, ddd), 5.709 (H_{12}, bdd), 5.683 (H_{15}, dd), 3.094 (H_1, m), 2.77 (H_{11}, m), 2.748 (H_{8a}, d), 2.565 (H_{10b}, dd), 2.401 (H_{8b}, ddd), 2.282 (H_{4b}, dd), 2.164 (H_{2b}, t), 2.07 (H_7, m), 2.04 (H_5, m), 1.99 (H_{10a}, m), 1.945 (H_{2a}, dd), 1.776 (H_{4a}). $J_{1,2a}$=7.8 Hz, $J_{1,2b}$=13.4 Hz, $J_{1,11}$=2.2 Hz, $J_{1,15}$=4.6 Hz, $J_{2,2b}$=13.4 Hz, $J_{4a,4b}$=15.3 Hz, $J_{4a,5}$=5.6 Hz, $J_{4b,5}$=10.0 Hz, $J_{7,8a}$=0 Hz, $J_{7,8b}$=9.5 Hz, $J_{8a,8b}$=17.3 Hz, $J_{10a,10b}$=13.7 Hz, $J_{10b,11}$=9.5 Hz, $J_{11,12}$=8.5 Hz, $J_{12,13}$=12.0 Hz, $J_{13,14}$=6.8 Hz, $J_{14,15}$=11.0 Hz. ^{13}C NMR (100 MHz) δ=129.7, 127.7, 127.3, and 123.1 (C_{12}, C_{13}, C_{14}, C_{15}), 105.7 (s, C_{16}), 81.9 (d, J_{CH}=7.3 Hz) and 79.2 (d, J_{CH}=7.3 Hz)(C_3, C_9), 50.8 (d, J_{CH}=125 Hz) and 45.1 (d, J_{CH}=131 Hz)(C_1, C_{11}), 38.5 (s, C_6), 37.1 (t, J_{CH}=135 Hz), 33.7 (t, J_{CH}=134 Hz), 29.0 (t, J_{CH}=130 Hz), and 26.5 (t, J_{CH}=127 Hz)(C_2, C_4, C_8, C_{10}), 26.9 (d, J_{CH}=166 Hz) and 26.3 (d, J_{CH}=169 Hz)(C_5, C_7). IR ($CHCl_3$) ν_{max} 3600 (s), 1780 (vs), 1365 (m), 1160 (vs), 1132 (m), 1185 (m), 1160 (m), 1100 (m) cm^{-1}.

This compound seems to be a hemiacetal (**31**) and was transformed to tropone **2** by prolonged heating with TFA in toluene.

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