72019-96-6; 18, 77612-52-3; 18 dibromide, 91760-19-9; *t*-BuOC(O)NHOH, 36016-38-3; $ClC(O)OCH_3$, 79-22-1; $NH_2OH{\cdot}HCl$, 5470-11-1; MeOC(O)NHOC(O)OMe, 6092-55-3; $PhCH_2C(O)Cl$, 103-80-0; $CH_2{=}CH(CH_2)_3C(O)Cl$, 36394-07-7; $CH_2{=}CH(CH_2)_3CO_2H$, 1577-22-6; $CH_3CH_2C({=}PPh_3)C(O)OEt$, 22592-13-8; $CH_3CH_2C(Br)HC(O)OEt$, 533-68-6; $CH_2{=}CHCH{=}C(Et)C(O)OEt$, 91760-17-7; $HOCH_2C(Et){=}CHCH{=}CH_2$, 91760-18-8; Ph_3P, 603-35-0; acrolein, 107-02-8.

Thermal Reorganizations of 1,2:3,4-Dibenzotropilidene (5*H*-Dibenzo[*a*,*c*]cycloheptene), 7,7′-Bi(1,2:3,4-dibenzotropyl) [5,5′-Bi(5*H*-dibenzo[*a*,*c*]cycloheptenyl)], and the 1,2:3,4-Dibenzotropyl (Dibenzo[*a*,*c*]cycloheptenyl) Free Radical

Martin Pomerantz,* Nissanke L. Dassanayake, Timothy R. McManus,[1] and Charles H. Reynolds[1]

Department of Chemistry, The University of Texas at Arlington, Arlington, Texas 76019-0065

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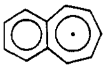
1,2:3,4-Dibenzotropilidene (5*H*-dibenzo[*a*,*c*]cycloheptene, **8**) has been shown to thermally produce phenanthrene (**12**), 9-methylphenanthrene (**13**), 9,10-dihydrophenanthrene (**14**), and 1,2:3,4-dibenzocycloheptadiene (6,7-dihydro-5*H*-dibenzo[*a*,*c*]cycloheptene, **15**). With added naphthalene, to trap the extruded one-carbon species, 1,2-benzotropilidene (**16**), α-methyl- and β-methylnaphthalene (**17** and **18**), 1,2-benzo-1,3-cycloheptadiene (**19**), and benzocycloheptene (**20**) were also produced. Reaction of 1,2-benzotropilidene with phenanthrene produced 1,2:3,4-dibenzotropilidene (**8**) and naphthalene, showing the reversibility of this thermal carbon extrusion reaction. 7,7-Bi(1,2:3,4-dibenzotropyl) [5,5′-bi(5*H*-dibenzo[*a*,*c*]cycloheptenyl), **10**] was prepared by VCl_2 reduction of the 1,2:3,4-dibenzotropylium cation. Thermally it underwent the same reactions as **8**, demonstrating that it is the 1,2:3,4-dibenzotropyl (dibenzo[*a*,*c*]cycloheptenyl) free radical (**9**) which lost a carbon atom (CH group) to the aromatic acceptor. At 200 °C the dimer **10** produced significant quantities of 9-methylphenanthrene (**13**), shown not to arise from **8**, in addition to phenanthrene, **12**. Mechanisms for the thermal transfer of a CH group from **9** to an aromatic acceptor and for the production of **13** from **9** are presented.

A number of years ago we noted that a one-carbon fragment could be thermally extruded from benzotropilidene[2,3] and this extruded species could be trapped by an aromatic acceptor such as benzene to produce naphthalene and toluene. The yield of naphthalene was in the range of 5–20%, showing that this pathway, while somewhat important, was not the major one. We further noted that in the thermolysis of the parent, tropilidene, the yield of benzene, also produced by the loss of a one carbon species, was only about 2–3%. In these cases the reactive intermediates were shown to be the benzotropyl (1) and tropyl (2) radicals by independent production from their respective dimers, 3 and 4,[2,4] and it was postulated that these radicals transferred a CH group to the aromatic acceptor.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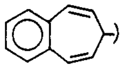
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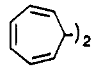
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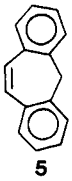
Examination of 1,2:5,6-dibenzotropilidene (5) and the corresponding dimer (6) showed that here too a carbon atom (CH group) was lost from the intermediate radical 7 and anthracene was produced. The yields of anthracene (up to about 45% absolute yield) were considerably higher than the yields of naphthalene from benzotropilidene and dimer 3, and thus CH loss represents an important pathway for radical 7.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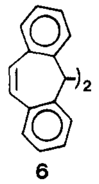
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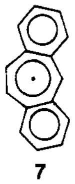
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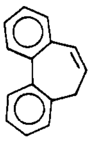
We now report on the thermal extrusion of a one-carbon species from 1,2:3,4-dibenzotropilidene (5*H*-dibenzo[*a*,*c*]cycloheptene, 8) and from the 1,2:3,4-dibenzotropyl (5*H*-dibenzo[*a*,*c*]cycloheptenyl) free radical (9) and its transfer to an aromatic acceptor (naphthalene). Radical 9 was formed independently from the dimer 7,7-bi(1,2:3,4-dibenzotropyl) [5,5′-bi(5*H*-dibenzo[*a*,*c*]cycloheptenyl), 10] by thermal cleavage of the central C–C bond. Absolute yields of up to 93% were observed, showing that this CH transfer is now the overwhelmingly preferred reaction.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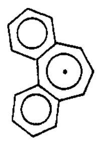
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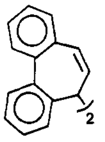
10

Results

Preparation and Pyrolysis of 1,2:3,4-Dibenzotropilidene (8). 1,2:3,4-Dibenzotropilidene (8) was prepared by the reactions shown in Scheme I.[5,6] The sequence for preparation of alcohol 11 was the same as that in the literature.[5,6] Although 1,2:3,4-dibenzotropilidene (8) has been prepared previously by other methods,[7,8] we prepared it by refluxing the alcohol (11) with *p*-toluenesulfonyl chloride in pyridine.

Two types of pyrolyses were run. Those we call "low pressure", which involved heating 20–40 mg of 8 in an evacuated 125-mL Pyrex ampule for 1 h at the specified

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[1] Participants in the NSF-URP program.

[2] Pomerantz, M.; Ross, A. S. *J. Am. Chem. Soc.* 1975, *97*, 5850.

[3] Pomerantz, M.; Ross, A. S.; Gruber, G. W. *J. Am. Chem. Soc.* 1972, *94*, 1403.

[4] Pomerantz, M.; Combs, G. L., Jr.; Fink, R. *J. Org. Chem.* 1980, *45*, 143.

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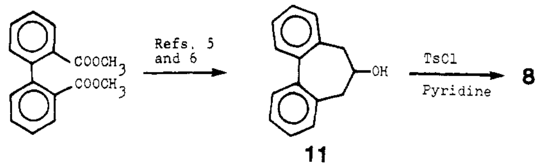
Table I. Pyrolysis of 8[a] (Absolute Percent Yields)

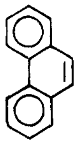
conditions, °C	recovered 8	12	13	14	15
	High Pressure				
260	95				
300	85	3	6	1	2
350	10	15	23	4	34
400	34	19	23	2	20
400 (with naphthalene[b])	11	23	37	1	10
	Low Pressure				
350	80	7	9		
400	9	63	6		

[a] Pyrolysis for 1 h. [b] Other products: 16, 2%; 17 + 18, 5%; 19 + 20, 3%.

Scheme I



temperature, and those we term "high pressure", where 20–40 mg of 8 were heated for 1 h at the specified temperature in an evacuated 0.75-mL Pyrex ampule. The analyses were by VPC using authentic products for comparison and known quantities for quantitative measurements. Table I gives the absolute yields of products from the pyrolysis of 8 at several temperatures at both "high" and "low pressures". The products identified were phenanthrene (12), 9-methylphenanthrene (13), 9,10-dihydrophenanthrene (14), and 1,2:3,4-dibenzo-1,3-cycloheptadiene (6,7-dihydro-5*H*-dibenzo[*a*,*c*]cyclopentene, 15), in addition to recovered 8. Thus, the most favorable conditions for the extrusion of the single carbon fragment was "low pressure" pyrolysis at 400 °C, where 63% absolute yield of phenanthrene (12) was produced. As with other pyrolytic free radical reactions, the hydrogenated products 14 and 15 were produced at higher pressures, since they are formed via bimolecular processes.[2-4] When 8 was heated at 400 °C (high pressure) with naphthalene as a trap for the extruded carbon species, 2% of 1,2-benzotropilidene (16), 5% of 1- and 2-methylnaphthalenes (17 and 18), and 3% of the hydrogenated products, 19 and 20, for a total yield of trapped products of 10%, were produced (Table I).[2-4] It should be noted that the trapping efficiency, which is close to 50%, is exceedingly good.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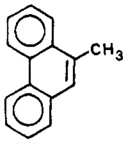

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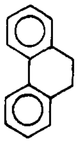
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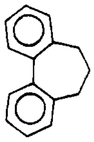
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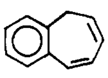
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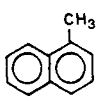

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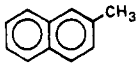

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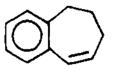
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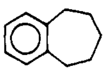
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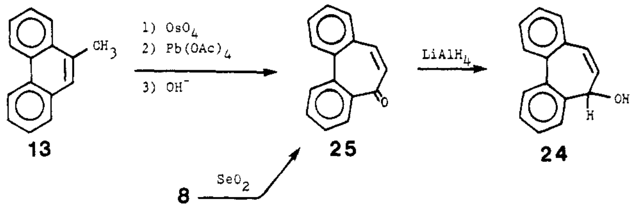
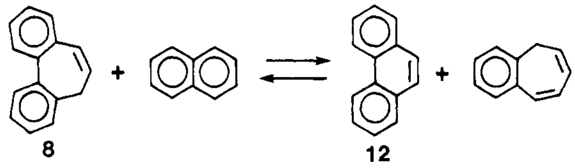
Scheme II

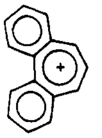


The reversibility of this trapping reaction (eq 1) was demonstrated by heating phenanthrene (12) with 1,2-benzotropilidene (16) at 400 °C (high pressure) and observing 2% of 1,2:3,4-dibenzotropilidene (8) along with 3% of 9-methylphenanthrene (13) and small amounts of the hydrogenated products (14 and 15). Compounds 8, 13, and 15 must have arisen from transfer of the one-carbon species from 16 [or, better, radical 1 (see Discussion below)] to 12.[2-4]



(1)

Preparation and Pyrolysis of 7,7′-Bi(1,2:3,4-dibenzotropyl) (10). Benzotropilidene-type dimers can be prepared from the respective benzotropylium cations by reduction with VCl_2.[4,9] Since the tropylium cations are aromatic they are usually easy to prepare. This is not true in the case of the 1,2:3,4-dibenzotropylium ion (21) as pointed out a number of years ago.[10,11] In our hands hydride abstraction from 8 using triphenylmethyl fluoborate failed, as did attempted bromination of 8 with NBS. Instead, this latter reaction produced a product tentatively identified, using spectral analysis, as the succinimidyl derivative 22.[12] This is analogous to the product 23 obtained from 1,2-benzotropilidene (16) upon attempted bromination.[13] Ultimately, the cation 21 was prepared from the dibenzotropyl alcohol 24, which was prepared by two methods. The first employed the sequence of Heilbronner and is shown in Scheme II.[11] The second was by SeO_2 oxidation of dibenzotropilidene (8) to give the tropone 25[8] followed, as in the Heilbronner sequence, by reduction with $LiAlH_4$ (Scheme II). It should also be mentioned that the 9-methylphenanthrene (13) was prepared by the oxidative photochemical ring closure of α-methylstilbene (26, eq 2). When the tropyl alcohol 24 was treated with concentrated H_2SO_4, the dibenzotropylium ion 21 was produced,[11] and when this, in turn, was reacted



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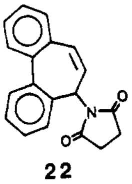

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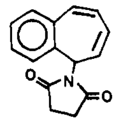

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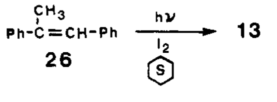

$$\underset{26}{\text{Ph-}\overset{CH_3}{\text{C}}\text{=CH-Ph}} \xrightarrow[I_2,\ S]{h\nu} 13 \qquad (2)$$

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(5) Eistert, B.; Minas, H. *Chem. Ber.* **1964**, *97*, 2479. Mutah, C. W.; Sung, W. L.; Papanstassiou, Z. B. *J. Am. Chem. Soc.* **1955**, *77*, 3393. Cope, A. C.; Smith, R. D. *J. Am. Chem. Soc.* **1956**, *78*, 1012. Kenner, J.; Turner, E. G. *J. Chem. Soc.* **1911**, *99*, 2101.

(6) Bartinger, W. F.; Schleyer, P. v. R.; Mislow, K. *J. Am. Chem Soc.* **1965**, *87*, 3168.

(7) Benciu, M.; Phan-Le-Thuy; Stanescu, L. *Rev. Roum. Chim.* **1979**, *24*, 957. Kenner, J. *J. Chem. Soc.* **1913**, 613.

(8) Cook, J. W.; Dickson, G. T.; Loudon, J. D. *J. Chem. Soc.* **1947**, 746.

(9) Pomerantz, M.; Combs, G. L., Jr.; Dassanayake, N. L. *Inorg. Synth.* **1982**, *21*, 185.

(10) Dewar, M. J. S.; Ganellin, C. R. *J. Chem. Soc.* **1959**, 3139.

(11) Naville, G.; Strauss, H.; Heilbronner, E. *Helv. Chim. Acta* **1960**, *43*, 1221.

(12) The ^1H NMR Spectrum of 22 (CCl_4) is δ 7.4 (m, 8 H), 6.23 (br d, 1 H, J = 11 Hz), 5.56 (br s, 1 H), 5.28 (d, 1 H, J = 11 Hz), 2.70 (s, 4 H).

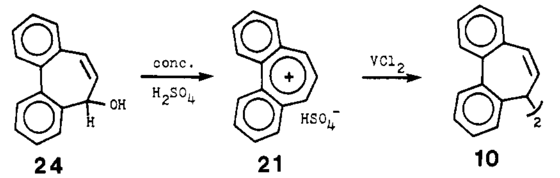
(13) Srivastava, K. C.; Dev, S. *Tetrahedron* **1972**, *28*, 1083.

Table II. Pyrolysis of 10[a] (Absolute Percent Yields)

conditions, °C	8	12	13	14	15
			products		
		High Pressure			
200	26	33	25	10	4
260	28	43	6	17	5
300[b]	45	36	2	15	2
400	41	43	10	4	1
		Low Pressure			
350	13	16	70		
400	1	93	0.8	2	2

[a] Pyrolysis for 1 h. [b] Pyrolysis at 300 °C in the presence of naphthalene also produced 1% of 16.

with VCl_2,[9] the dimer 7,7-bi(1,2:3,4-dibenzotropyl) 10, was obtained in 43% yield (eq 3). This substance was identified by its ^1H NMR and UV spectra which were very similar to those of the monomer 8.



(3)

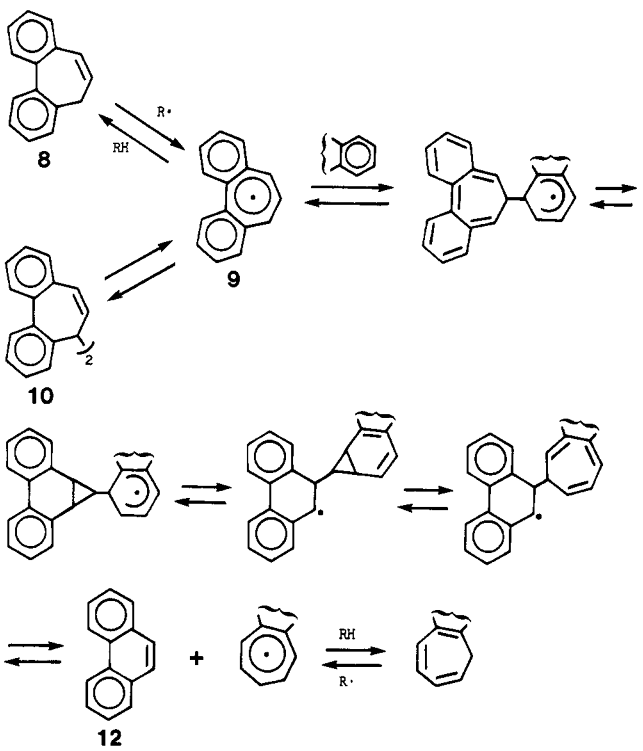
The pyrolysis of the dimer 10 was also carried out under two sets of conditions. "Low pressure" corresponds to 5 mg of 10 in an evacuated 125-mL Pyrex ampule and "high pressure" to 5 mg of 10 in an evacuated 0.75-mL Pyrex ampule. The results are shown in Table II. In addition, at 300 °C, "high pressure" pyrolysis in the presence of naphthalene resulted in the production of 1,2-benzotropilidene (16) as the adduct of the extruded carbon species. Attention should be drawn to the 400 °C "low pressure" pyrolysis which produces 93% (absolute yield) of phenanthene (12) which shows that carbon extrusion is now, by far, the major reaction.

Discussion

The following summarizes the significant observations concerning the reactions described above. The products from the pyrolysis of 8 and 10 are the same. Slight differences in yields reflect differences in reaction conditions particularly with pressure-dependent reactions. At all temperatures the amount of phenanthrene (12) was considerably greater from the dimer 10 than from the monomer 8. Further, at temperatures where most of the monomer 8 was recovered unchanged when it was pyrolyzed, the dimer produced phenanthrene (12) and significant quantities of 9-methylphenanthrene (13). This proves that the dimer is giving products directly (via 9) and not through the intermediacy of 8 which is then undergoing secondary pyrolysis. Control experiments indicate that at 350 °C (and below) 9-methylphenanthrene (13) did not produce any measurable amount of phenanthrene (12). At 400 °C, 13 did produce 12 very slowly, but it is clear that this reaction is much too slow to account for the vast majority of 12, which, therefore, must have been produced directly in the reactions.

Since it is well-known that tropyl dimers thermally produce tropyl free radicals,[4,14] the mechanism shown in Scheme III can be postulated for the transfer of a one-carbon species to an aromatic acceptor. It shows free radical 9 produced from both 8 and 10 as the first formed intermediate and is similar to the mechanism postulated for the pyrolysis of the other tropyl derivatives.[2-4] Of course the mechanism in Scheme III shows only one of several possibilities for attack at various positions in 9 and the aromatic acceptor. The reactions are shown as reversible since we have demonstrated that phenanthrene (12) reacts with 1,2-benzotropilidene (16) to give hydrocarbon 8 and naphthalene (reverse of eq 1). On the basis of previous studies,[2-4] this (reverse) reaction must involve the benzotropyl radical (1) and is depicted in Scheme III as the final seven-membered ring radical intermediate.

Scheme III



Finally, we note that at 200 °C the dimer 10 produced significant quantities of 9-methylphenanthrene (13), in addition to phenanthrene (12). Control experiments (see Table I) showed that hydrocarbon 8 was not the source of 13. This type of reaction was also observed in the pyrolysis of the benzotropyl dimer 3 which produced the methylnaphthalenes.[4] A possible mechanism for the production of 13 is shown in Scheme IV. The important step is formation of an isomeric dimer which enables a double bond to come into conjugation with the three-membered ring in order to allow cleavage in the proper direction. At this point without any additionl evidence, it must remain a purely speculative mechanism but one which involves reactions for which there is analogy.[15] It should also be pointed out that since there are different pathways involved in the formation of 12 and 13 from 10 and likewise different pathways involved in going from 8 to 12 and 13,[15] product ratios from 10 and 8 can not be directly compared. In conclusion, we point out that with suitable substitution, cycloheptatrienes or cycloheptatrienyl radicals can extrude a carbon atom (CH group) in nearly quantitative yield.

Experimental Section

General Methods. Melting points are uncorrected. IR spectra were determined on a Perkin-Elmer 257 spectrometer, NMR

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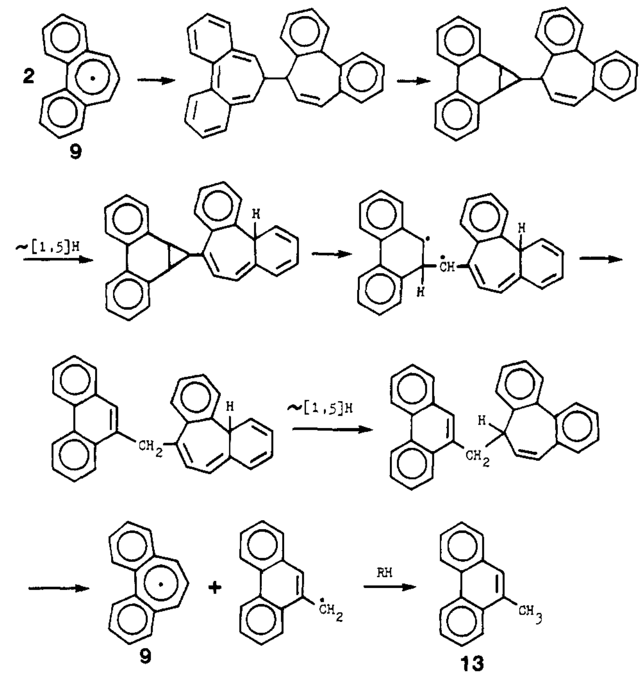
(14) Vincow, G.; Dauben, H. J., Jr.; Hunter, F.; Volland, W. V. *J. Am. Chem. Soc.* **1969**, *91*, 2823. Gerson, F.; Huber, W.; Müllen K. *Helv. Chim. Acta* **1979**, *62*, 2109; **1981**, *64*, 2766. Wittig, G.; Hahn, E.; Tochtermann, W. *Chem. Ber.* **1962**, *95*, 431. Pomerantz, M.; Strom, E. T.; Harris, M.; Combs, G. L., Jr.; Dassanayake, N. L., unpublished observations.

(15) Gajewski, J. J. "Hydrocarbon Thermal Isomerization"; Academic Press: New York, 1981.

Scheme IV



spectra on either a Varian T-60, HA-100, or EM-390 instrument, and UV spectra on a Cary 14 spectrometer. Gas chromatography was performed with a Varian 3700 instrument with an FID detector using the following columns: (A) 10 ft × 0.25 in 10% Apiezon L on 60/80 mesh Chromosorb P; (B) 5 ft × 0.25 in. 15% Carbowax 20 M on 60/80 mesh Chromosorb P; or with a Matronic Model 500 instrument with TC detectors using the following columns: (C) 5 ft × 0.25 in. 10% Apiezon L on 60/80 mesh Chromosorb P; (D) 3 m × 0.25 in. 15% Carbowax 20 M on 60/80 mesh Chromosorb P. All peak areas were calibrated with known quantities of substances so absolute yield determinations could be made from peak areas.

1,2:3,4-Dibenzocyclohepta-1,3-dien-6-ol (6,7-Dihydro-5*H*-dibenzo[*a*,*c*]cyclohepten-6-ol, 11). The sequence shown in Scheme I, starting with dimethyl diphenate, was used and was essentially the same as that in the literature.[5,6]

1,2:3,4-Dibenzotropilidene (5*H*-Dibenzo[*a*,*c*]cycloheptene, 8). A solution of 1,2:3,4-dibenzocycloheptadien-6-ol (11; 10.87 g, 0.0523 mol) and *p*-toluenesulfonyl chloride (10.00 g, 0.0525 mol) in pyridine (50 mL) was refluxed for 24 h. After cooling, 50 mL of water was added, and the mixture was extracted with three 100-mL portions of ether. The combined ether extract was washed with three 100-mL portions of 0.1 M HCl and 100 mL of H_2O and dried ($MgSO_4$), and the ether was removed in vacuo. Compound 8 was distilled; bp 114 °C (0.2 torr) yield 1.72 g, 17%; 100-MHz ^1H NMR (CCl_4) δ 6.9–7.7 (m, 8 H), 6.46 (d, 1 H, J = 10 Hz), 6.08 (dt, 1 H, J = 10 and 7 Hz), 2.93 (d, 2 H, J = 7 Hz). Anal. ($C_{15}H_{12}$) C, H.

1,2-Diphenylpropene (1-Methylstilbene, 26). 1,2-Diphenyl-2-methylethanol (2.50 g, 10.0 mmol) was heated for 24 h with 1 mL of 85% H_3PO_4 at 100 °C. Water (50 mL) was added and this was extracted with three 50-mL portions of ether, washed with 50 mL of Na_2CO_3 solution, and dried ($MgSO_4$). After treatment with charcoal and removal of the solvent in vacuo, 1.43 g (62%) of 1,2-diphenylpropene (1-methylstilbene, 26) was obtained: mp 79–81 °C [lit.[16,17] mp 81–82 °C (*Z* isomer)].

9-Methylphenanthrene (13). 1,2-Diphenylpropene (1.43 g, 7.34 mmol) in 1.4 L of cyclohexane containing 0.127 g of I_2 was irradiated with a General Electric 100-W medium pressure mercury lamp (H 100 A4/T), which had the outer shield removed, in a quartz immersion well. After photolysis for 24 h the solvent was removed in vacuo and the solid obtained was recrystallized from ethanol to give 0.940 g (67%) of 9-methylphenanthrene, mp 90–91 °C (lit.[18] mp 91–92.5 °C).

1,2:3,4-Dibenzo-7-hydroxytropilidene (5*H*-Dibenzo[*a*,*c*]cyclohepten-5-ol, 24). Compound 24 was prepared from 9-methylphenanthrene by the method of Naville et al.[11] using the sequence shown in Scheme II.

2,3:4,5-Dibenzotropone (Dibenzo[*a*,*c*]cycloheptenone, 25). Compound 25 was not only prepared as part of the above sequence (Scheme II) but also by SeO_2 oxidation of 8 as described.[8]

7,7′-Bi(1,2:3,4-dibenzotropyl) [5,5′-Bi(5*H*-dibenzo[*a*,*c*]cycloheptenyl), 10]. Concentrated H_2SO_4 was added to 0.50 g (2.4 mmol) of 1,2:3,4-dibenzo-7-hydroxytropilidene (24) to give a deep red solution: UV λ_{max} 248, 282, 300, 321 nm (lit. for 1,2:3,4-dibenzotropylium cation:[11] 248, 281, 300, 317 nm). The red solution was poured onto a solution of VCl_2 (ca. 1 N),[9] and the white crystals which formed immediately were extracted with three 30-mL portions of ether, washed with three 30-mL portions of saturated $NaHCO_3$ solution, and dried, ($MgSO_4$) and the ether was removed in vacuo to give a white gum. Trituration with pentane gave a white solid which was washed with ethanol and filtered to give 7,7′-bi(1,2:3,4-dibenzotropyl) (10): 0.20 g, 43%; mp 180–185 °C. Chromatography on silica gel (benzene eluent) gave a colorless oil which solidified upon tituration with ethanol. The white solid was recrystallized from ethanol/CH_2Cl_2 to give pure 10: mp 188–190 °C; 90-MHz ^1H NMR (CCl_4) 7.4 (m, 16 H), 6.5 (m, 4 H), 3.6 (m, 2 H); UV λ_{max}^{EtOH} 239 nm (ϵ 7800) [8 has λ_{max}^{EtOH} 239 nm (ϵ 4000)]. Anal. ($C_{30}H_{22}$) C, H.

"Low Pressure" Pyrolyses. A sample of 20–40 mg of 8 or 5 mg of 10 was put into a Pyrex ampule of about 125-mL volume. It was cooled in dry ice, evacuated to 0.2 torr, sealed, and heated in a tube furnace for 1 h at the specified temperature. After removal from the furnace the narrow end of the tube was cooled in dry ice to condense the products. Analysis was by gas chromatography using column C for the products from 8 (8 and 12–15) and column A for the products from 10 (16–20).

"High Pressure" Pyrolysis. A sample of 20–40 mg of 8 or 5 mg of 10 was put in a heavy walled piece of Pyrex capillary tubing (2.25–3 mm i.d. × 8–10 mm o.d.) whose volume was about 0.75 mL. The tube was cooled in dry ice, evacuated to 0.2 torr, sealed, and heated for 1 h in a tube furnace at the specified temperature. It was then removed and one end was cooled in dry ice to condense the products. Analysis was by gas chromatography using column C for the products from 8 (8 and 12–15) and column D for the trapping products (16–20) from reaction 8 with with naphthalene. Column A was used with dimer 10 to analyze for products 8 and 12–15 and column B was used to analyze for 16–20, the products from trapping of 10 with naphthalene.

1,2:3,4-Dibenzocycloheptadiene (6,7-Dihydro-5*H*-dibenzo[*a*,*c*]cycloheptene, 15). Hydrogen was bubbled through a solution of 500 mg of 8 (2.6 mmol) in 15 mL of ethanol containing 100 mg of PtO_2 for 6 h. The solvent was removed in vacuo, and the product was passed through a silica gel column impregnanted with $AgNO_3$ using benzene as eluent. Removal of the benzene in vacuo followed by distillation gave 200 mg (40%) of 15 as a colorless oil: bp 99 °C (0.2 torr) (lit.[19] bp 99–100 °C (0.3 torr)); ^1H NMR (CCl_4) 7.1 (m, 8 H), 2.4 (m, 6 H).

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