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(48) E.g., the products resulting from the Birch reduction of the aromatic ring of *exo*- and *endo*-1 are readily aromatized by DDQ.[1]
(49) NOTE ADDED IN PROOF. We are indebted to Professor H. Prinzbach for sending us a copy of the ^{1}H NMR spectrum of the endo,endo isomer.

Conversion of Benzo- and Naphthonorcaradien-7-yl to Benzo- and Naphthotropyl Radicals

Martin Pomerantz* and N. L. Dassanayake

Contribution from the Department of Chemistry, The University of Texas at Arlington, Arlington, Texas 76019. *Received January 22, 1979*

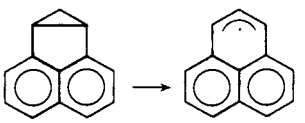
Abstract: Thermal decompositions of *tert*-butyl 2,3-benzonorcaradiene-7-percarboxylate (**7**), *tert*-butyl 2,3-(2′,3′-naphtho)-norcaradiene-7-percarboxylate (**8**), bis(2,3-benzonorcaradiene-7-carbonyl) peroxide (**9**), and bis[2,3-(2′,3′-naphtho)norcaradiene-7-carbonyl] peroxide (**10**) have been studied with particular attention paid to the hydrocarbon products, 2,3-benzonorcaradiene (**11**) and 1,2-benzotropilidene (**12**) from **7** and **9**, and 2,3-(2′,3′-naphtho)norcaradiene (**14**) and 1,2-(2′,3′-naphtho)-tropilidene (**15**) from **8** and **10**. The variation of product ratio with solvent from **7** and **8** suggests that the intermediate benzo- and naphthonorcaradien-7-yl radicals competitively abstract a hydrogen atom or undergo ring opening to the corresponding tropyl radical. A similar study of **9** and **10** suggests that there is an additional, polar component to formation of seven-membered ring products **12** and **15**. Since the hydrocarbon products are free radical in origin, it is suggested that the intermediates, whether highly polarized species or free cations, must revert back to free radicals before giving these products. It is further suggested that the greater degree of ring opening from the diacyl peroxides, **9** and **10**, is due to the greater allowedness of the ring opening of the norcaradienyl type cations relative to the corresponding radicals. It is also demonstrated that benzonorcaradienyl intermediates undergo ring opening more readily than the corresponding naphthonorcaradienyl intermediates.

Introduction

Our interest in the reactions of tropyl and benzotropyl radicals[1] has led us to explore the possibility of the electrocyclic ring opening of norcaradien-7-yl radicals to provide the corresponding tropyl radicals.

While a number of thermal ring openings of cyclopropyl radicals have been reported,[2,3] calculations indicate that the reaction, at least of the cyclopropyl radical to allyl itself, is forbidden.[4] The calculations further point out that, of the two possible modes of ring opening, conrotatory and disrotatory, the latter is preferred, although both modes should have large activation energies. In general, liquid phase reactions of simple cyclopropyl radicals show few, if any, products of ring opening. This is not surprising considering the activation energy for ring opening, estimated to be 22 kcal/mol for the cyclopropyl to allyl conversion in the gas phase,[5] is considerably higher than that for hydrogen abstraction, reported to be 7.3 kcal/mol.[6]

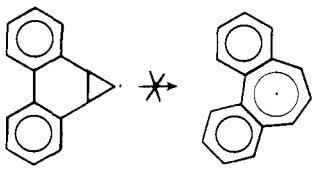
When phenyl substituents are put on the 2 and 3 positions of the cyclopropyl radical, the ring opening seems to be more facile.[3] Thus, for example, the 2,3-diphenylcyclopropyl radical has been observed to open in competition with hydrogen abstraction.[2b] Consistent with these observations is the report that free radical **1** readily undergoes ring opening to the radical shown, even using ethylbenzene as solvent and as hydrogen



1

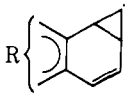
donor.[7] What appears quite puzzling, however, is the report[7] that the dibenzonorcaradien-7-yl radical **2**, under the same conditions, does not open to the dibenzotropyl radical. This is in spite of the known aromaticity of the tropyl radical.[8]

This paper describes our attempts to observe the ring

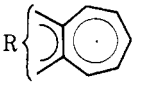


2

opening of the 2,3-benzonorcaradien-7-yl radical (**3**) to produce the benzotropyl radical (**4**) and also the ring opening of the 2,3-(2′,3′-naphtho)norcaradien-7-yl (**5**) radical to produce the naphthotropyl radical (**6**). We felt that ring opening might



3, R = benzo
5, R = 2,3-naphtho



4, R = benzo
6, R = 2,3-naphtho

be observable under an appropriate set of conditions since these should be highly exothermic reactions. Not only is the strain inherent in the three-membered ring being lost, but also the resonance energy associated with the tropyl radical[8] is being gained in these ring opening reactions.

Results and Discussion

In an attempt to observe the ring opening of norcaradienyl radicals, we have studied the thermal decomposition of *tert*-butyl 2,3-benzonorcaradiene-7-percarboxylate (**7**), *tert*-butyl 2,3-(2′,3′-naphtho)norcaradiene-7-percarboxylate (**8**), bis(2,3-benzonorcaradiene-7-carbonyl) peroxide (**9**), and bis[2,3-(2′,3′-naphtho)norcaradiene-7-carbonyl] peroxide (**10**) at 180 °C in a variety of solvents. We examined the hydrocarbon products, 2,3-benzonorcaradiene (**11**) and 1,2-benzotropilidene (**12**) from **7** and **9**, and 2,3-(2′,3′-naphtho)norcaradiene (**14**) and 1,2-(2′,3′-naphtho)tropilidene (**15**) from

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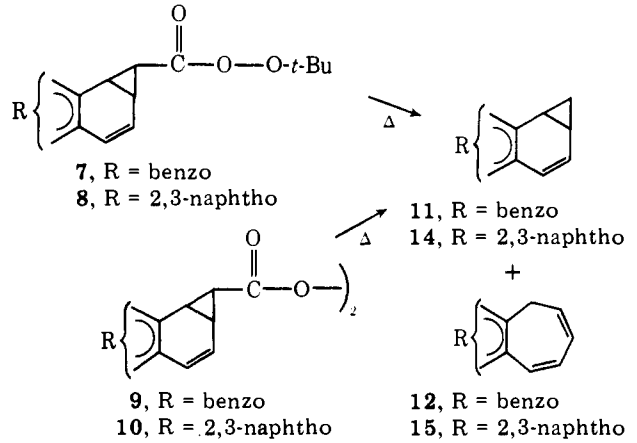
Table I. Absolute Percent Yields of Products (180 °C)

peroxide[a]	solvent	hydrocarbons (**11** + **12** or **14** + **15**)	carboxylic acid[a]	arene (**13** or **16**)	other compds[b]
7	C_6H_6	11	27	4	18
	o-$Cl_2C_6H_4$	16	28	3	20
	CH_3CN	9	21	trace	30
9	C_6H_6	27	33	2	32
	CH_3CN	22	40	6	27
8	C_6H_6	36	23	11	15
10	C_6H_6	21	40	3	32

[a] R = benzo for **7** and **9** and R = 2,3-naphtho for **8** and **10**. [b] Consists of material which was insoluble in benzene and of a large number of other compounds none of which amounted to more than a few percent. Because of the small amount of each component, none was identified. This number does not include the gases produced.

8 and **10**. In addition we also observed some naphthalene (**13**), from **7** and **9**, and anthracene (**16**), from **8** and **10**.



The *tert*-butyl peresters (**7** and **8**) were prepared by known methods[9,10] by reaction of the corresponding acid chlorides with *tert*-butyl hydroperoxide. The diacyl peroxides were prepared by reaction of the acid chlorides with potassium superoxide.[11] In addition, the products **11–16** were identified by comparison with authentic samples,[1,12] Naphthotropilidene (**15**) was prepared by Claisen condensation of diethyl naphthalene-2,3-dicarboxylate with diethyl glutarate[13] followed by bis-decarboethoxylation with NaCl in Me_2SO.[14] This latter

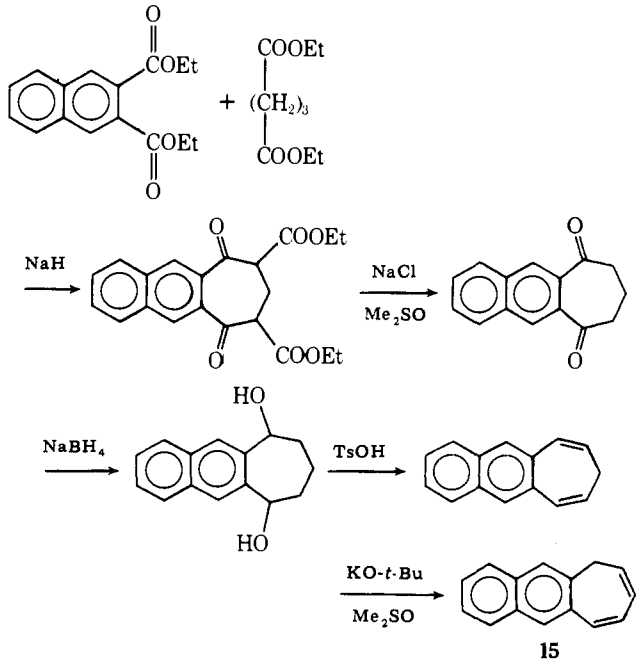


Table II. Ratio of Three-Membered Ring Product (**11** or **14**) to Seven-Membered Ring Product (**12** or **15**) from Thermal (180 °C) Decompositions

peroxide	solvent	product ratio: 3-memb ring prod	:	7-memb ring prod
7	cyclohexane	1	:	0
	cumene	1	:	0
	Nujol	1	:	0
	benzene	1	:	1
	acetonitrile	1	:	1.3
	o-dichlorobenzene	1	:	3.7
	hexafluorobenzene	1	:	5.6
8	cyclohexane	1	:	0
	cumene	1	:	0
	acetonitrile	1	:	0
	hexane	1	:	0.12
	benzene	1	:	0.24
9	cyclohexane	1	:	0.43
	hexane	1	:	0.67
	cumene	1	:	1
	Nujol	1	:	1
	benzene	1	:	2.0
	hexafluorobenzene	1	:	2.0
	acetonitrile	0	:	1
10	cyclohexane	1	:	0
	cumene	1	:	0
	acetonitrile	1	:	0.2
	benzene	1	:	0.43
	hexafluorobenzene	1	:	0.63

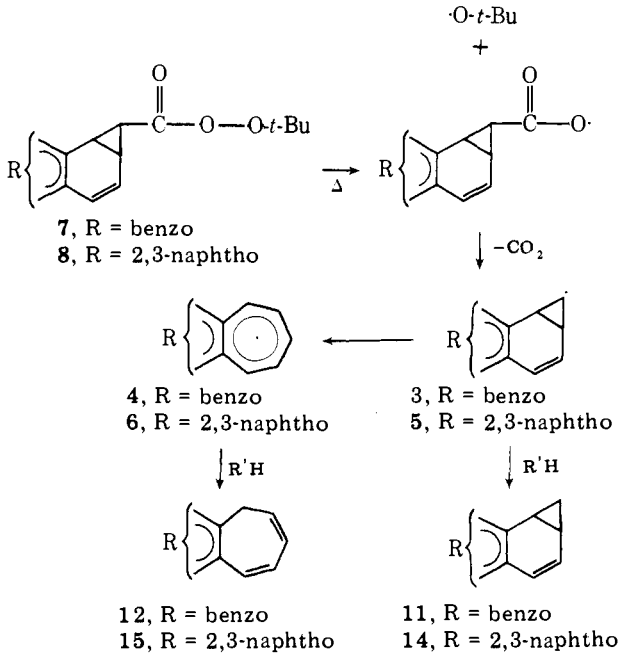
procedure was found to be necessary since most of the more conventional decarboxylation procedures[13] failed. Instead, these reactions gave the reverse Claisen condensation. The 2,3-benzocycloheptene-1,7-dione was reduced by $NaBH_4$ to the diol which was dehydrated with a catalytic amount of *p*-toluenesulfonic acid. The naphthotropilidene thus obtained was isomerized, with KO-*t*-Bu in Me_2SO to 1,2-(2′,3′-naphtho)tropilidene (**15**). The NMR spectrum of **15** was quite similar to that of 1,2-benzotropilidene.

The absolute yields of the products from the decomposition of **7–10** were determined for selected runs by first performing preparative thick-layer chromatography and then gas chromatographic or high pressure liquid chromatographic analysis. Table I summarizes the results.

Although we have not assessed the exact extent of cage recombination, the data indicate that it is at most a minor pathway under our conditions. We will omit this from further discussions since it will not affect the qualitative discussions which follow.

The results of the thermal decomposition studies are shown in Table II. Once again it should be mentioned that naphtha-

Scheme 1



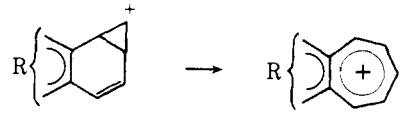
lene (**13**) and anthracene (**16**) are formed in variable amounts in the decompositions of **7** and **9** and of **8** and **10**, respectively, but there is no apparent correlation of the yield with any reaction variable. Two very preliminary experiments have been run, one of which indicates that the arenes may be rising from the benzonorcardiene portion of the molecule being oxidized by the peroxide. Another experiment shows that naphthalene is a product when the benzotropylium cation reacts with a perester. This seems to be analogous to the known reaction of the tropylium cation with peroxides such as *m*-chloroperoxybenzoic acid, hydrogen peroxide, sodium peroxide, or potassium superoxide to give up to 80% of benzene.[15] It is not clear if the arene production is related to the production of the other hydrocarbons and thus we will omit the arene from the discussions which follow.

tert-Butyl peresters are known to generally decompose by free radical pathways, particularly when CO_2 is lost.[16] This, coupled with Rüchardt's report that perester **7** decomposes by initial homolytic cleavage of the O–O bond,[10a] allows the mechanism shown in Scheme I to be postulated for the formation of **11** and **12** from **7** and of **14** and **15** from **8**. From the data in Table II, it can be seen that hydrogen donor solvents trap the benzo- and naphthonorcaradienyl radicals, **3** and **5**, respectively, prior to ring opening, but in nonhydrogen donor solvents ring opening to the corresponding benzo- and naphthotropyl radicals (**4** and **6**, respectively) successfully competes with hydrogen abstraction.

Table II also shows that the overall trends in the decomposition of the diacyl peroxides **9** and **10** are similar to those in the perester decompositions except that the actual ratios are somewhat different. In fact, in all cases but one, and excluding the results in acetonitrile solvent which will be discussed below, the amount of ring opening is greater for the diacyl peroxides than for the peresters. Since it is known that diacyl peroxides have a polar component to their decomposition,[17-21] we attempted to see if the differences noted in product ratios from **7** and **8** and from **9** and **10** were due to this (polar) phenomenon. To this end we ran the four decompositions of **7**, **8**, **9**, and **10** in acetonitrile (also at 180 °C), the solvent used typically to enhance polar reactions.[17,18] The results of this study are also shown in Table II.

Thus, assuming **7** and **8** decompose exclusively by radical pathways,[16] it is clear that **9** and **10** do indeed have polar pathways for production of the hydrocarbon products and these are enhanced in acetonitrile. In particular the results show a very much larger increase in the proportion of seven-membered ring products (**12** and **15**) in the decompositions of **9** and **10** compared with **7** and **8** than in any of the less polar solvents.

Polar reactions are well known in diacyl peroxide decompositions[17-21] and there is recent CIDNP evidence that rearranged cationic products are formed from free radical precursors.[18,19] In the present study it appears as though we are dealing with a cationic or highly polarized, cationic like intermediate or transition state. We postulate a cationic type intermediate since the benzo- or naphthonorcaradienyl cations (**16** and **17**), or high polarized, cation like intermediates, would be expected to undergo ring opening to the corresponding seven-membered ring cationic system (such as **18** or **19** or related polarized species) much more readily than the corresponding radical species (**3** and **5** or related species) due to the greater allowedness of the former reactions.

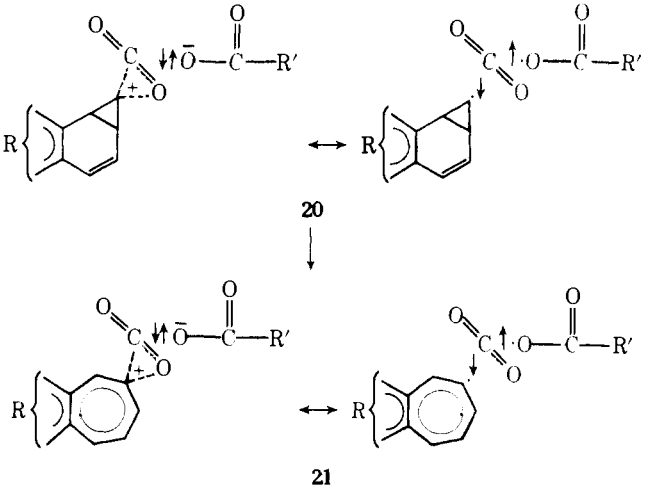


16, R = benzo
17, R = 2,3-naphtho

18, R = benzo
19, R = 2,3-naphtho

The most interesting and significant aspect of the present study is that the hydrocarbon products (**11**, **12**, **14**, and **15**) are formed in 20–30% absolute yield from the diacyl peroxides (**9** and **10**) and are derived, at least in part, from a polar intermediate. In general this extensive amount of hydrocarbon products is not produced from diacyl peroxides undergoing polar reactions. Since hydrocarbon products are generally accepted to be free radical products,[22] we must postulate that, whatever the nature of the polar intermediate, it must revert to a free radical, or must itself be a high polarized form of a free radical-like species, in order to produce the benzo- and naphthotropilidenes (**12** and **15**).

A number of cationic species might be postulated which can undergo ring opening either stepwise or concerted with formation of these ring-opened intermediates (allowed norcaradienyl to tropyl cation rearrangement). We can, as Walling[17] and subsequent workers postulated,[18,21] propose the intermediate **20** (or others involving less bridging to oxygen), which can either produce three-membered ring hydrocarbons, **11** and **14**, or open to **21** which would give seven-membered ring

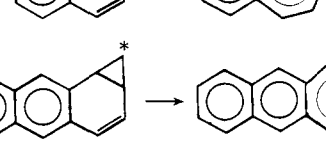


products **12** and **15**. In this instance, since these intermediates are postulated to be polar resonance hybrids,[17,18,21] they could give free radical products directly and would not require an electron transfer step. On the other extreme, there are polar

reactions of diacyl peroxides which are postulated to go through carbonium ion-ion pairs,[18-20] If we postulate that free tropyl cations (**18** or **19**) are formed in the reaction as intimate ion pairs, then an electron transfer from the carboxylate anion to the tropyl cation would have to occur. There is no precedent at this time for such a reaction.[18]

In addition, when the decomposition of the diacyl peroxides is carried out in the presence of 25-200% of diphenylpicrylhydrazyl (a free radical scavenger) in acetonitrile, the hydrocarbon products are no longer produced confirming they have a free radical precursor. Unfortunately the carboxylic acid production is also quenched and so it is not clear whether the hydrocarbon and acyloxy radicals are all scavanged or whether the acyloxy radicals alone are being intercepted and thus not surviving long enough to lose CO_2 and produce the hydrocarbons.

A final conclusion from the present study is that, in both the radical and cationic or polar reactions, ring opening of the benzonorcaradienyl system occurs more readily than ring opening of the naphthonorcaradienyl system. This can be reasonably ascribed to less gain in resonance energy for the latter ring openings than the former. That is, eq 1 (* is radical



(1)

(2)

or cation) is more exothermic than eq 2. The reason is that eq 1 shows a single aromatic ring system going to a two-ring aromatic system, while eq 2 shows a two-ring aromatic system producing a three-ring aromatic system. Since the difference in resonance energy between benzene and naphthalene (25 kcal/mol; a one- and two-ring aromatic system, respectively) is larger than the difference in resonance energy between naphthalene and anthracene (22.5 kcal/mol; a two- and three-ring aromatic system, respectively),[23] it follows that reaction 1 should be more exothermic than reaction 2. This can then be reflected in the transition states for eq 1 and 2 and so the benzo systems open more readily than the naphtho systems.

We plan to study these interesting systems further and to hopefully elucidate the nature of the polar intermediates involved in the formation of the hydrocarbon products.

Experimental Section

Melting points are uncorrected. Infrared spectra were taken on either a Perkin-Elmer 257 or 237B spectrometer and NMR spectra on a Varian T-60 spectrometer. HPLC was performed on a Glenco system using UV detection and a Whatman 25 cm × 4.6 mm i.d. column packed with Partisil 10-ODS (5%-C18). VLPC was on a 3 m × 0.25 in. column packed with 15% Carbowax 20M on 60-80 mesh Chromosorb P.

2,3-Benzonorcaradiene-7-carbonyl Chloride. 2,3-Benzonorcaradiene-7-carboxylic acid was prepared from naphthalene and ethyl diazoacetate.[24,25] This was converted, by reaction with $SOCl_2$ in ether,[24,25] to the acid chloride, in 72% yield: IR (CCl_4) 1750 (C=O) cm^{-1}; NMR (CCl_4) δ 7.2 (m, 4, Ar*H*), 6.2 (m, 2, -C*H*=C*H*-), 3.2 (m, 1, Ar-C*H*-CH-), 3.0 (m, 1, =CH-C*H*-CH), and 1.2 (m, 1, >C*H*-COCl) ppm.

***tert*-Butyl 2,3-Benzonorcaradiene-7-percarboxylate (7).** *tert*-Butyl hydroperoxide (0.720 g, 7.9 mmol) in ether (10 mL) was maintained in an ice bath, and 2,3-benzonorcaradiene-7-carbonyl chloride (0.744 g, 4.0 mmol) in ether (10 mL) was added dropwise along with pyridine (0.316 g, 4.0 mmol). The mixture was allowed to come to room temperature and then stirred for 24 h. The solution was washed with sodium carbonate (5%, 3 × 10 mL) and water (2 × 10 mL), dried ($MgSO_4$), and filtered, and the ether removed in vacuo to give a syrupy liquid. Vacuum distillation gave *tert*-butyl 2,3-benzonorcaradiene-7-percarboxylate (**7**) as a thick liquid which solidified upon standing: yield, 0.586 g, 56%; mp 74 °C (lit.[26] mp 73-74 °C); IR (neat liq) 1750 (C=O) cm^{-1}; NMR ($CDCl_3$) δ 7.4 (m, 4, Ar*H*), 6.4 (m, 2, -C*H*=C*H*-), 3.2 (m, 1, Ar-C*H*-CH-), 2.8 (m, 1, =CH-C*H*-CH-), 1.4 (s, 9, -C*H*$_3$), 0.8 (t, 1, >C*H*-COO-) ppm.

Bis(2,3-benzonorcaradiene-7-carbonyl) Peroxide (9). 2,3-Benzonorcaradiene-7-carbonyl chloride (0.612 g, 3.0 mmol) was dissolved in benzene (10 mL) which contained potassium superoxide (0.213 g, 3.0 mmol). The mixture was stirred for 3 h, 30 mL of a saturated solution of NaCl was added, and this mixture was extracted with CH_2Cl_2 (3 × 30 mL). The dried ($MgSO_4$) organic mixture was reduced in volume to about one-third and petroleum ether (bp 30-60 °C) was added until the solution was turbid. Crystallization afforded white crystals of bis(2,3-benzonorcaradiene-7-carbonyl) peroxide (**9**; 0.210 g, 31%): mp 100-120 °C (dec); IR (CCl_4) 1800, 1775 cm^{-1}; NMR (CCl_4) δ 7.0 (m, 4, Ar*H*), 6.2 (m, 2, -C*H*=C*H*-), 3.0 (m, 1, Ar-C*H*-CH-), 2.6 (m, 1, =CH-C*H*-CH-), 0.8 (m, 1, >C*H*-C(=O)-) ppm. Titration[27] indicated 94.4% peroxide purity.

2,3-(2′,3′-Naphtho)norcaradiene-7-carboxylic Acid. The procedure of Badger[27] using 59 g of anthracene (0.33 mol), 9.5 g of ethyl diazoacetate (0.08 mol), and 300 mL of dodecane gave 2.20 g of 2,3-(2′,3′-naphtho)norcaradiene-7-carboxylic acid (12%), mp 282-284 °C (lit.[27] mp 282 °C).

2,3-(2′,3′-Naphtho)norcaradiene-7-carbonyl Chloride. 2,3-(2′,3′-Naphtho)norcaradiene-7-carboxylic acid (1.28 g, 5.7 mmol) was suspended in ether (100 mL) and a few drops of pyridine was added. Thionyl chloride (10 mL) was added to the mixture dropwise and, after addition was complete, the mixture was refluxed overnight and filtered. The ether and excess $SOCl_2$ were removed in vacuo. The yellow solid residue was dissolved in the minimum amount of $CHCl_3$ and petroleum ether (bp 30-60 °C) was added until the solution was turbid. Cooling afforded tan crystals of 2,3-(2′,3′-naphtho)norcaradiene-7-carbonyl chloride (1.2 g, 82%): mp 153-155 °C; IR (Nujol) 1760 cm^{-1}; NMR ($CDCl_3$) δ 7.5 (m, 6, Ar*H*), 6.2 (m, 2, -CH=CH-), 3.3 (m, 1, Ar-C*H*-CH-), 2.9 (m, 1, =CH-C*H*-CH-), 1.3 (t, 1, >C*H*-COCl) ppm.

***tert*-Butyl 2,3-(2′,3′-Naphtho)norcaradiene-7-percarboxylate (8).** The same procedure as for the preparation of **7** using 0.5 mL of *tert*-butyl hydroperoxide, 1.01 g of 2,3-(2′,3′-naphtho)norcaradiene-7-carbonyl chloride (4.0 mmol) and a few drops of pyridine afforded a thick yellow liquid (0.480 g): IR (neat liquid) 1770, 1720 cm^{-1}. **8** was purified by column chromatography (neutral alumina). Elution with *n*-hexane gave anthracene. Further elution with *n*-hexane:benzene (1:1 v/v) gave a yellow solid identified by IR and NMR spectroscopy as *tert*-butyl 2,3-(2′,3′-naphtho)norcaradiene-7-carboxylate. Further elution with benzene gave a pale yellow solid which was recrystallized from methanol to give *tert*-butyl 2,3-(2′,3′-naphtho)-norcaradiene-7-percarboxylate (**8**, 0.180 g, 14%): mp 131 °C; IR (Nujol) 1740 cm^{-1}; NMR ($CDCl_3$) δ 7.5 (m, 6, Ar*H*), 6.2 (m, 2, -C*H*=C*H*-), 3.1 (m, 1, Ar-C*H*-CH-), 2.8 (m, 1, =CH-C*H*-CH-), 1.4 (m, 10, >C*H*-CO and -C*H*$_3$) ppm. Anal. ($C_{20}H_{20}O_3$): C, H.

Bis[2,3-(2′,3′-Naphtho)norcaradiene-7-carbonyl] Peroxide (10). The same procedure as for the preparation of **9** using 0.762 g of 2,3-(2′,3′-naphtho)norcaradiene-7-carbonyl chloride (3.0 mmol) and 0.213 g of potassium superoxide (3.0 mmol) afforded bis[2,3-(2′,3′-naphtho)norcaradiene-7-carbonyl] peroxide (**10**, 0.160 g, 11%) as a pale yellow solid: mp 140 °C (dec); IR (Nujol) 1750, 1770 cm^{-1}; NMR ($CDCl_3$) δ 7.4 (m, 6, Ar*H*), 6.3 (m, 2, -C*H*=C*H*-), 3.4 (m, 1, Ar-C*H*-CH-), 3.1 (m, 1, =CH-C*H*-CH-), 1.4 (m, 1, >C*H*-CO-) ppm. Titration[27] indicated 90.7% peroxide purity.

Pyrolysis of 7, 8, 9, or 10. About 0.5 mL of a 0.02-0.03 M solution of **7, 8, 9,** or **10** in the appropriate solvent was put into a heavy-walled Pyrex tube (7 mm o.d., 2.5 mm i.d. and ca. 10 in. long). The tube was cooled in either dry ice/isopropyl alcohol or liquid N_2 (if the solution did not freeze at −80 °C), evacuated to <0.2 Torr, and sealed. The tube was then heated in a furnace at 180 °C for 1 h and cooled. The contents of the tube were removed and the solvent was stripped in vacuo. For the product analysis of the reactions of **7** and **9**, the residue was dissolved in the minimum amount of acetone and analyzed by gas chromatography (column temp. 210 °C, He flow 50 mL/min) by comparison with authentic samples. For the product analysis of the reactions of **8** and **10**, the residue was chromatographed (TLC-silica gel-benzene) and the fraction having the same R_f value as anthracene was collected. Further analysis was by high pressure liquid chroma-

tography (LC) (room temp., 63 mL/h; 60:40 MeOH/H_2O, v/v) by comparison with authentic samples.

Typical pyrolyses involved 5 mg of **9** in 0.5 mL of solvent (0.021 M), 3.2 mg of **7** in 0.5 mL of solvent (0.026 M), 6 mg of **10** in 0.5 mL of solvent (0.032 M), and 4 mg of **8** in 0.5 mL of solvent (0.026 M).

2,3-(2′,3′-Naphtho)norcaradiene (14). The procedure of Müller[12] using CH_2N_2 from 28.8 g of *N*-nitroso-*N*-methylurea (0.25 mol), 3.0 g of anthracene (16 mmol), and Cu_2Cl_2 catalyst in 200 mL of CH_2Cl_2 gave, after chromatography on a column of basic alumina impregnated with picric acid, treatment with 1.7 g of maleic anhydride, additional chromatography with the same type of column, and finally recrystallization from MeOH, 0.670 g of 2,3-(2′,3′-naphtho)norcaradiene (**14**; 20%), mp 100–101 °C (lit.[12] mp 103 °C).

3,4-(2′,3′-Naphtho)-1,6-dicarboethoxycyclohept-3-ene-2,5-dione. To a stirred mixture of sodium hydride (9.28 g, 0.38 mol) and diethyl glutarate (13.82 g, 0.073 mol) heated to 100 °C (oil bath) was added dropwise, over a period of about 45 min, diethyl 2,3-naphthalenedicarboxylate[28] in 50 mL of bis(methoxyethyl) ether. The mixture was then heated and stirred at 100–110 °C until gas evaluation ceased (about 50 mL more solvent was added during the approximately 1 h of reaction time to dissolve the solid which formed). The reaction mixture was cooled (10 °C); ether (100 mL) was added carefully (H_2 evolution) followed by 200 mL of crushed ice. The orange aqueous layer was acidified (litmus) with concentrated HCl and extracted with ether (3 × 100 mL). The combined ether extracts were washed with H_2O (50 mL) and dried ($MgSO_4$) and the solvent removed in vacuo to give a semisolid. This material was cooled (refrigerator) overnight and filtered. The orange solid was recrystallized from ethyl acetate to give 3,4-(2′,3′-naphtho)-1,6-dicarboethoxycyclohept-3-ene-2,5-dione (3.03 g, 23%): mp 146–150 °C; IR (Nujol) 1620 cm^{-1}; NMR ($CDCl_3$) δ 8.6 (s, 2, Ar*H*), 7.6 (m, 4, Ar*H*), 4.4 (m, 4, $-CH_2CH_3$), 3.05 (s, 2, C-CH_2-C), and 1.4 (m, 6, $-CH_3$) ppm. Anal. ($C_{21}H_{20}O_6$): C, H.

2,3-(2′,3′-Naphtho)cyclohept-2-ene-1,4-dione. Following the procedure of Krapcho,[14] 3,4-(2′,3′-naphtho)-1,6-dicarboethoxycyclohept-3-ene-2,5-dione (0.736 g, 2.0 mmol), sodium chloride (0.290 g, 5.0 mmol), 10 mL of Me_2SO, and a few drops of water were mixed, heated at 120 °C for 7 h, and cooled. Water (50 mL) was added, and the mixture was extracted with ether (3 × 20 mL) and dried ($MgSO_4$). Removal of the ether in vacuo gave a brown solid, which upon recrystallization from EtOH gave orange crystals of 2,3-(2′,3′-naphtho)cyclohept-2-ene-1,4-dione (0.240 g, 54%): mp 110 °C; IR (Nujol) 1675 cm^{-1} (>C=O); NMR ($CDCl_3$) δ 8.4 (s, 2, Ar*H*), 7.6 (m, 4, Ar*H*), 3.0 (t, 4, $-C(=O)-CH_2-$, J = 7 Hz), and 2.2 (t, 2, $-CH_2CH_2CH_2-$, J = 7 Hz).

2,3-(2′,3′-Naphtho)cyclohept-2-ene-1,4-diol. Following the procedure of Gruber and Khan et al.[13] for the benzo analogue, 0.340 g (1.5 mmol) of 2,3-(2′,3′-naphtho)cyclohept-2-ene-1,4-dione was dissolved in 15 mL of THF and to this was added 0.600 g of $NaBH_4$ in 10 mL of absolute EtOH. The mixture was stirred at room temperature for 2 h, acidified with 0.1 N HCl, extracted with ether (3 × 25 mL), and dried ($MgSO_4$) and the ether removed in vacuo to give tan crystals of 2,3-(2′,3′-naphtho)cyclohept-2-ene-1,4-diol (0.230 g, 66%): IR (Nujol) 3200 cm^{-1} (broad, OH).

1,2-(2′,3′-Naphtho)tropilidene (15). A benzene (25 mL) solution of 2,3-(2′,3′-naphtho)cyclohept-2-ene-1,4-diol (0.230 g, 1.0 mmol) and a catalytic amount of *p*-toluenesulfonic acid was refluxed for 6 h. The reaction mixture was washed with water (30 mL), extracted with ether (3 × 10 mL), and dried ($MgSO_4$), and upon removal of the ether in vacuo a yellow oil (0.140 g) was obtained. This was dissolved in 30 mL of Me_2SO, 20 mg of KO-*t*-Bu was added, and this mixture was stirred overnight at room temperature. It was washed with water (25 mL), extracted with ether (3 × 25 mL), and dried ($MgSO_4$), and the ether was removed in vacuo to give a yellow oil. Chromatography on silica gel with benzene as eluent gave a yellow solid (0.110 g, 57%): mp 230 °C (dec); NMR ($CDCl_3$) δ 7.5 (*m*, 7, Ar*H* and Ar-C*H*=), 6.2 (*m*, 3, >C=C*H*-), and 3.3 (d, 2, $>CH_2$, $J \cong 6$ Hz). Anal. ($C_{15}H_{12}$): C, H.

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