addition promoter cupric acetate monohydrate.[19] The trans/cis ratio was 83:17 by NMR integration (doublets at δ 3.9 and 4.1, respectively). HPLC purification (10-μm silica gel column; 20% CH_2Cl_2; 0.1% ethanol, 80% hexane; retention time 13.5 min at a 5-mL/min flow rate) gave **18**: 99.8% pure; n^{21}_D 1.5532; NMR (CCl_4) δ 2.3 (s, 3 H) 3.2 (d, 2 H, J = 4 Hz) 3.6 (s, OH), 3.9 (d, 2 H, J = 4 Hz), 5.6 (m, 2 vinyl H), 7.0 (s, 4 aromatic H); IR (AgCl disks) 3200–3600 (OH), 960 (trans C=C), 800 (para) cm^{-1}; mass spectrum, calcd for $C_{11}H_{14}O$ (M^+) 162.1044, m/e found 162.1048.

1,4-Di-*o*-tolyl-*trans*-2-butene (Isomer of 19). The Grignard of *o*-bromotoluene (2 equiv) was combined with 1,4-dibromo-2-butyne. After a typical workup, 0.95 g of the alkyne was forced under a mixture of 0.28 g of sodium and 20 mL of anhydrous ammonia. A normal reaction time and workup gave 0.5 g of product, which was purified by preparative GC (6 ft OV17 column, 180 °C): NMR (CCl_4) δ 2.3 (s, 6 H), 3.3 (d, 4 H), J = 4 Hz), 5.6 (m, 2 H), 7.0 (s, 4 H); IR (AgCl disks) 965 (m, trans C=C), 740 (ortho) cm^{-1}.[26] The GC retention time and spectra agreed with those of the sample from the Friedel–Crafts reaction (see below).

General Friedel–Crafts Procedure for 1,2-Epoxy-3-butene (Regular Addition). A solution of 1.0 g of the epoxide (14 mmol) in 9 mL of toluene was added dropwise over 6–8 min to a solution of 0.46 or 1.08 equiv of Lewis acid in 50 mL of dry toluene (initially at 27 °C; the temperature increased to 33 °C after the addition began). The addition time was varied only slightly to control the temperature at 33 °C. The solution was stirred at 33 °C for the time described in Tables I–III, washed with 10% sodium hydroxide and water, and dried ($MgSO_4$). The organic layer was evaporated overnight in an evaporating dish. The concentrate (1.2–1.5 g) was analyzed by GC, IR, and NMR. The NMR and IR data for these compounds are given above; GC data are footnoted.[25b]

(26) The 1,4-di-*m*-tolyl-*trans*-2-butene has been reported: bp 168–170 °C (2 mm); n^{20} 1.5788. See: Askerov, A. K.; Mustafaeva, P. R.; Sadyleh-Zade, S. I. *Soobshch. Akad. Nauk. Gruz. SSR* **1966**, *42*, 589.

Inverse Addition Procedure. A solution of 0.46 or 1.08 equiv of Lewis acid in 9 mL of toluene was added dropwise over 6–8 min to a mixture of 50 mL of toluene and 1.0 g of 1,2-epoxy-3-butene, controlling the reaction temperature at 33 °C (see above). After the addition was complete and the reaction was stirred at 33 °C for the time specified in the tables, the workup procedure above was followed.

Procedure for Isolating 19 Isomers. The procedure described in entry 12 of Table I was repeated on a larger (7 times) scale. The product was distilled: bp 120–126 (0.2 mm);[25] NMR ($CDCl_3$) δ 2.3 (at least 2 s, 6 H), 3.3 (at least 2 d, 4 H), 5.6 (vinyl, 2 H), 7.1 (2 s, 8 H) IR (AgCl disks) 960 (trans C=C), 800 (m, para), 740 (s, ortho) cm^{-1}; mass spectrum, m/e (relative intensity) 236 (21, M^+) 131 (100), 105 (45), 91 (32). A 60-m DB-1 capillary column (J&W Scientific) separated the isomers of **19** (temperature programmed from 100 to 240 °C at 2 °C/min). Retention times: cis isomers overlapping peaks centered at 53.2 min; *o,o* isomer, 53.6 min; *o,p* isomer, 53.8 min; *p,p* isomer, 54.1 min (16:45:39 ratio).

Acknowledgment. We thank M. Beeny, C. E. McEwen, Sidney Bourne, and John Schneider (Argonne National Labs) for instrumental assistance. Also, we thank Olivet Research Associates, Research Corp. (Grant No. C1108), and the National Science Foundation (Grant No. CDP-8006131) for financial support. Encouragement and discussions with John Hanson were also helpful.

Registry No. 1, 96-09-3; **2**, 84174-30-1; **3**, 84174-31-2; **7**, 13107-39-6; **8**, 6388-72-3; **9**, 84192-53-0; **9** 3,5-dinitrobenzoate, 84174-32-3; **10**, 84174-33-4; **15**, 84174-34-5; **15** 3,5-dinitrobenzoate, 84174-35-6; **16**, 84174-36-7; **16** 3,5-dinitrobenzoate, 84174-37-8; *cis*-**17**, 84174-38-9; *trans*-**17**, 84174-39-0; *cis*-**18**, 84174-40-3; *trans*-**18**, 84174-41-4; *trans*-**19** (*o,o* isomer), 84174-42-5; *trans*-**19** (*o,p* isomer), 84174-43-6; *trans*-**19** (*p,p* isomer), 60155-90-0; 4-chloro-2-butynol, 13280-07-4; *p*-bromotoluene, 106-38-7; *o*-bromotoluene, 95-46-5; 1,2-epoxy-3-butene, 930-22-3; 1,4-dibromo-2-butyne, 2219-66-1.

Preparation and Properties of Annelated Tropylium Salts

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The insertion of methylene into the aromatic ring of benzocyclobutene leads to a mixture of cyclobutane-fused cycloheptatrienes. Treatment of this mixture with a trityl salt affords the cyclobutane-fused tropylium salt in essentially pure form. If this same synthetic approach is applied to other annelated benzenes, bis- and tris-annelated salts can be prepared. The proton and carbon-13 NMR spectra of a series of annelated tropylium salts have been analyzed and interpreted in terms of a rehybridization theory. Small but meaningful trends have been observed in the ultraviolet absorption spectra and pK_{R^+} values.

The synthesis and properties of benzocyclobutene have been thoroughly studied.[1] The properties of this molecule represent a unique compromise between the thermodynamic stability associated with a benzenoid aromatic system and the kinetic reactivity of a strained cyclobutene. The effects of further strain on benzene have been probed by the fusion of additional small rings to the aromatic nucleus.[2] The effect of ring strain on several polynuclear hydrocarbons[3] as well as on certain heteroaromatic rings[4] has recently been given increased attention. Thus far, however, there have been relatively few accounts of small ring-fused charged aromatic systems. It is the purpose of this paper to present some initial investigations in this area.

The two simplest cyclobutene-fused aromatic hydrocarbons which would be isoelectronic with benzocyclo-

(1) (a) Thummel, R. P. *Acc. Chem. Res.* **1980**, *13*, 70. (b) Klundt, I. L. *Chem. Rev.* **1970**, 471.

(2) (a) Thummel, R. P.; Nutakul, W. *J. Org. Chem.* **1977**, *42*, 300. (b) Davalian, D.; Garratt, P. J.; Koller, W.; Mansuri, M. M. *Ibid.* **1980**, *45*, 4183. (c) Hillard, R. L., III; Vollhardt, K. P. C. *J. Am. Chem. Soc.* **1976**, *98*, 3579. (d) Saward, C. J.; Vollhardt, K. P. *Tetrahedron Lett.* **1975**, 4539. (e) Heilbronner, E.; Kovac, B.; Nutakul, W.; Taggart, A. D.; Thummel, R. P. *J. Org. Chem.* **1981**, *46*, 5279.

(3) (a) Bilyard, K. G.; Garratt, P. J.; Underwood, A. J.; Zahler, R. *Tetrahedron Lett.* **1979**, 1815. (b) Doecke, C. W.; Garratt, P. J. *J. Chem. Soc., Chem. Commun.* **1981**, 873. (c) Hart, H.; Teuerstein, A.; Jeffares, M.; Kurg, W.-J. H.; Ward, D. L. *J. Org. Chem.* **1980**, *45*, 3731. (d) Thummel, R. P.; Nutakul, W. *J. Am. Chem. Soc.* **1978**, *100*, 6171.

(4) (a) Garratt, P. J.; Nicolaides, D. N. *J. Org. Chem.* **1974**, *39*, 2222. (b) Thummel, R. P.; Kohli, D. K. *Ibid.* **1978**, *43*, 4882. (c) Thummel, R. P.; Kohli, D. K. *Tetrahedron Lett.* **1979**, 143.

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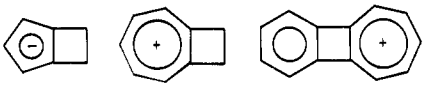
butene (6 π electrons) would be the analogous cyclopentadienyl anion **1** and tropylium cation **2**. The former

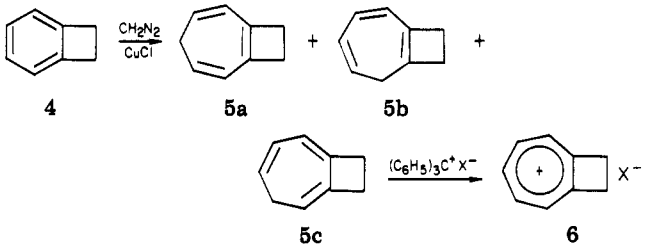


1 2 3

of these systems has been mentioned briefly in a paper by Breslow and Oda[5] while the latter has been reported in unpublished work of Redecker and Grimme at the University of Cologne.[6] Cava and co-workers have prepared the biphenylene analogue of **1** in which one of the fused benzo rings has been replaced by a cyclopentadienyl anion.[7] The corresponding tropylium cation, **3**, as its hexafluorophosphate salt, has been synthesized and studied by Lombardo and Wege.[8] Their preparation of **3** involves the initial [2 + 2] cycloaddition of benzyne to cycloheptatriene followed by a five-step sequence to derive the appropriate oxidation state of the seven-membered ring. Although conceptually more direct, the carbenoid-type ring expansion of biphenylene to give the cycloheptatriene precursor to **3** leads mainly to products having the fluorene ring skeleton.[9] Rearrangement to a fluorene derivative also occurs from the adduct formed by the reaction of sodium methoxide with cation **3**.[8] We have found, however, that this sort of skeletal rearrangement does not pose a problem in the preparation of annelated derivatives of the parent tropylium nucleus.

Synthesis

The synthetic approach to annelated tropylium salts involves two simple steps. In the first step the aromatic ring of an annelated benzene derivative is expanded to provide an annelated cycloheptatriene. Redecker and Grimme found that if diazomethane is bubbled into benzocyclobutene containing copper(I) chloride, a mixture of triene isomers **5a–c**, is obtained.[6] The reaction is ter-



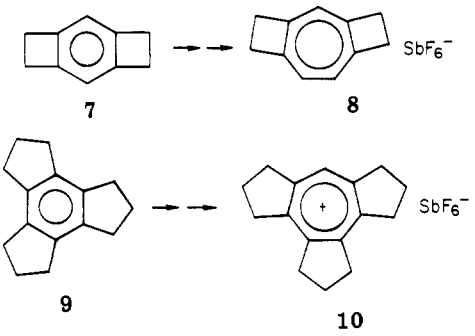
4 5a 5b 5c 6

X = BF_4, $PtCl_6$, $SbCl_6$, SbF_6

minated at about 15% conversion. Beyond this point higher molecular weight products begin to appear, presumably from the insertion of a second methylene unit into the triene **5**. Unreacted benzocyclobutene can be recovered by distillation and recycled. The distillation fraction containing the trienes (as well as other volatile impurities) may be treated with a trityl salt which effects hydride abstraction to generate the tropylium salt which precipitates in essentially pure form. All three trienes **5a–c** lead to the same salt, **6**, so that isolation or purification of these triene isomers is unnecessary.

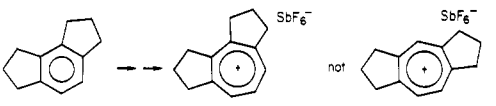
With regard to isolation and characterization of the salt **6**, the choice of counterion is quite important. In several cases the fluoroborate salt is both air and moisture sensitive; the hexachloroplatinate is quite stable but is readily soluble only in sulfuric acid. The hexafluoroantimonate (X = SbF_6) is the counterion of choice, being both stable and soluble in polar solvents such as water and acetonitrile.

Application of this synthetic method to other annelated benzenes leads to the corresponding tropylium salts. Thus 1,2:4,5-dicyclobutenobenzene gives **8**, and trindan (tri-



7 8 9 10

cyclopentenobenzene) gives **10**. The yields of these salts, which depend upon the optimum conversion of triene, appear to improve somewhat as more rings are annelated to the benzene nucleus, but no clear trend is evident. If the reaction sequence is applied to 1,2:3,4-dicyclopentenobenzene, two isomeric products are possible. We observe only the formation of compound **12** which would result from methylene insertion into the less substituted side of the benzene precursor **11**.



11 12 13

Physical Properties

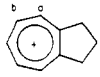
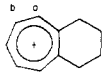
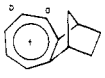
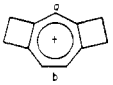
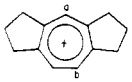
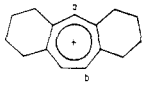
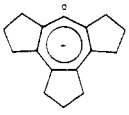
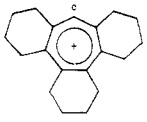
A detailed analysis of the proton and carbon-13 NMR spectra of a series of annelated tropylium salts has been carried out. The data are summarized in Table I. Chemical shift assignments were made on the basis of C–H coupling information as well as relative peak intensities. The same general trends are exhibited by these systems as were observed previously for the corresponding para-bis-annelated benzene precursors.[10] Thus the chemical shift of the unsubstituted aromatic carbon (a) in systems **8**, **13**, and **18** and in systems **10** and **19** is seen to move upfield as the size of the annelated rings is decreased while the C–H coupling constant is found to increase from 156 to 169 Hz. As before, these observations are explained by invoking the Streitweiser–Finnegan rehybridization theory which has been set forth earlier.[10] Application of this theory to systems **6** and **15** allows us to make a tentative assignment of the aromatic carbons C_a and C_b. Due to rehybridization of the bridgehead carbon atom, it uses an orbital of higher s character to bond the adjacent ortho carbon atom. Thus the ortho C–H bond should be more polarized (higher C–H coupling constant), and C_a should exhibit a higher field chemical shift.

The anomalous high-field chemical shift of H_a for system **8** is consistent with observations for other benzocyclobutene derivatives, but the explanation of this shift is still unclear.

Lombardo and Wege have examined the 90-MHz ^1H NMR spectrum of **3** and found three well-resolved signals for the tropylium ring protons at δ 8.20, 7.80, and 7.48

(5) Oda, M.; Breslow, R. *Tetrahedron Lett.* **1973**, 2537.
(6) Redecker, K. "Diplomarbeit"; University of Cologne: Cologne, 1967.
(7) Cava, M. P.; Narasimhan, K.; Zeiger, W.; Radonovich, L. J.; Glick, M. D. *J. Am. Chem. Soc.* **1969**, *91*, 2378.
(8) Lombardo, L.; Wege, D. *Aust. J. Chem.* **1978**, *31*, 1569.
(9) Kende, A. S.; MacGregor, P. T. *J. Am. Chem. Soc.* **1964**, *86*, 2088.
(10) Thummel, R. P.; Nutakul, W. *J. Org. Chem.* **1978**, *43*, 3170.
(11) Lombardo, L.; Wege, D. *Tetrahedron Lett.* **1972**, 4859.

Table I. Selected Proton and Carbon-13 NMR Data[a] for Annelated Tropylium Salts

cation	no.	carbons				hydrogens			aromatic J_{C-H}, Hz
		bridgehead	arom a	arom b	α-carbon	arom a	arom b	α-hydrogen	
	14		155.0			9.37			
	6	180.2	148.9	154.6	32.8	8.76	8.99	3.69	167.2 (a) 165.6 (b)
	14	178.3	150.0	152.0	41.1			3.67	165.6 (a) 165.6 (b)
	16	172.8	150.4 or 155.5		37.2			3.4	167.2 165.6 (a or b)
	17	179.2	147.1 or 153.5		51.1			4.08	165 (a and b)
	8	178.6 173.0	142.9	147.6	32.4 32.3	8.38	8.52	3.58	168.7 (a) 165.6 (b)
	13	172.5 171.0	144.1	145.7	40.2 40.1	8.73	8.57	3.55	162.5 (a) 162.5 (b)
	18	166.8 164.8	155.1	149.5	36.1 35.4	8.54	8.42	3.8	156 (a) 160.9 (b)
	10	169.3 167.3 165.1	140.3		40.4 39.5 39.3	8.53		3.35	162.5 (a)
	19	166.6 162.6 159.7	152.4		33.0 32.8 36.1	8.22		3.12	156.2 (a)

[a] All chemical shifts are given in parts per million downfield from Me_4Si.

ppm.[11] At 80 MHz we observe the tropylium ring protons of **6** to be an unresolved multiplet centered at 8.86 ppm. At 400 MHz, however, this same system exhibits a well-resolved, essentially first-order pattern for these five protons. By use of the observed chemical shifts and coupling constants, an excellent computer-simulated fit is obtained (see Figure 1). The upfield doublet at 8.76 ppm is assigned to H_a which also shows some broadening due to long-range couplings. The one-proton signal at 8.86 ppm is H_c, and the six-line pattern at 8.99 ppm is H_b. It is interesting to note that the carbon and proton resonances in this system follow the same trend with regard to field strength. Thus H_b and C_b appear at lowest field and H_a and C_a at highest field. This observation implies that a localized charge model which places the highest positive charge density on C_b and the lowest on C_a might explain the data as well as the aforementioned rehybridization model.

The ultraviolet spectra in acetonitrile of this same series of annelated tropylium salts have been determined (Table II). A general, though somewhat inconsistent, trend has been observed in which the absorption maxima shift to longer wavelength upon increasing annelation. A similar trend has been reported for a series of methyl-substituted derivatives.[12]

The pK_{R^+} values for this series of compounds has been determined by titration of dilute aqueous solutions with 0.1 N sodium hydroxide. The pH at half neutralization (pK_{R^+}) may be determined graphically (Table II).[13] Small but meaningful increases in pK_{R^+} are observed as the size of the annelated rings is decreased. This observation would imply that the tropylium cation becomes slightly more stable as the size of the annelated rings is decreased. Unlike the parent tropylium ion, hydrolysis of any one of the given annelated tropylium salts might give rise to as many as four different isomeric cycloheptatrienols. These alcohols are generally unstable, and no attempt was made to isolate or characterize them. In considering the relative

(12) Peter-Katalinic, J.; Zsindely, J.; Schmid, H. *Helv. Chim. Acta* **1973**, *56*, 2796.

(13) One reviewer raised the question that the equilibrium being measured might not involve hydroxide attack on the tropylium nucleus but rather α-proton elimination to yield a heptafulvene derivative. In the case of methyl-substituted tropylium salts there is evidence favoring nucleophilic attack.[12] Nevertheless we wish to mention three additional pieces of experimental evidence which support alcohol formation. First, the titration experiments are reversible. Back-titration with 0.1 N hydrochloric acid yields a mirror image titration curve having the same equivalence point. Second, if methyltropylium hexafluoroantimonate is treated with 1 equiv of NaOD in D_2O followed by 1 equiv of DCl in D_2O, NMR analysis of the regenerated tropyllium salt shows no evidence for α-deuterium incorporation. Third, it is very unlikely that the bicyclo[2.2.1]heptenotropylium salt **17** would undergo α-proton abstraction as this would produce a highly strained bridgehead double bond. The pK_{R^+} value for this system (4.08) is quite similar to those for other monoannelated systems, supporting the belief that they all react by the hydroxide addition pathway.

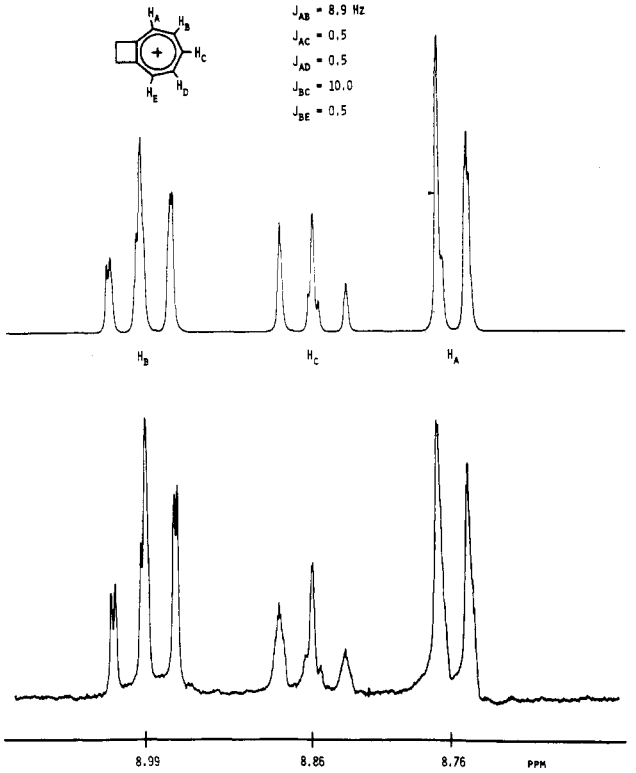


Figure 1. Downfield ^1H NMR spectrum of cyclobutenotropylium hexafluoroantimonate (**6**): bottom spectrum was measured at 400 MHz; top spectrum is a computer simulation using the indicated parameters.

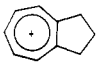
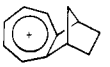
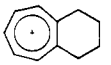
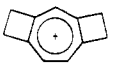
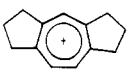
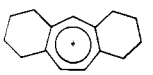
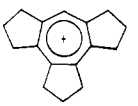
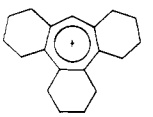
stabilities of the tropylium cations therefore, it is difficult to make arguments based on the influence of ring strain on bond orders. A priori one would expect that an alkyl inductive effect should stabilize the tris-annelated species **19** with respect to the parent **14**. Both systems, however, exhibit the same pK_{R^+} value which seems to indicate that more than simple inductive effects are involved.

Experimental Section

Proton and carbon nuclear magnetic resonance spectra were obtained on a Varian Associates T-60 or FT-80 spectrometer, and chemical shifts are reported in parts per million downfield from Me_4Si. The 400-MHz NMR spectra were obtained by Dr. Ruth Inners at the University of South Carolina Magnetic Resonance Laboratory, Columbia, SC. Infrared spectra were obtained on a Beckman IR-4250 spectrometer. Ultraviolet spectra were obtained on a Cary-14 spectrometer. Propionic anhydride was Eastman practical grade, and antimony pentafluoride was purchased from PCR Research Chemicals, Inc. Methylene chloride was dried by distillation from phosphorous pentoxide.

Trityl Hexafluoroantimonate.[14] A solution of 26.4 g (0.1 mol) of triphenylcarbinol in 200 mL of propionic anhydride was prepared by warming it on a steam bath under a nitrogen atmosphere. After the mixture cooled to room temperature, 4.06 mL (0.1 mol) of 50% hydrofluoric acid was slowly added, followed by 22.1 g (0.1 mol) of antimony pentafluoride.[15] With stirring to maintain the temperature at 25–30 °C, trityl hexafluoroantimonate separated slowly as a brown solid. The bulk of the supernatant liquid was removed by decantation, and the residual solvent was removed by a dropper. The remaining solid was triturated with anhydrous ether (3 × 200 mL). Vacuum drying of the solid material afforded 27.4 g (57%) of trityl hexafluoroantimonate, mp 190–202 °C dec.

Table II. Ultraviolet Absorption Data and pK_{R^+} Values for Annelated Tropylium Salts

tropylium cation ($X^- = SbF_6^-$)	acetonitrile λ_{max}, nm	ϵ	pK_{R^+}
	275 226	3 610 13 380	4.52
	295 230	3 470 19 270	4.33
	304 223	5 120 17 870	4.15
	295 232	3 650 25 880	4.08
	297 224	5 090 17 770	4.12
	308 233	3 840 19 470	4.83
	327 242	5 490 15 660	4.6
	314 247	5 930 13 920	4.08
	308 257	4 520 44 700	4.83
	315 258	4 510 15 660	4.52

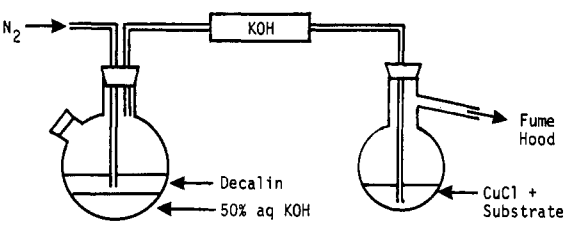


Figure 2.

General Procedure for Diazomethane Reaction. Diazomethane was generated by utilizing the apparatus shown in Figure 2. All-glass openings were fire polished smooth and neoprene rubber stoppers were used to make connections. In the 250-mL flask on the left, 50 mL of 50% aqueous KOH and 20 mL of decalin were cooled to ice-bath temperature. To this flask was added *N*-methyl-*N*-nitrosourea[16] in small portions (0.5 g/15 min). Diazomethane was generated in the aqueous layer, was dissolved in the organic layer, and was swept with a stream of nitrogen through the drying tube into the reaction flask on the right. This second flask contained the benzocycloalkene and 20 mg of freshly prepared anhydrous copper(I) chloride.[17]

The progress of the reaction was monitored by removing a small aliquot of the reaction mixture and analyzing it by gas chromatography on a 7 ft × $^1/_8$ in. column of 2% OV-101 on Chromsorb W (60/80 mesh) at 110 °C and a flow rate of 30 cm^3/min of nitrogen. The formation of cycloheptatrienes was indicated by the appearance of three or more closely overlapping peaks at the expense of the peak for the starting benzocycloalkene. Reaction was continued until additional longer retention time peaks were

(14) This procedure is modified from the preparation of trityl fluoroborate: Dauben, H. J., Jr.; Honnen, L. R.; Harmon, K. M. *J. Org. Chem.* **1960**, *25*, 1442.

(15) Antimony pentafluoride is toxic and sensitive to moisture. The container should be chilled in a refrigerator prior to opening. Weighing and transferring of this material should be done in a drybox.

(16) Arndt, F. "Organic Syntheses"; Wiley: New York, 1943; Collect. Vol. II, p 461.

(17) Keller, R. N.; Wycoff, H. D. *Inorg. Synth.* **1946**, *2*, 1.

observed, indicating the probable formation of secondary insertion products. The system was flushed with nitrogen to purge unreacted diazomethane and then filtered to remove the copper(I) chloride. In general this crude reaction mixture was used directly in the subsequent salt formation step.

Preparation of Tropylium Hexafluoroantimonates. By use of the above-described VPC analysis, the approximate molar amount of cycloheptatrienes in the crude diazomethane reaction mixture could be calculated. Under a nitrogen atmosphere at 0 °C, this crude mixture was added with stirring to an equimolar amount of trityl hexafluoroantimonate dissolved in a minimum amount of dry methylene chloride. The color of the mixture changed immediately from brown to dark green, and hexane was added to accelerate the precipitation. The solid product was collected by suction filtration, washed with ether, dried under vacuum, and analyzed spectroscopically. Elemental analysis of these salts was not feasible. They all exhibited very low volatility and often decomposed upon being heated.

1,2-Cyclobutenotropylium Hexafluoroantimonate (6). A mixture of 12.0 g (0.115 mol) of benzocyclobutene[18] and 20 mg of anhydrous copper(I) chloride was heated at 60 °C and treated with diazomethane as described above. The crude reaction product was purified by spinning-band distillation to give 7.8 g of unreacted benzocyclobutene [bp 91 °C (100 mm)] and cycloheptatrienes: (1.0 g, 21% based on consumed benzocyclobutene); bp 108 °C (100 mm). This triene mixture (0.3 g, 2.6 mmol) was added to 1.23 g (2.6 mmol) of trityl hexafluoroantimonate to afford 0.50 g (54%) of a gray solid: mp >250 °C; 80-MHz ^{1}H NMR (CD_3CN) δ 8.91 (m, 5 H, Ar H), 3.68 (s, 4 H, Ar CH_2); ^{13}C NMR (CD_3CN) δ 180.2, 154.6, 150.0, 148.2, 32.76; UV λ_{max} (CH_3CN) 295 nm (ϵ 3470), 230 (19 270).

1,2-Cyclopentenotropylium Hexafluoroantimonate (15). A mixture of 10.0 g (0.085 mol) of indan and 20 mg of anhydrous copper(I) chloride was heated to 130 °C and treated with diazomethane generated from 5.0 g of *N*-methyl-*N*-nitrosourea as described above. After filtration, VPC analysis (120 °C) showed 95% unreacted indan at a 1.2-min retention time and two new overlapping peaks (5%) at a 2.0-min retention time.[19] Part of this mixture (5.2 g) was treated with 0.9 g (2 mmol) of trityl hexafluoroantimonate to afford 450 mg (62% based on consumed indan) of a gray solid: mp 180 °C dec); 80-MHz ^{1}H NMR (CD_3CN) δ 8.86 (m, 5 H, Ar H), 3.67 (t, 4 H, Ar CH_2, J = 8 Hz), 2.34 (t, 2 H, CH_2, J = 8 Hz); ^{13}C NMR (CD_3CN) δ 178.3, 152.0, 151.0, 150.0, 41.1, 25.2; UV λ_{max} (CH_3CN) 304 nm (ϵ 5120), 223 (17 870).

1,2-Cyclohexenotropylium Hexafluoroantimonate (16). A mixture of 10.0 g (0.076 mol) of 1,2,3,4-tetrahydronaphthalene (tetralin) and 20 mg of anhydrous copper(I) chloride was heated to 160 °C and treated with diazomethane generated from 5.0 g of *N*-methyl-*N*-nitrosourea as described above. After filtration, VPC analysis (150 °C) showed 75% unreacted tetralin at 1.0 min and 25% of poorly resolved new peaks at a 1.5-min retention time. Part of this mixture (0.88 g) was added to a solution of 0.72 g (1.5 mmol) of trityl hexafluoroantimonate in 20 mL of dry methylene chloride to afford 400 mg (70% based on consumed tetralin) of a gray precipitate: mp 131–133 °C; 80-MHz ^{1}H NMR (CD_3CN) δ 8.83 (br s, 5 H, Ar H), 3.4 (m, 4 H, Ar CH_2), 1.96 (m, 4 H, CH_2); ^{13}C NMR (CD_3CN) δ 172.8, 155.5, 152.2, 150.4, 37.2, 20.6; UV λ_{max} (CH_3CN) 279 nm (ϵ 5090) 224 (17 770).

1,2-Bicyclo[2.2.1]heptenotropylium Hexafluoroantimonate (17). A mixture of 1.0 g (7 mmol) of 2,3-benzobicyclo[2.2.1]-heptene[20] and 20 mg of anhydrous copper(I) chloride in 20 mL of dry methylene chloride was treated at room temperature with diazomethane generated from 1.4 g of *N*-methyl-*N*-nitrosourea as described above. After filtration, VPC analysis (110 °C) indicated 40% unreacted 2,3-benzobicyclo[2.2.1]heptene at 1 min and three new peaks (60%) at 1.8-, 1.9- (2 overlapping), and 2.3- (shoulder) min retention times. The entire mixture was added to a solution of 1.8 g (3.8 mmol) of trityl hexafluoroantimonate in 20 mL of dry methylene chloride. After the mixture had been allowed to stand at room temperature for 30 min, 50 mL of ether–hexane (1:1) was added to the solution to effect precipitation. The precipitate was collected by filtration, washed with ether (3 × 20 mL), and vacuum dried to give 0.9 g (60% based on consumed 2,3-benzobicyclo[2.2.1]heptene) of a gray solid: mp 155–160 °C; 60-MHz ^{1}H NMR (CD_3CN) δ 9.0 (m, 5 H, Ar H), 4.08 (m, 2 H, Ar CH), 2.38 (m, 4 H, CH_2), 1.4 (m, 2 H, CH_2); ^{13}C NMR (CD_3CN) δ 179.2, 153.5, 149.4, 147.1, 51.1, 50.0, 24.4; UV δ_{max} (CD_3CN) 295 nm (ϵ 3650), 232 (25 880).

1,2:4,5-Dicyclobutenotropylium Hexafluoroantimonate (8). A mixture of 0.10 g (0.77 mmol) of 1,2:4,5-dicyclobutenobenzene[21] and 20 mg of anhydrous copper(I) chloride in 10 mL of dry methylene chloride was treated at room temperature with diazomethane generated from 80 mg of *N*-methyl-*N*-nitrosourea as described above. After filtration, VPC analysis (150 °C) showed about 40% unreacted 1,2:4,5-dicyclobutenobenzene at a 1.2-min retention time and three new peaks (about 60%) at slightly longer retention times. The entire mixture was added to a solution of 0.21 g (0.44 mmol) of trityl hexafluoroantimonate in 10 mL of dry methylene chloride. After the mixture had been allowed to stand at room temperature for 30 min, the solvent was evaporated, and the residue was triturated with ethyl ether (3 × 20 mL). Vacuum drying afforded 70 mg (41% based on consumed 1,2:4,5-dicyclobutenobenzene) of a black solid: mp >250 °C; 80-MHz ^{1}H NMR (CD_3CN) δ 8.52 (s, 2 H, Ar H), 8.38 (s, 1 H, Ar H), 3.58 (s, 8 H, Ar CH_2); ^{13}C NMR (CD_3CN) δ 178.6, 173.0, 147.6, 142.9, 32.4, 32.3; UV λ_{max} (CH_3CN) 308 nm (ϵ 3840), 233 (19 470).

1,2:4,5-Dicyclopentenotropylium Hexafluoroantimonate (13). A mixture of 0.5 g (3 mmol) of 1,2:4,5-dicyclopentenobenzene[22] and 20 mg of anhydrous copper(I) chloride in 20 mL of dry methylene chloride was treated at room temperature with diazomethane generated from 0.66 g of *N*-methyl-*N*-nitrosourea as described above. After filtration, VPC analysis (180 °C) indicated 65% of unreacted 1,2:4,5-dicyclopentenobenzene at a 1.4-min retention time and three new overlapping peaks (35%) at a 1.8-min retention time. This entire mixture was added to a solution of 0.48 g (1.0 mmol) of trityl hexafluoroantimonate in 20 mL of dry methylene chloride. After the mixture had been allowed to stand at room temperature for 30 min, the solvent was evaporated, and the residue was triturated with ethyl ether (3 × 20 mL). Vacuum drying afforded 0.25 g (61% based on consumed 1,2:4,5-dicyclopentenobenzene) of a black solid: mp 90–95 °C; 80-MHz ^{1}H NMR (CD_3CN) δ 8.73 (s, 1 H, Ar H), 8.57 (s, 2 H, Ar H), 3.55 (t, 8 H, Ar CH_2, J = 7.5 Hz), 2.32 (quintet, 4 H, CH_2, J = 7.5 Hz); ^{13}C NMR (CD_3CN) δ 172.5, 170.9, 145.7, 144.1, 40.2, 40.1, 24.3; UV λ_{max} (CD_3CN) 327 nm (ϵ 5490), 242 (15 660).

1,2:4,5-Dicyclohexenotropylium Hexafluoroantimonate (18). A mixture of 0.5 g (2.7 mmol) of 1,2,3,4,5,6,7,8-octahydroanthracene[23] and 20 mg of anhydrous copper(I) chloride in 20 mL of dry methylene chloride was treated at room temperature with diazomethane generated from 0.83 g of *N*-methyl-*N*-nitrosourea as described above. After filtration, VPC analysis (160 °C) indicated about 70% of unreacted 1,2,3,4,5,6,7,8-octahydroanthracene at a 3.2-min retention time and several overlapping new peaks (30%) at slightly longer retention times. The entire mixture was added to a solution of 0.36 g (0.75 mmol) of trityl hexafluoroantimonate in 20 mL of dry methylene chloride. After standing at room temperature for 30 min, the solvent was evaporated, and the residue was triturated with ethyl ether (3 × 20 mL). Vacuum drying afforded 0.2 g (61% based on consumed 1,2,3,4,5,6,7,8-octahydroanthracene) of a black semisolid: 80-MHz ^{1}H NMR ($CDCl_3$) δ 8.54 (s, 1 H, Ar H), 8.42 (s, 2 H, Ar H), 3.28 (m, 8 H, Ar CH_2), 1.92 (m, 8 H, CH_2); ^{13}C NMR ($CDCl_3$) δ 166.8, 164.8, 155.1, 149.5, 36.1, 35.4, 20.4, 20.3, UV λ_{max} (CH_3CN) 314 nm (ϵ 5930), 247 (13 920).

1,2:3,4:5,6-Tricyclopentenotropylium Hexafluoroantimonate (10). A mixture of 0.5 g (2.5 mmol) of 1,2:3,4:5,6-tricyclopentenobenzene[24] (trindan) and 20 mg of anhydrous copper(I) chloride in 20 mL of dry methylene chloride was treated at room temperature with diazomethane generated from 0.26 g

(18) Schiess, P.; Heitzmann, M.; Rutschmann, S.; Staheli, R. *Tetrahedron Lett.* **1978**, 4569.
(19) In later runs conversion to cycloheptatrienes was as high as 50%.
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(21) Gray, R.; Harruff, L. G.; Krymowski, J.; Peterson, J.; Boekelheide, V. *J. Am. Chem. Soc.* **1978**, *100*, 2892.
(22) Arnold, R. T.; Barnes, R. A. *J. Am. Chem. Soc.* **1944**, *66*, 960.
(23) Schroeter, G. *Chem. Ber.* **1924**, *57B*, 2003.
(24) Mayer, R. *Chem. Ber.* **1956**, *89*, 1443.

of *N*-methyl-*N*-nitrosourea as described above. After filtration, VPC analysis (150 °C) indicated 70% of unreacted trindan at a 5.8-min retention time and four new peaks (30%) at 3.6-, 4.6- (2 overlapping), and 6.8- (shoulder) min retention times. The entire mixture was added to a solution of 0.34 g (0.7 mmol) of trityl hexafluoroantimonate in 20 mL of dry methylene chloride. After standing at room temperature for 30 min, the solvent was evaporated, and the residue was triturated with ethyl ether (3 × 20 mL). Vacuum drying afforded 0.2 g (64% based on consumed trindan) of a black solid: mp 150–155 °C; 80-MHz ^{1}H NMR (CD_3CN) δ 8.53 (s, 1 H, Ar H), 3.35 (m, 12 H, Ar CH_2), 2.28 (m, 6 H, CH_2); ^{13}C NMR (CD_3CN) δ 169.3, 167.3, 165.1, 140.3, 40.4, 39.5, 39.3, 24.1, 23.3; UV λ_{max} (CH_3CN) 308 nm (ε 4520), 257 (44 700).

1,2:3,4:5,6-Tricyclohexenotropylium Hexafluoroantimonate (19). A mixture of 0.5 g (2 mmol) of dodecahydrotriphenylene (Aldrich Chemical Co.) and 20 mg of anhydrous copper(I) chloride in 30 mL dry methylene chloride was treated at room temperature with diazomethane generated from 0.4 g of *N*-methyl-*N*-nitrosourea as described above. After filtration, VPC analysis (240 °C) indicated 20% unreacted dodecahydrotriphenylene at a 4.5-min retention time and a new peak (80%) at a 2.2-min retention time. The entire mixture was added to a solution of 0.77 g (1.6 mmol) of trityl hexafluoroantimonate in 20 mL dry methylene chloride. After the mixture had been allowed to stand at room temperature for 30 min, the solvent was evaporated, and the residue was triturated with ethyl ether (3 × 20 mL). Vacuum drying afforded 0.5 g (64% based on consumed dodecahydrotriphenylene) of black solid: mp 190–193 °C; 80-MHz ^{1}H NMR ($CDCl_3$) 8.22 (s, 1 H, Ar H), 3.12 (m, 12 H, Ar CH_2), 1.89 (m, 12 H, CH_2); ^{13}C NMR ($CDCl_3$) δ 166.6, 162.6, 159.7, 152.4, 36.1, 33.0, 32.8, 20.8, 20.5, 20.2; UV λ_{max} (CH_3CN) 315 nm (ε 4510), 258 (15 660).

Measurement of pK_{R^+} Values. The pK_{R^+} values of the annelated tropylium salts were determined according to the method of Michael and co-workers[25] by potentiometric titration with a Radiometer RTS 622 Recording Titration System fitted with a glass indicator electrode and a staturated calomel reference electrode. Titrations were carried out at 25.00 ± 0.05 °C under a nitrogen atmosphere in a water-jacketed cell connected to a constant-temperature bath and fitted with a neoprene cover drilled to accommodate two electrodes, a buret, a thermometer, and a nitrogen inlet tube. In a typical run, an accurately weighed amount of the annelated tropylium hexafluoroantimonate (ca. 2×10^{-4} M) was dissolved in carbon dioxide free, distilled water in a nitrogen-swept 50-mL volumetric flask. Ultrasonic agitation was utilized to effect total dissolution. A 25-mL aliquot was transferred to the titration cell and with magnetic stirring was titrated with 0.10 N sodium hydroxide solution. The end point and half-neutralization potential were determined graphically. All runs were carried out in duplicate, with a precision of ±2 mV.

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Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the Robert A. Welch Foundation for support of this research. We also thank Dr. Ruth Inners of the University of South Carolina Magnetic Research Laboratory for obtaining the 400-MHz NMR spectra, Professor Harold Kohn for use of the recording titration system, and Professor Wolfram Grimme for helpful discussions.

Registry No. **6**, 84176-05-6; **6** cation, 84176-04-5; **8**, 84176-13-6; **8** cation, 84176-12-5; **10**, 84176-19-2; **10** cation, 84176-18-1; **13**, 84176-15-8; **13** cation, 84192-63-2; **14** cation, 26811-28-9; **15**, 84176-07-8; **15** cation, 84176-06-7; **16**, 84176-09-0; **16** cation, 84176-08-9; **17**, 84176-11-4; **17** cation, 84176-10-3; **18**, 84176-17-0; **18** cation, 84176-16-9; **19**, 84176-21-6; **19** cation, 84176-20-5; H^-, 12184-88-2; triphenylcarbinol, 76-84-6; trityl hexafluoroantimonate, 437-18-3; diazomethane, 334-88-3; benzocyclobutene, 4026-23-7; bicyclo[5.2.0]nona-1(7),2,5-triene, 84176-22-7; bicyclo[5.2.0]-nona-1,3,6-triene, 84176-23-8; bicyclo[5.2.0]nona-1(7),2,4-triene, 84176-24-9; indan, 496-11-7; bicyclo[5.3.0]deca-1(7),2,5-triene, 84176-25-0; bicyclo[5.3.0]deca-1,3,6-triene, 84176-26-1; bicyclo-[5.3.0]deca-1(7),2,4-triene, 84176-27-2; tetralin, 119-64-2; bicyclo[5.4.0]undeca-1(7),2,4-triene, 84176-28-3; bicyclo[5.4.0]undeca-1(7),2,5-triene, 84176-29-4; bicyclo[5.4.0]undeca-1,3,6-triene, 84176-30-7; tricyclo[5.4.0.1^{8,11}]dodeca-1(7),2,4-triene, 84176-31-8; tricyclo[5.4.0.1^{8,11}]dodeca-1(7),2,5-triene, 84176-32-9; tricyclo-[5.4.0.1^{8,11}]dodeca-1,3,6-triene, 84176-33-0; 2,3-benzobicyclo-[2.2.1]heptene, 4486-29-7; [1,2:4,5]dicyclobutenobenzene, 1610-51-1; [1,2:4,5]dicyclopentenobenzene, 495-52-3; [1,2:5,6]dicyclobutenocyclohepta-1,3,5-triene, 84176-35-2; [1,2:5,6]dicyclopentenocyclohepta-1,3,5-triene, 84176-36-3; [1,2:4,5]dicyclopentenocyclohepta-1,3,5-triene, 84176-37-4; 1,2,3,4,5,6,7,8-octahydroanthracene, 1079-71-6; [1,2:4,5]dicyclohexenocyclohepta-1,3,5-triene, 84176-38-5; [1,2:5,6]dicyclohexenocyclohepta-1,3,5-triene, 84176-39-6; [2,3:6,7]dicyclohexenocyclohepta-1,3,5-triene, 84176-40-9; [1,2:3,4:5,6]tricyclopentenobenzene, 1206-79-7; [1,2:3,4:5,6]tricyclopentenocyclohepta-1,3,5-triene, 84176-41-0; [2,3:6,7]dicyclopentenocyclohepta-1,3,5-triene, 84176-42-1; [1,2:3,4:6,7]tricyclopentenocyclohepta-1,3,5-triene, 84176-43-2; [1,2:4,5:6,7]tricyclopentenocyclohepta-1,3,5-triene, 84176-44-3; dodecahydrotriphenylene, 1610-39-5; [1,2:3,4:5,6]tricyclohexenocyclohepta-1,3,5-triene, 84176-45-4; [2,3:4,5:6,7]tricyclohexenocyclohepta-1,3,5-triene, 84176-46-5; [1,2:4,5:6,7]tricyclohexenocyclohepta-1,3,5-triene, 84176-47-6; [1,2:3,4:6,7]tricyclohexenocyclohepta-1,3,5-triene, 84176-48-7; [3,4:6,7]dicyclohexenocyclohepta-1,3,5-triene, 84176-49-8; [3,4:6,7]dicyclobutenocyclohepta-1,3,5-triene, 84176-50-1; [2,3:6,7]dicyclobutenocyclohepta-1,3,5-triene, 84176-51-2; bicyclo[5.4.0]undeca-1,3,5-triene, 84176-52-3; tricyclo[5.4.0.1^{8,11}]dodeca-1,3,5-triene, 84176-53-4; bicyclo[5.2.0]nona-1,3,5-triene, 84176-54-5; bicyclo-[5.3.0]deca-1,3,5-triene, 33877-87-1; [2,3:6,7]dicyclopentenocyclohepta-1,3,5-triene, 84176-42-1; [3,4:6,7]dicyclopentenocyclohepta-1,3,5-triene, 84176-55-6.