

**Thermal Extrusion of a One-Carbon Species from 1,2-Benzotropilidene (5*H*-Benzocycloheptene), the Benzotropryl (Benzocycloheptenyl) Free Radical, 1,2:5,6-Dibenzotropilidene (5*H*-Dibenzo[*a,d*]cycloheptene), and the 1,2:4,5-Dibenzotropryl (Dibenzo[*a,d*]cycloheptenyl) Free Radical**

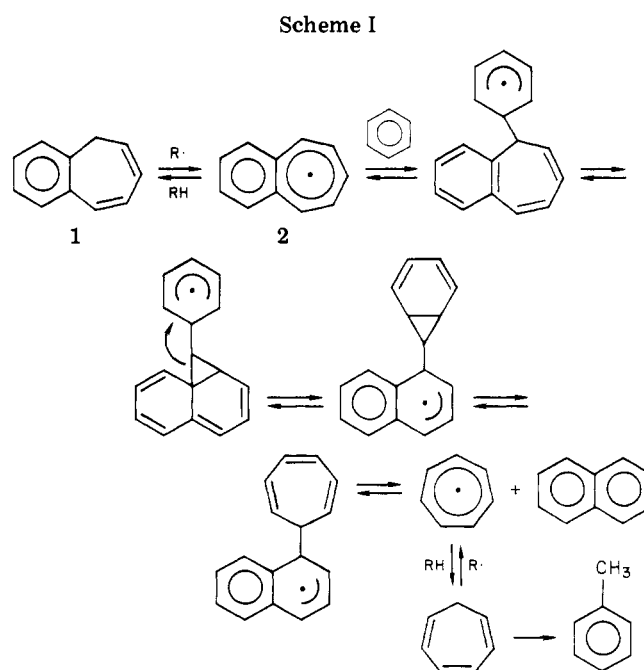
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The benzotropryl dimer 7,7'-bis(3,4-benzotropryl) (6) has been prepared and thermolyzed (400 °C) both without and with added benzene. In addition, 1,2:5,6-dibenzotropilidene (3) and 7,7'-bis(1,2:5,6-dibenzotropyl) (7) have been pyrolyzed (430 °C) both without and with added naphthalene. The similarity of the products obtained in the former pyrolysis, namely, naphthalene (12),  $\alpha$ -methylnaphthalene (13),  $\beta$ -methylnaphthalene (14), 1,2-benzocyclohepta-1,3-diene (15), benzocycloheptene (16), and toluene (when benzene is used), with those obtained from pyrolysis of 1,2-benzotropilidene (1) confirms that both thermolyses involve the benzotropryl radical. The similarity of the products from the latter two pyrolyses (of 3 and 7), namely, anthracene (4), 9-methylanthracene (5), 9,10-dihydroanthracene (17), 1,2:4,5-dibenzo-1,4-cycloheptadiene (20), 1- and 2-methylanthracene (18 and 19), and, when naphthalene (12) was used, benzotropilidene (1) and 1- and 2-methylnaphthalene (13 and 14), shows that both of these go through a common intermediate, the 1,2:4,5-dibenzotropryl radical (8). 9-Methylanthracene (5) was shown to thermally produce anthracene (4) and 1- and 2-methylanthracene (18 and 19), but, even with this complication, anthracene (4) was shown to be a primary product from the pyrolysis of dibenzotropilidene (3). Attempts to use di-*tert*-butyl nitroxide (21) as an initiator (400 °C) gave primarily Diels-Alder addition of the isobutylene formed by decomposition of the nitroxide with both 1,2:4,5-dibenzotropilidene (the product of a 1,5-hydrogen shift in 3) and 9-methylanthracene (5). A lower temperature (345 °C) reaction of 3 with naphthalene in the presence of nitroxide 21 did produce anthracene (4) and benzotropilidene (1) in addition to the Diels-Alder adduct, confirming the free-radical nature of the reaction. Low-temperature control experiments employing the benzotropryl dimer (6) (280 °C) and the dibenzotropryl dimer (7) (345 °C) showed that they were undergoing cleavage to their respective radicals (2 and 8) and that these were giving products directly, rather than the benzo- and dibenzotropilidenes (1 and 3), which were being formed in the reactions by hydrogen abstraction, giving the products. It has thus been demonstrated that the benzo- and dibenzotropryl radicals (2 and 8) can transfer a CH group to an aromatic acceptor and that the pyrolytic reactions of benzo- and dibenzotropilidenes (1 and 3) to give naphthalene and anthracene are CH-transfer reactions of the tropryl radicals formed by hydrogen abstraction. Yields of up to 65% of anthracene (4) have been realized in the pyrolyses of dibenzotropilidene (3). Mechanisms for these CH-transfer reactions are presented. A contrast is made between the low-temperature reaction of the dibenzotropryl dimer (7) which (345 °C) gives only anthracene and dibenzotropilidene (3), by CH loss and hydrogen abstraction, respectively, and the low-temperature (280 °C) reaction of benzotropryl dimer (6) which not only gives naphthalene (12) and benzotropilidene (1) by CH loss and hydrogen abstraction but also produces significant amounts of the methylnaphthalenes (13 and 14, 25%) and 1,2-benzocyclohepta-1,3-diene, (15, 15%).

Our interest in the thermal reorganization reactions of 1,2-benzotropilidene (1)<sup>2-4</sup> has led us to uncover an unprecedented pyrolytic loss of a "CH<sub>2</sub>" group from 1 to produce naphthalene in about 10-20% yield.<sup>2,3</sup> We found that benzene could trap the extruded "CH<sub>2</sub>" group and that toluene was produced. A similar study involving troprilidene showed that the small amount of extruded "carbon atoms", which produced about 2% of benzene, could be trapped with naphthalene. This time, however, under carefully controlled conditions, which included the utilization of a free-radical initiator, the first-formed product was the seven-membered-ring compound 1,2-benzotropilidene (1) rather than the methylnaphthalenes. Since bitropryl, a well-known source of tropryl radicals, gave similar results (formation of 1 from naphthalene), the mechanism shown in Scheme I was postulated.<sup>4</sup> Because of the similarity of the reactions of benzotropilidene and troprilidene the reactions were presented as reversible, and the benzotropryl free radical (2) was the hypothesized in-



intermediate for the forward reaction as shown.<sup>4</sup>

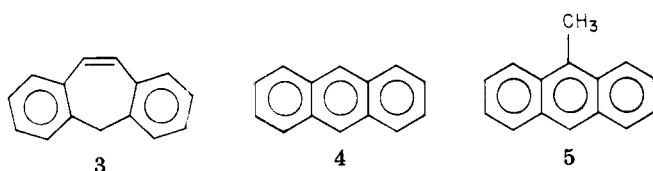
In a previous preliminary paper<sup>3</sup> we also reported, very preliminarily, that 1,2:5,6-dibenzotropilidene (3) loses a "CH<sub>2</sub>" group to produce anthracene (4), rearranges in part

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(2) Pomerantz, M.; Gruber, G. W. *J. Org. Chem.* 1968, 33, 4501.

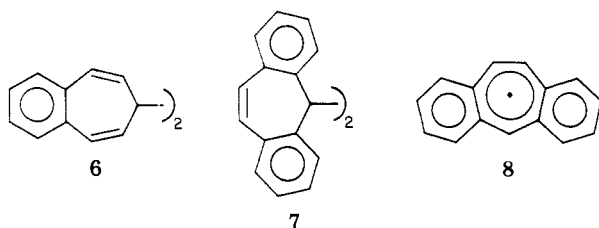
(3) Pomerantz, M.; Ross, A. S.; Gruber, G. W. *J. Am. Chem. Soc.* 1972, 94, 1403.

(4) Pomerantz, M.; Ross, A. S. *J. Am. Chem. Soc.* 1975, 97, 5850.

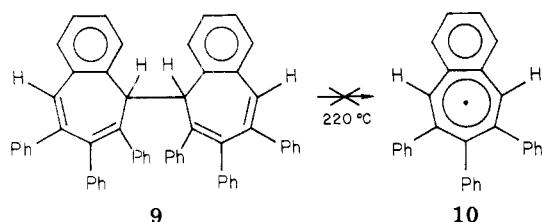


to produce 9-methylantracene (5), and, in the presence of naphthalene, gives 1,2-benzotropilidene and 1- and 2-methylnaphthalene.

We now wish to report the preparation of 7,7'-bis(3,4-benzotropyl) (6) and its thermolysis to the benzotropyl radical (2), detailed studies of the thermal reorganizations of 1,2:5,6-dibenzotropilidene (3), 9-methylantracene (5), and 7,7'-bis(1,2:5,6-dibenzotropyl) (7) as a source of the 1,2:4,5-dibenzotropyl free radical (8).



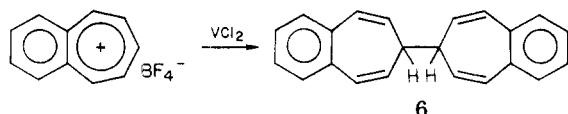
At this point, it should be mentioned that there is a rather interesting but curious report of the preparation and properties of a triphenylbenzotropyl dimer **9**.<sup>5</sup> The dimer



**9**, whose structure was not convincingly proven to be that shown, was reported not to decompose to the triphenylbenzotropyl radical **10** at temperatures up to 220 °C. This is surprising since **10** is expected to be a rather stable radical, and dimer **9** is quite sterically congested.

## Results and Discussion

**Pyrolytic Reactions of 1,2-Benzotropilidene (1), 7,7'-Bis(3,4-benzotropyl) (6), and the Benzotropyl Radical (2).** A recent report that divalent vanadium ( $VCl_2$ ) could successfully reduce tropylium and 1,2:4,5-dibenzotropylium salts to the corresponding dimers<sup>6</sup> led us to attempt the reductive dimerization of the benzotropylium cation with this reagent. When a solution of  $VCl_2$  was added to benzotropylium fluoborate<sup>7</sup> in tetrahydrofuran, the dimer **6** immediately formed. Recrys-



tallization gave yellow crystals (mp 127.5 °C), but repeated crystallizations ultimately afforded pale yellow crystals. The structure proof for **6** rests principally on its NMR spectrum which shows an aromatic multiplet at  $\delta$  7.27, a

Table I. Yields (Relative Percent) for the Pyrolysis (400 °C) of **1** and **6**<sup>a</sup>

product	1 <sup>4,7</sup>		6	
	LP	HP	LP	HP
12	14	11	9	14
13	50	15	13	18
14	18	18	10	6
15	17	30	3	13
16	1	3	<1	50
1			66	<1

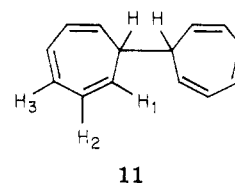
<sup>a</sup> LP = low pressure and HP = high pressure.

Table II. Yields (Relative Percent) for the Pyrolysis (400 °C) of **1** and **6** with Benzene<sup>a</sup>

product	1, HP	6	
		LP	HP
12	17	12	13
13	17	10	33
14	16	7	11
15		12	12
16	51	3	26
toluene	0.6	0.6	2.6
1		55	2.2

<sup>a</sup> LP = low pressure and HP = high pressure.

vinyl doublet at  $\delta$  6.64 ( $J = 10$  Hz), a second vinyl "doublet", where each of the two peaks is clearly a tight multiplet, at  $\delta$  5.71 ( $J = 10$  Hz), and a multiplet for the methine hydrogens at  $\delta$  2.53. The relative areas of the peaks are 4:2:2:1 in agreement with the proposed structure. The symmetry and appearance of the <sup>1</sup>H NMR spectrum shows unequivocally that the dimer has the symmetrical structure shown (**6**). The similarity of this <sup>1</sup>H NMR spectrum to that of bitropyl (**11**), which is also a symme-



trical dimer, is quite striking.<sup>7</sup>  $H_3$  (in **11**) appears as a narrow multiplet at  $\delta$  6.67,  $H_2$  as a "doublet", where each peak is a tight multiplet, at  $\delta$  6.23 ( $J \approx 9$  Hz),  $H_1$  as a doublet, where, again, each peak is a tight multiplet at  $\delta$  5.27 ( $J \approx 9$  Hz), and the methine hydrogen as a narrow multiplet at  $\delta$  1.97. In addition, **6** shows a small parent ion in its mass spectrum at  $m/e$  282.

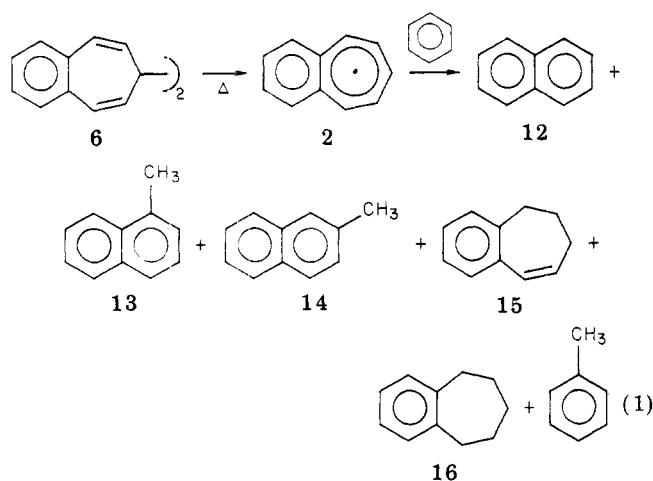
Pyrolyses of the dimer **6**, both neat and with benzene as a trap for the extruded "CH" group, were examined, and these results were then compared to the comparable pyrolyses of 1,2-benzotropilidene (**1**) itself (eq 1). The products obtained from both **1** and **6** were identical, while the product ratios were somewhat different, with the exception that the dimer produced 1,2-benzotropilidene (**1**). Most significantly, naphthalene is produced from **6** (Table I), and, in addition, toluene is obtained when benzene is a reactant. Indeed, when account is taken of the 1,2-benzotropilidene (**1**) produced from the dimer **6**, it appears as though there is at least as much, if not more, naphthalene produced from **6** as from **1**. In addition, the toluene production (Table II) is greater from that fraction of **6** not producing **1** than from **1** itself.

Table I shows the relative yields (analysis by GLC) for the reactions of **1** and **6** at 400 °C (1 h) in both "low-pressure" (50 mg of **1** or **6** in an evacuated, 125-mL, Pyrex ampule) and "high-pressure" (20 mg of **1** or **6** in an evacuated, heavy-walled, 0.75-mL, Pyrex ampule) vessels. The

(5) Tochterman, W.; Schnabel, G.; Mannschreck, A. *Justus Liebigs Ann. Chem.* **1968**, *711*, 88.

(6) Olah, G. A.; Ho, T.-L. *Synthesis* **1976**, 798.

(7) Ross, A. S. Ph.D. Dissertation, Yeshiva University, New York, NY, 1974; *Diss. Abstr. B* **1975**, *35*, 1582.



products were naphthalene (12),  $\alpha$ -methylnaphthalene (13),  $\beta$ -methylnaphthalene (14), 1,2-benzocyclohepta-1,3-diene (15), and benzocycloheptene (16), all of which were identified by comparison with authentic samples. It should also be pointed out that the absolute yields of products were reasonably good. For example, the low-pressure pyrolysis of the dimer gave about 31% of material which was insoluble in ether, with essentially all of the 69% ether soluble material being hydrocarbons 1 and 12-16. Thus, the absolute yield of naphthalene is 6% from the 54% of dimer 6 which reacted to produce products (including polymeric material) other than 1,2-benzotropolidene (1; 66% relative, 46% absolute yield). This compares quite favorably with the 14% relative, 12% absolute, yield of naphthalene from 1,2-benzotropolidene<sup>4</sup> (100% reaction) and completely supports the contention that the benzotropolyl radical (2) is an intermediate in the production of naphthalene (12). Further, 13 and 14 are unexceptional products (from 1) expected for a tropilidene to methylarene rearrangement, and 15 and 16 are hydrogenated products which are commonly found in free-radical reactions.

Table II shows the results of pyrolyses in both high- and low-pressure evacuated ampules, in the presence of ca. 0.3-0.5 mL of benzene. Once again the absolute yields of these hydrocarbons were reasonably good. There was about 51% ether-soluble material in the low-pressure dimer reaction, and the absolute yield of the naphthalene was ca. 6%. In the high-pressure reaction the absolute yield of naphthalene was 8.2%. Once again the similarity between the reactions of 1 and 6 is apparent (except for the production of 1 from 6), supporting the hypothesis that the same intermediate, the benzotropolyl radical (2), is producing the naphthalene and toluene in both reactions.

We were able to show that the products from dimer 6 were indeed primary products and were not arising from a secondary reaction of the 1,2-benzotropolidene (1) which was being formed. Pyrolysis of 6 at 280 °C, a temperature at which we have shown that 1,2-benzotropolidene (1) produces none of the observed products (12-16), produced the results shown in Table III. The observation that 1,2-benzotropolidene (1) was produced, particularly at this low temperature, proves that the dimer was indeed cleaving to yield the benzotropolyl radical (2).

In order to determine whether the first-formed product from benzene was toluene or tropilidene (which was predicted by the mechanism shown in Scheme I), we ran a pyrolysis of the dimer 6 (high pressure) in the presence of benzene at 250 °C along with parallel pyrolyses of tropilidene and a mixture of 6, benzene, tropilidene, and decane, as internal standard. This temperature was chosen since we felt that the rearrangement of tropilidene to

Table III. Pyrolysis of 6 at 280 °C

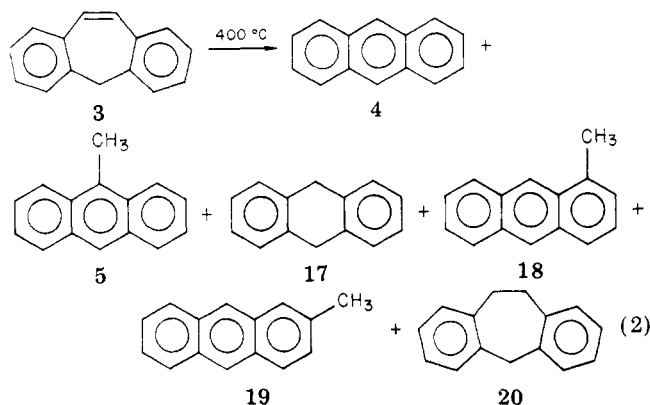
product	relative yield, <sup>a</sup> %	product	relative yield, <sup>a</sup> %
12	11 (7)	15	14
13	17	1	50 (31)
14	8		

<sup>a</sup> Absolute yields in parentheses.

toluene would be slow enough to allow us to observe the tropilidene if it were formed. Unfortunately, we were not able to observe either tropilidene or toluene from 6 by using FID-GLC (column G; see Experimental Section). We did note that the majority of the tropilidene survived when it was pyrolyzed neat, but less than 50% of it survived when heated with 6 and benzene. Thus, the postulated production of tropilidene as a precursor of toluene must still remain speculative.

**Pyrolytic Reactions of 1,2:5,6-Dibenzotropolidene (3) and 9-Methylanthracene (5).** Since pyrolysis of tropilidene produces only ca. 2-3% of benzene and pyrolysis of benzotropolidene produces ca. 5-20% of naphthalene, we reasoned that pyrolysis of dibenzotropolidene might produce a considerably greater yield of arene. This expectation has been realized.

When 1,2:5,6-dibenzotropolidene (3) was heated at 400 °C for 24 h and the pyrolysate was analyzed by GLC, the products were shown to be anthracene (4, 65%), 9-methylanthracene (5; 3%), 9,10-dihydroanthracene (17; 14%), a mixture of 1- and 2-methylanthracenes (18 and 19; 14% total, ratio ca. 2:1 by NMR spectroscopy), and 1,2:4,5-dibenzo-1,4-cycloheptadiene (20; 4%) (Table IV, entry 1) as shown in eq 2. All products were identified by comparison of NMR spectra and GLC retention times, with those of authentic samples.



When the pyrolysis of 3 was carried out for a shorter period of time (2.5 h), the most significant observation was that the 1- and 2-methylanthracenes (18 and 19) were not formed although 9-methylanthracene (5) was formed. About 60% of 3 remained unreacted (Table IV, entry 2). Only after longer periods of time were 18 and 19 formed, and it appeared they were being formed while 9-methylanthracene (5) was disappearing. A control pyrolysis demonstrated that it was indeed 9-methylanthracene (5) which was producing the 1- and 2-methylanthracenes (18 and 19) but also, more significantly, that the major product from 5 was anthracene (4; Table IV, entry 3). When the pressure in the ampule was approximately doubled (twice as much 3), the ratio of 9-methyl- to 1- and 2-methylanthracenes [5:(18 + 19)] changed from about 1:1 to about 1:5, strongly suggesting that 18 and 19 are formed by some type of intermolecular process.

Since we showed that the major product from 5 was anthracene (4), it was necessary to demonstrate that

Table IV. Pyrolysis of 1,2:5,6-Dibenzotropolidene (3) and of 9-Methylanthracene (5)

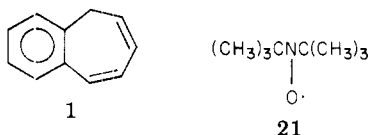
entry no.	reactant(s) and conditions <sup>a</sup>	products: relative % yield <sup>d</sup>						
		3	4	5	17	18 + 19	20	other
1	3, 400 °C, 24 h, HP		65	3	14	14	4	
2	3, 400 °C, 2.5 h, HP	60	20	10	5			
3	5, 400 °C, 24 h, HP		70	5	3	15		
4	5, 400 °C, 3 h, HP		15	80	1			
5	3, 430 °C, 1 h, naphthalene, HP	50	26 (24)	17	2	0.2	4	0.3 <sup>b</sup>
6	3, 430 °C, 1 h, naphthalene, LP	78	14 (13)	7		0.7		0.6 <sup>b</sup>
7	3, 345 °C, 1 h, naphthalene, 21, HP	23	13	8	3	1.7	3	48 <sup>c</sup>

<sup>a</sup> HP = high-pressure reaction: ca. 90 mg of reactant in a 3-mL ampule or 20–40 mg of reactant in a 0.75-mL ampule; LP = low-pressure reaction: ca. 150 mg of reactant in a 125-mL ampule. <sup>b</sup> 1,2-Benzotropolidene (1). <sup>c</sup> Consists of 47% of Diels–Alder adduct and 0.8% of 1,2-benzotropolidene. <sup>d</sup> Absolute yields in parentheses.

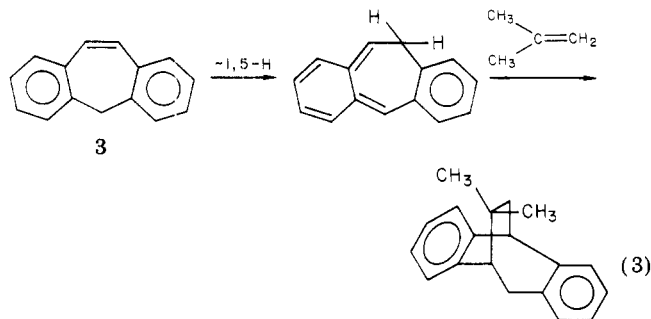
1,2:5,6-dibenzotropolidene (3) does indeed produce anthracene (4) in a primary reaction, in addition to that produced from the secondary reaction of 5. This was accomplished by pyrolyzing both 3 and 5 at the same temperature and approximate pressure. Entries 2 and 4 in Table IV show that the anthracene is produced from 3 in greater quantity than can be accounted for by secondary pyrolysis of 5 since even after 3 h 80% of 5 remains unreacted.

When 1,2:5,6-dibenzotropolidene (3) was heated in the presence of naphthalene (Table IV, entries 5 and 6), the most significant observation was the production of 1,2-benzotropolidene (1). This result indicates that the naphthalene is trapping the carbon species which is being lost from 3, and the primary product is 1,2-benzotropolidene (1).

In order to verify the presumed free-radical nature of the above reactions, we attempted the pyrolyses of 3 and 5 in the presence of di-*tert*-butyl nitroxide (21). Previ-

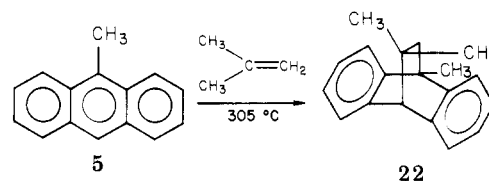


ously we showed that 21 was an effective initiator for the 1,2-benzotropolidene (1) CH-transfer reaction.<sup>4</sup> Pyrolysis of both 3 and 5 at 400 °C with 21 produced, after 24 h, in both cases, a 4:1 mixture of anthracene (4) and 1- and 2-methylanthracenes (18 and 19). The situation was clouded, however, since both compounds formed Diels–Alder adducts with isobutylene, one of the decomposition products of 21.<sup>8</sup> In a previous publication we demonstrated that the Diels–Alder reaction of 3 was that shown in eq 3.<sup>9</sup> The Diels–Alder adduct from 9-methyl-

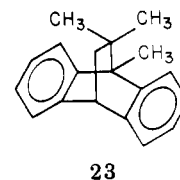


anthracene (5), and the isobutylene produced from the di-*tert*-butyl nitroxide (21), formed in about 30% yield at

300 °C, could also be produced from 5 and isobutylene at 305 °C. It was demonstrated to have structure 22 by its



NMR spectrum which shows a six-proton singlet at  $\delta$  0.72 [ $C(CH_3)_2$ ], a two-proton singlet at  $\delta$  1.25 ( $CH_2$ ), a three-proton singlet at  $\delta$  1.83 ( $CCH_3$ ), a one-proton singlet at  $\delta$  3.56 ( $CH$ ), and an eight-proton multiplet at  $\delta$  6.89–7.18 (ArH). The presence of all singlets uniquely defines the Diels–Alder adduct as 22. The regioselectivity can be accounted for on thermodynamic grounds since the methyl groups are as far apart as possible. Interestingly, when the Diels–Alder reaction is carried out at lower temperatures, 205–245 °C, two adducts are obtained (25% yield) in about equal amounts. One was 22 while the other was identified as 23 also by its NMR spectrum which showed the fol-



lowing:  $\delta$  0.68 [s, 6,  $C(CH_3)_2$ ], 1.59 (d, 2,  $J = 3$  Hz,  $CH_2$ ), 4.05 (t, 1,  $J = 3$  Hz,  $CH$ ), 6.92–7.26 (m, 8, ArH).

Thus, at the lower temperatures either 23 or both 22 and 23 are the kinetically controlled products, but at the higher temperatures, the thermodynamically favored product 22 is formed. This is presumably because of the reversible nature of the Diels–Alder reaction.

A further, careful, pyrolysis of 1,2:5,6-dibenzotropolidene (3) with di-*tert*-butyl nitroxide (21) and naphthalene (345 °C, Table IV, entry 7) gave about 47% of the Diels–Alder adduct, along with 23% of recovered 3 and, what is most significant, 0.8% of 1,2-benzotropolidene (1). A control experiment has shown that 1 is not formed at 345 °C when the nitroxide is omitted. Thus, we can conclude that the di-*tert*-butyl nitroxide (21) is initiating the reaction and that the carbon-transfer reaction is free radical in nature and, as a result, is completely analogous to the pyrolysis of 1,2-benzotropolidene (1) and tropilidene.

**Pyrolysis of 7,7'-Bis(1,2:5,6-dibenzotropyl) (7) and the 1,2:4,5-Dibenzotropyl Radical (8).** We next chose to prepare what we assumed, by analogy to the tropylium and benzotropylium reactions, to be the intermediate in the " $CH_2$ "-transfer reaction, namely, the 1,2:4,5-dibenzotropyl radical (8). We prepared the dimer of dibenzotropylium,

(8) Hoffmann, A. K.; Feldman, E.; Gelblum, E.; Hodgson, H. G. *J. Am. Chem. Soc.* 1964, 86, 639.

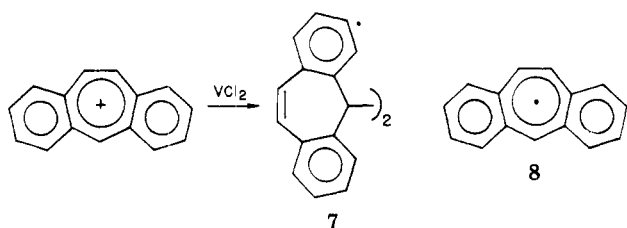
(9) Pomerantz, M.; Fink, R. *J. Org. Chem.* 1977, 42, 2788.

Table V. Pyrolysis of 7,7'-Bis(1,2:5,6-dibenzotropylyl) (7)

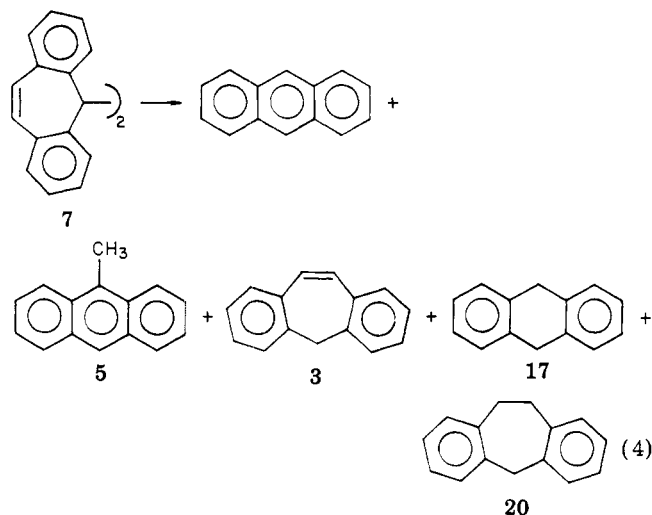
en- try no.	reactant(s) and condi- tions <sup>a</sup>	products: relative % yield <sup>b</sup>					
		3	4	5	17	20	1
1	7, 430 °C, 1 h, HP	11	52 (41)	27	3	9	
2	7, 430 °C, 1 h, LP	67 (54)	23 (18)	10			
3	7, 430 °C, 1 h, naph- thalene, LP	59	36				5
4	7, 345 °C, 1 h, LP	93 (74)	7 (6)				
5	7, 345 °C, 1 h, naph- thalene, LP	93	7				trace

<sup>a</sup> HP = high-pressure reaction: 20–40 mg of reactant in a 0.75-mL ampule; LP = low-pressure reaction: ca. 150 mg of reactant in a 125-mL ampule. <sup>b</sup> Absolute yield in parentheses.

7,7'-bis(1,2:5,6-dibenzotropylyl) (7)<sup>6</sup> by VCl<sub>2</sub> reduction of the dibenzotropylyl cation.



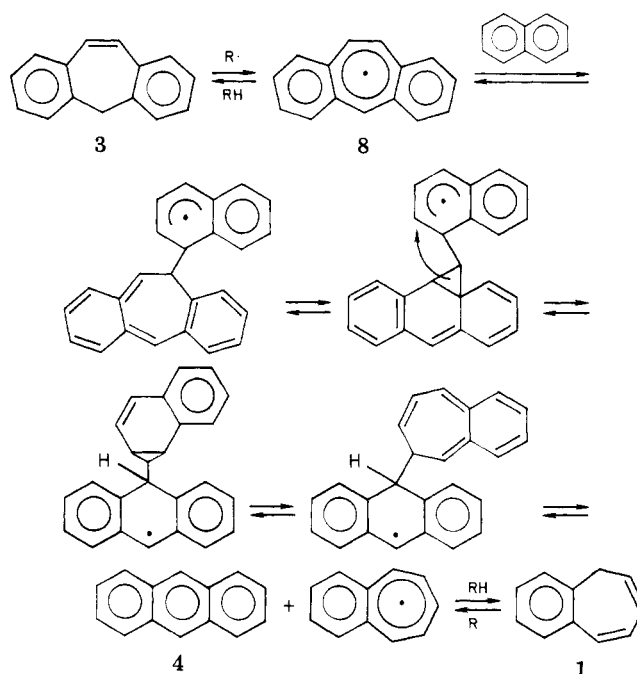
Pyrolysis of 7 (430 °C, eq 4) gave results (Table V, entry 1), particularly in the formation of anthracene (4), which were similar to those of the pyrolysis of 3. Entries 2 and



3 in Table V compare pyrolyses of the dimer 7 both without and with added naphthalene. The significant point is the formation of 5% of 1,2-benzotropylylene (1) in the latter reaction. It should also be noted that there is a distinct similarity between the pyrolysis of 1,2:5,6-dibenzotropylylene (3) in the presence of naphthalene (Table IV, entry 6) and the comparable pyrolysis of the dimer 7 (Table V, entry 3) and that there is a marked increase in the 1,2-benzotropylylene (1) formation in the latter.

Thus it appears that the pyrolytic production of anthracene (4) from dibenzotropylylene 3 and from the dibenzotropylyl dimer 7 proceeds through a common intermediate, namely, the dibenzotropylyl radical 8. Of course

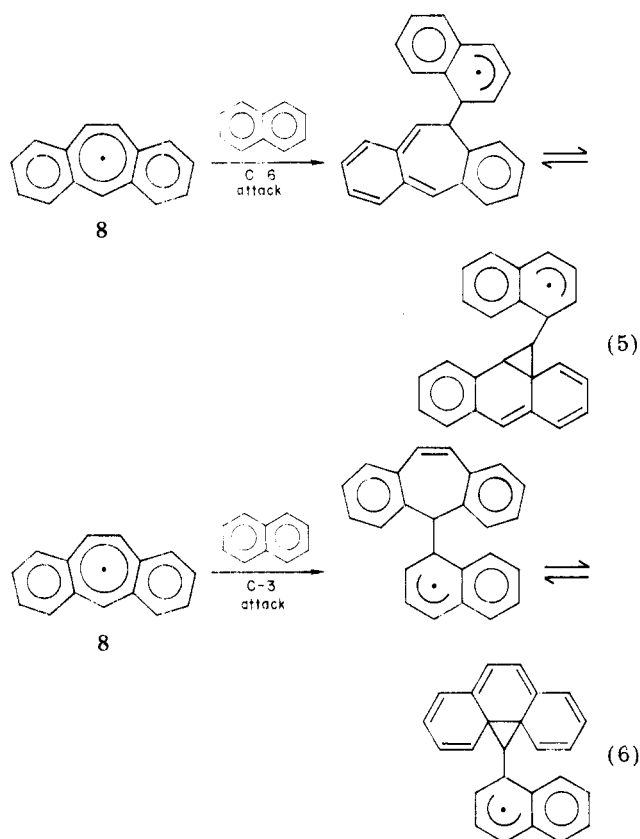
Scheme II



there still exists an alternate explanation, namely, that the dimer 7 produces dibenzotropylylene 3 as the primary product, and this gives the observed products in a subsequent reaction. This possibility was quite easily eliminated by showing that 3 could be recovered unchanged (low-pressure pyrolysis) after 1 h at 345 °C whereas under the same conditions 7 gave a 93% relative (74% absolute) yield of dibenzotropylylene 3 and a 7% relative (6% absolute) yield of anthracene (4) (Table V, entry 4). Also, under these conditions, dimer 7 with naphthalene produced a trace of 1,2-benzotropylylene (1) in addition to the monomeric 3 (93%) and anthracene (7%) (Table V, entry 5). The observations of these products prove that the dimer does indeed cleave to the radical 8 and that this radical then goes on to produce anthracene (4) by transfer of a CH group. Since no 9-methylanthracene (5) was observed here, it also proves that the anthracene (4) is indeed a primary product from the benzotropylyl radical 8.

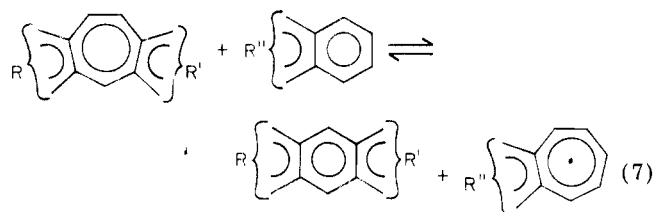
We can now write a mechanism (Scheme II) whereby dibenzotropylylene 3 produces the dibenzotropylyl radical 8 which then reacts with an aromatic acceptor to transfer a CH group. This mechanism is completely analogous to that written for the 1,2-benzotropylylene (1) and tropylylene reactions (vide supra), and as such, the reactions are written as reversible reactions, although we have not examined the reaction of 1,2-benzotropylylene (1) with anthracene (4). The yields of up to 65% of anthracene (4) indicate that the CH transfer is the major reaction of the dibenzotropylyl radical 8, except, of course, for hydrogen abstraction to produce dibenzotropylylene (3; Table V, entry 4).

It should be pointed out that the only arene observed from 3 or 7 was anthracene (4), and no phenanthrene could be detected. This means that C-6 in the dibenzotropylyl radical 8 is lost (attacks the aromatic acceptor) and not C-3. This is reasonable on two grounds. First, C-6 is less sterically hindered than C-3, and second, the next valence tautomerism in the mechanistic sequence would be much less favorable after C-3 attack than after C-6 attack. This is shown in eq 5 and 6. In eq 5 the  $\sigma$ -complex radical has the same number of aromatic rings after the valence tautomerism while the  $\sigma$ -complex radical in eq 6 loses two aromatic rings upon valence tautomerism.



### Conclusion

We have shown that the dimer 6 is formed on reduction of the benzotropylium cation with  $VCl_2$  and that pyrolyses of dimer 6 and the dibenzotropyli dimer 7 give the corresponding benzo- and dibenzotropyli radicals (2 and 8, respectively). On the basis of the experiments described, we have concluded that benzotropyli free radicals (2) and dibenzotropyli free radicals 8 can transfer a CH group to an aromatic acceptor. The tropyli radicals form arene products, and the aromatic acceptors form tropyli-type radicals. This is summarized in eq 7, where the R, R', and

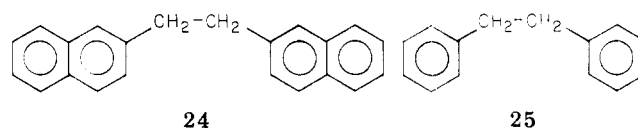


R'' groups can be hydrogen or benzo. We have further demonstrated, since both the hydrocarbons 1,2-benzotropyliidene (1) and dibenzotropyliidene 3 lose a "CH<sub>2</sub>" group and produce the same arenes (12 and 4) and the same tropyliidenes as the corresponding radicals (2 and 8) formed from the dimers (6 and 7, respectively), that these radicals are involved in the "CH<sub>2</sub>" loss and that the reactions, as above, are really CH-transfer reactions. Although we have herein reported that 9-methylanthracene (5) thermally produces anthracene (4) and 1- and 2-methylanthracenes (18 and 19), any mechanistic speculation must await further study.

There is a rather interesting contrast between the reactions of the benzotropyli dimer 6 and the dibenzotropyli dimer 7. At the lowest temperatures studied (350 °C) the latter dimer only gives two products, dibenzotropyliidene 3, by cleavage to radical 8 followed by hydrogen abstraction, and anthracene (4), by cleavage to 8 followed by loss

of a CH group. On the other hand, the benzotropyli dimer 6, at 280 °C, not only produces 1,2-benzotropyliidene (1) by cleavage to 2 followed by hydrogen abstraction and naphthalene (12) by CH transfer but also gives large amounts (25%) of 1- and 2-methylnaphthalenes (13 and 14) along with hydrogenated product, 15, in 14% relative yield. Clearly dimer 6 or the radical 2, or both, are undergoing reactions which the dibenzo systems are not. There are several routes, particularly to form the methylnaphthalenes, which one can write involving either reorganizations within the dimer prior to cleavage or reorganizations within the radical 2 itself. We are currently actively involved in trying to elucidate the origin of these products (13, 14, and 15), which amount to nearly 40% of the observed products. These results will be reported when the study is complete.

Several additional points deserve mention. First, the dimer 6 appears not to decompose at its melting point (127.5 °C) since it does not develop a color on melting and, after solidification, is remelted quite sharply again at 127.5 °C. Second, in none of the reactions of 6 was 1,2-bis(β,β'-naphthyl)ethane (24) observed. This product would



be analogous to the bibenzyl (25) which is formed upon pyrolysis of 7,7'-bitropyli (11).<sup>10</sup> Third, in none of the reactions of 6 (all reaction times were of 1-h duration) was there any dimer which remained unreacted. Fourth, we believe that all reactions, including those of the dimers, are gas phase since the ampules were usually sealed at -78 °C and <0.05 torr. Thus the pressure at 350 °C would be about 0.2 torr which we estimate to be above the boiling point of dimer 7 and as a result above the boiling point of all lower molecular weight substances. Finally, it should be pointed out that there is some variability in the amounts of hydrogenated products produced. Hydrogen transfer reactions are common in free-radical reactions, and in this study they are competitive with carbon loss and with the other concurrent reactions. Hence, the variability of hydrogenated products is not surprising.

### Experimental Section

Melting points and boiling points are uncorrected. Infrared spectra were recorded on either a Perkin-Elmer 700, 467, 257, or 237B spectrometer, and nuclear magnetic resonance spectra were taken on a Varian A-60A or T-60 spectrometer as 10–20% solutions in  $CCl_4$  or  $CDCl_3$ . GLC was done on a thermal-conductivity instrument or a Varian Aerograph 1200 FID instrument using the following columns: column A, 3 m × 0.25 in. column packed with 15% Carbowax 20M on 60/80 mesh Chromosorb P; column B, 5 ft × 0.25 in. column packed with 10% Carbowax 20M on 60/80 mesh Chromosorb P; column C, 5 ft × 0.25 in. column packed with 10% Apiezon L on 60/80 mesh Chromosorb P; column D, 5 ft × 0.25 in. column packed with 10% DC-710 silicone oil on 60/80 mesh Chromosorb P; column E, 12 ft × 0.25 in. column packed with 15% Carbowax 20M on 60/80 mesh Chromosorb P; column F, 5 ft × 0.25 in. column packed with 10% Apiezon L on 45/60 mesh Chromosorb P; column G, 6 ft × 0.125 in. column packed with 5% SE-30 on 100/120 mesh Chromosorb W and used on a Hewlett-Packard 5750 FID instrument. High-pressure LC was done on a Glenco instrument using UV detection and a 25 cm × 4.6 mm i.d. Whatman column packed with Partisil 10-ODS (5% C<sub>18</sub>) and 60/40 v/v or 70/30 v/v CH<sub>3</sub>CN-H<sub>2</sub>O as eluent. Mass spectra were taken on a Du Pont

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321 GC/MS spectrometer equipped with a Riber 400 data system including a PDP 8/m computer or a Du Pont 21-492 mass spectrometer.

**Vanadium Dichloride.**<sup>11</sup> To 11 g of Zn powder (0.17 mol) in a three-necked flask equipped with an addition funnel, condenser with drying tube, and nitrogen inlet was added 5.7 g (31 mmol) of V<sub>2</sub>O<sub>5</sub>. To this was added dropwise, with stirring, under oxygen-free nitrogen, 60 mL of 15% HCl. After being stirred at room temperature for 0.5 h, the solution was filtered to produce a purple VCl<sub>2</sub> solution which was ~1 N (titrated against standard KMnO<sub>4</sub>).

**7,7'-Bis(3,4-benzotropylium) (6).** To an ice-cooled solution of 5.2 g of triphenylmethanol (20 mmol) in 85 mL of acetic anhydride, under nitrogen, was added 3.4 mL of 48% fluoboric acid dropwise followed by 3.0 g (21 mmol) of 1,2-benzotropolidene (1), also dropwise. The resulting brown solution of benzotropylium fluoborate<sup>7,12</sup> was stirred for 1 h, and 100 mL of ether was added. The excess Ac<sub>2</sub>O was decanted from the yellow solid which was washed with pentane. After most of the pentane was decanted, 100 mL of dry THF was added, while a nitrogen atmosphere was maintained, with vigorous stirring, followed by 60 mL of VCl<sub>2</sub> solution (1 N). Water was added, and the mixture was extracted with ether, which was washed with Na<sub>2</sub>CO<sub>3</sub> solution and dried (MgSO<sub>4</sub>). Removal of the ether in vacuo gave a yellow oil which gave a yellow solid when triturated with pentane. Recrystallization from pentane (charcoal) gave pale yellow crystals of 7,7'-bis-(3,4-benzotropylium) (6): 0.32 g, 11% of theoretical; mp 127.5 °C. Anal. (C<sub>22</sub>H<sub>18</sub>) C, H. See the Results and Discussion section for the NMR spectrum. The reaction has been run without the nitrogen atmosphere without a significant diminution of the yield.

**1,2,5,6-Dibenzotropolidene (3).** This was prepared by aluminum isopropoxide reduction of 2,3:6,7-dibenzotropone.<sup>13</sup>

**1-Methylanthracene (18).** This was prepared by the Diels-Alder addition-oxidation reaction between 1,3-pentadiene and 1,4-naphthoquinone which gave 1-methylanthraquinone, and this in turn was reduced with Zn/HOAc.<sup>14</sup>

**1,2,4,5-Dibenzo-1,4-cycloheptadiene (20).**<sup>15</sup> Catalytic hydrogenation (Raney Ni/EtOH) gave an 82% yield of 20, mp 74-77 °C (lit.<sup>15</sup> mp 77-78 °C).

**Pyrolysis of 9-Methylanthracene (5) with Di-tert-butyl Nitroxide (21).** 9-Methylanthracene (5; 200 mg, 1.04 mmol) and 0.5 mL of di-tert-butyl nitroxide (21) were sealed in an evacuated, 15-mL, Pyrex ampule (previously washed with aqueous NH<sub>3</sub>) and heated at 300 °C for 24 h. GLC analysis of the product (column C, 200 °C) showed 70% of recovered 5 and 30% of Diels-Alder adduct 22 which was collected by preparative GLC; mp 90-91 °C. The NMR spectrum of 22 is presented in the Results and Discussion section. The mass spectrum (70 eV) had a very small parent at *m/e* 248, and the base peak was at *m/e* 192 (*P* - 56) corresponding to a retro-Diels-Alder reaction. Anal. (C<sub>19</sub>H<sub>20</sub>) C, H.

**Diels-Alder Reaction of 9-Methylanthracene (5) with Isobutylene.** 9-Methylanthracene (5; 200 mg, 1.04 mmol) and 1.5 g of isobutylene (27 mmol) were placed in a 200-mL Parr steel bomb, heated at 205 °C for 36 h, cooled, and removed with ether. The mixture was filtered and evaporated to dryness, and analysis by GLC (column C, 200 °C) revealed 75% recovered 5 and 25% of an approximately equal mixture of Diels-Alder adducts 22 and 23. Purification was by preparative GLC. The NMR spectrum

of 23 is presented in the Results and Discussion section. Anal. (C<sub>19</sub>H<sub>20</sub>) C, H.

A similar result was obtained when the reaction was carried out at 245 °C. When the reaction was performed at 305 °C (300 mg of 5 and 3 g of isobutylene), 22 was by far the major product since only a trace of 23 could be detected (GLC, column C).

**7,7'-Bis(1,2:5,6-dibenzotropylium) (7).**<sup>6</sup> Dibenzosuberone was reduced with NaBH<sub>4</sub> in 99.6% yield by the method of Berti to give 2,3:6,7-dibenzocycloheptatrien-1-ol.<sup>16</sup> To a solution of 2.0 g (9.6 mmol) of 2,3:6,7-dibenzocycloheptatrien-1-ol in 50 mL of CH<sub>3</sub>CN was added 48% HBF<sub>4</sub>, under nitrogen, until the solution was a very deep red (ca. 3 mL) followed by 60 mL of the above VCl<sub>2</sub> solution (~1 N). The white crystals which precipitated immediately were filtered and washed with acetone: mp 316 °C (lit.<sup>6</sup> mp 316 °C); yield 1.6 g, 86% of theory. We found this modification of Olah's procedure<sup>6</sup> to be an improvement since we experienced difficulty in working with the isolated dibenzotropylium perchlorate and fluoborate salts.

**General Pyrolysis Procedure.** "High-pressure" pyrolyses were carried out by using either medium- or heavy-walled Pyrex ampules of about 0.75- or 3-mL capacity and about 20-40 or 90 mg of sample, respectively. The ampules were previously washed with ammonium hydroxide and distilled water and dried (110 °C), and the charged ampule was cooled in dry ice and sealed under vacuum. Usually pressures of <0.05 torr were used, except in a few runs where a pressure of 15 torr was employed. The tube was heated in an oven, cooled, and opened. Some samples, particularly when GLC collection was required, were dissolved in benzene, filtered through a very short column of silica gel, concentrated, and analyzed by GLC or high-pressure LC. Other samples were simply analyzed by GLC directly after removal from the ampule.

"Low-pressure" pyrolyses were carried out by using a 125-mL Pyrex ampule [previously washed with ammonium hydroxide and water and dried (110 °C)] and about 50-200 mg of sample. The ampule was cooled in dry ice, evacuated to <0.05 torr, sealed, heated at the appropriate temperature, cooled, and analyzed by GLC or high-pressure LC.

Analysis of the fused bicyclic molecules, 1 and 12-16, was with column A or E. Preparative GLC was usually with column A. Analysis of the fused tricyclic molecules 3-5 and 17-20 was with GLC columns B, C, or F (or occasionally D) and by high-pressure LC. Preparative GLC was usually with column B.

When benzene was a reactant in the pyrolysis of 6, typically 50 mg of 6 and 0.5 mL of benzene were used in a low-pressure ampule (125 mL) or 20 mg of 6 and 0.3 mL of benzene in a high-pressure ampule (0.75 mL).

When naphthalene was used in the pyrolyses of 3 or 7, typically 20-50 mg of 3 or 7 and about 100-200 mg of naphthalene were employed. This quantity was used in either a 125-mL ampule (low pressure) or a 0.75-mL ampule (high pressure).

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**Registry No.** 1, 264-08-4; 3, 256-81-5; 4, 120-12-7; 5, 779-02-2; 6, 72017-20-0; 7, 15224-49-4; 12, 91-20-3; 13, 90-12-0; 14, 91-57-6; 15, 7125-62-4; 16, 1075-16-7; 17, 613-31-0; 18, 610-48-0; 19, 613-12-7; 20, 833-48-7; 22, 72030-09-2; 23, 72017-21-1; 2,3:6,7-dibenzotropone, 2222-33-5; 1,3-pentadiene, 542-92-7; 1,4-naphthoquinone, 130-15-4; 1-methylanthraquinone, 954-07-4; isobutylene, 115-11-7; dibenzosuberone, 1210-35-1; 2,3:6,7-dibenzocycloheptatrien-1-ol, 10354-00-4; VCl<sub>2</sub>, 10580-52-6.

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