The Electron-Transfer Reduction of Dibenzonorcaradiene. Orbital Symmetry Considerations in an Ion Radical Reaction

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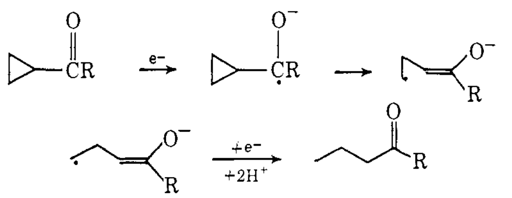
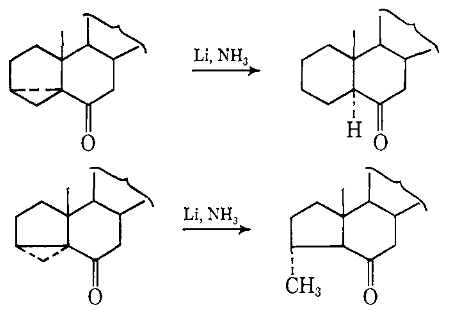
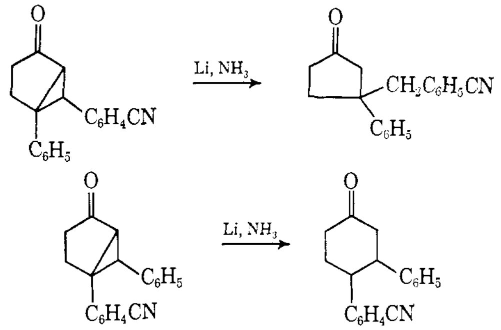
Abstract: Dibenzonorcaradiene has been treated with various electron-transfer reducing agents in anhydrous dimethoxyethane (glyme) solvent in order to study possible cyclopropane isomerizations by the dibenzonorcaradiene anion radical. The products of reduction with sodium metal after 12 hr at room temperature were 9-methylphenanthrene (25.4%), 9-methyl-9,10-dihydrophenanthrene (47.9%), and 6,7-dihydro-5H-dibenzo[*a*,*c*]cycloheptene (26.6%). Shorter reaction periods and reductions with lithium metal or sodium naphthalenide gave very similar product ratios. The latter result indicates that cyclopropane ring opening is a homogeneous process. Formation of these products could be simply rationalized in terms of competitive unimolecular cleavage of the internal and external cyclopropane bonds of the dibenzonorcaradiene anion radical except for the consideration of orbital symmetry. Unimolecular cleavage of the internal bond is an electrocyclic reaction and is sterically constrained to occur in a disrotatory fashion. This disrotatory process does not, however, conserve orbital symmetry and should be very difficult. Several alternative mechanisms in which an unsymmetrical intermediate is generated prior to internal bond cleavage are, therefore, considered. It has also been demonstrated that cleavage of the external bonds can be assisted by acids since reduction in the presence of *t*-butyl alcohol gave only 9-methylphenanthrene and 9-methyl-9,10-dihydrophenanthrene.

Although mass spectrometric studies indicate that cation radical (molecular cation) rearrangements are common in the vapor phase, very little is known about such reactions in solution. We are, therefore, exploring this possibility and report here on a solution-phase cyclopropylcarbinyl-type isomerization which is initiated by anion radical formation. The proclivity of cyclopropylcarbinyl cations, radicals, and anions toward rearrangement is well documented[1] and suggests the feasibility of similar reactions for ion radicals in which the odd electron is held in a π orbital adjacent to a cyclopropyl group. Reductive rearrangements of cyclopropyl ketones have, in fact, been reported to occur in metal ammonia solutions[2-5] and can be rationalized in terms of a radical anion intermediate.



Alternate mechanisms would involve a more difficultly formed, but more reactive, dianion or protonation before, rather than after, isomerization. Dauben and Deviney[2] have summarized much of the data on such reactions and have demonstrated that in certain cases the direction of bond cleavage is highly specific for cleavage of the cyclopropyl bond which best overlaps the π orbital of the ketone. The following isomeric cholestanones were, for example, cleaved quite stereospecifically. The importance of electronic effects in these reactions is well illustrated by the work of Zimmerman and coworkers,[3] who found that a *p*-cyano group could control the bond cleavage process.





A very interesting and pertinent example of an isomerization of a hydrocarbon anion radical is found in the reduction of bicyclo[6.1.0]nonatriene. Reduction with sodium in glyme[6] or electrochemically in ammonia[7] gave

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(1) R. Breslow in "Molecular Rearrangements," Vol. I, P. de Mayo, Ed., Interscience Publishers, New York, N. Y., 1963, Chapter 4.

(2) W. G. Dauben and E. J. Deviny, *J. Org. Chem.*, **31**, 3794 (1966).

(3) H. E. Zimmerman, R. Rieke, and J. R. Scheffer, *J. Am. Chem. Soc.*, **89**, 2033 (1967).

(4) H. O. House and C. J. Blakely, *J. Org. Chem.*, **33**, 47 (1968).

(5) T. Norin, *Acta Chem. Scand.*, **19**, 1289 (1965); **17**, 738 (1963).

(6) (a) S. Winstein, International Symposium on Aromaticity, Sheffield, England, July 6–8, 1966; (b) R. Rieke, M. Ogliaruso, R. McClung, and S. Winstein, *J. Am. Chem. Soc.*, **88**, 4729 (1966).

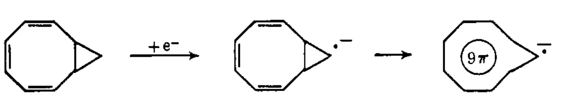
(7) T. J. Katz and C. Talcott, *ibid.*, **88**, 4732 (1966).

Table I. Products of Dibenzonorcaradiene Reduction[a]

Reducing agent (equiv)[b]	Quenching agent	Reaction time, hr	Yield, %			
			Unreacted dibenzonorcaradiene	Dibenzo[*a*,*c*]cycloheptene	9-Methyl-9,10-dihydrophenanthrene	9-Methylphenanthrene
Na (2)	H_2O	5	37.5	24.7	24.2	13.6
Na (6)	D_2O	18	<1.0	53.5	39.8	6.8
Na (8)	H_2O	12	<1.0	25.4	47.9	26.6
Na (8)	NH_4Cl	11	<1.0	41.8	38.1	20.1
Na (8)	D_2O	10.5	<1.0	37.9	42.7	19.3
Na^+, $C_{10}H_8\cdot^-$ (20)	H_2O	11	<1.0	10.2	55.4	34.3
Li (10)	H_2O	9.5	3.3	12.6	20.7	63.3
Na (8)	*t*-BuOH[c]	96	67.0	<1.0	14.5	18.4
Na (0.1)	H_2O	9	88.7	4.3	2.1	4.9

[a] All runs at room temperature in glyme with about 150 mg of dibenzonorcaradiene. [b] Equivalents with respect to dibenzonorcaradiene. [c] *t*-Butyl alcohol present during the run.

a metastable anion radical which was characterized by esr as a cyclononatetraene ion. It is of further chemical interest to note that although Katz and Talcott[7] reported eventual isomerization to a methylcyclooctatetraene anion radical in ammonia, Ogliaruso and Winstein[6] found evidence for bicyclo[6.1.0]nonadiene upon quenching the sodium in glyme reaction with methanol. Winstein and coworkers have also studied the esr spectrum of the radical anion derived from transfused bicyclo[6.1.0]nonatriene[8] and found that this species does not undergo ring opening at −90°. The comparative reluctance of the *trans* isomer to isomerize was rationalized in terms of the conformations of the radical anions. *trans*-I was expected to be somewhat more stable than *cis*-I because the triene π system in the former is more nearly planar making delocalization effective without introducing conformational strain. The ring opening is predicted to be disrotatory in order to preserve orbital symmetry. This process, however, generates a *trans* double bond in the ring-opened species from *trans*-I, again making isomerization relatively unfavorable.



I

Results and Discussion

Dibenzonorcaradiene (II) was selected for initial study because it provides a convenient electrophore[9] for formation of both the anion radical and cation radical in solution, and we hoped to investigate and compare the reactivities of each. These ion radicals were of particular interest because (1) they were expected to have a high proclivity toward cyclopropane ring opening reactions and (2) they presented an interesting competition between stereoelectronic, orbital symmetry, and conjugative effects with respect to the direction of ring opening. Although the external cyclopropane bonds are well oriented for overlap with the π system, the internal bond is nearly perpendicular to that system. This obviously favors cleavage of an external bond. Conjugative considerations on the other hand predict that cleavage of the internal bond should take place since this produces a fully conjugated ion radical which could, in principle, be even further stabilized by homoconjugation between the two benzylic carbons. Simple cleavage of this internal bond is, furthermore, an electrocyclic reaction, and is expected to be controlled to a large degree by the conservation of orbital symmetry.

Dibenzonorcaradiene[10] was readily prepared by the method alluded to by Richardson and coworkers.[11] Purification proved tedious, however, because of difficulty in removing all of the phenanthrene precursor. Treatment of II with 1–2 equiv of sodium metal in dry 1,2-dimethoxyethane (glyme) under nitrogen produced a green reaction mixture characteristic of many aromatic anion radicals. Quenching after various reaction periods with water or ammonium chloride gave three major products: 9-methylphenanthrene, 16–24%, 9-methyl-9,10-dihydrophenanthrene, 33–43%, and 6,7-dihydro-5H-dibenzo[*a*,*c*]cycloheptene (III), 23–34%. These products were isolated by preparative gas chromatography. 9-Methylphenanthrene and 9-methyl-9,10-dihydrophenanthrene were identified by comparison with independently synthesized samples. Dibenzocycloheptene (III) had intense mass spectral peaks at *m*/*e* 194, 179, 178, and 165. Its nmr spectrum had multiplets at τ 2.6–2.9 (8 H) and 7.5–7.9 (6 H), and the uv and ir spectra corresponded to literature values.[12] The nmr spectra of the crude reaction mixtures clearly indicated the formation of these products before chromatography and demonstrated that they comprise >90% of the products after a 12-hr reduction period at room temperature. As can be seen in Table I, shorter reaction times gave lower conversions, but essentially unchanged product ratios. A reduction with lithium metal led to the same products but increased relative yields of 9-methylphenanthrene.

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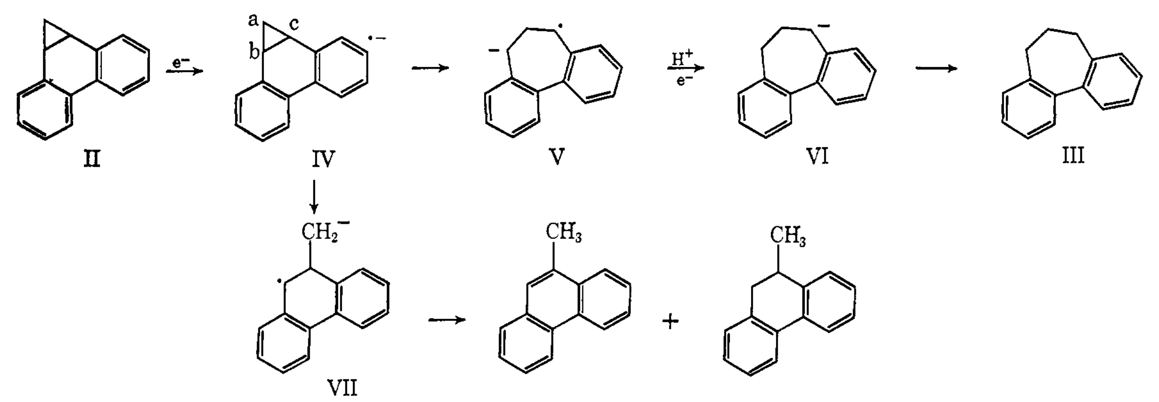
(8) G. Moshuk, G. Petrowski, and S. Winstein, *J. Am. Chem. Soc.*, **90**, 2179 (1968).

(9) We define electrophore in analogy with chromophore as a group capable of bearing an extra electron or a hole, *i.e.*, entering into electron-transfer reactions.

(10) E. Muller, H. Kessler, and H. Sahr, *Tetrahedron Letters*, 423 (1965).

(11) D. B. Richardson, *et al.*, *J. Am. Chem. Soc.*, **87**, 2763 (1965).

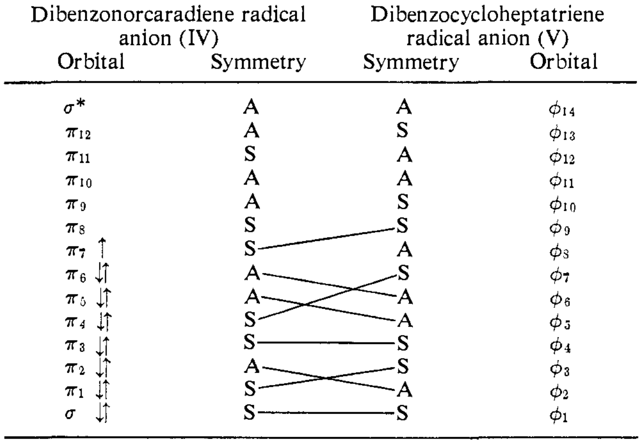
(12) P. B. D. de la Mare, E. A. Johnson, and J. S. Lomas, *J. Chem. Soc.*, 5317 (1964).



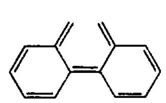
The initial reaction under these conditions is undoubtedly electron transfer from sodium to the aromatic molecule. Although electron addition to cyclopropane had been discussed[13] there is little doubt that in the present case the biphenyl electrophore or an electrophore which encompasses both the biphenyl and cyclopropyl groups will have the most positive reduction potential and, therefore, initially hold the extra electron.

The simplest mechanism for formation of the above products would then involve competitive cleavage of the a,b and b,c bonds in the anion radical IV. The efficiency of this cleavage is of interest in itself since biphenyl and dibenzonorcaradiene have similar electrophores, but show contrasting anion radical stability. According to this simple scheme b,c bond cleavage is an example of an electrocyclic ion radical reaction and subject to control by the conservation of orbital symmetry.[14] We presume that this bond cleavage is sterically constrained to occur in a disrotatory fashion giving a reaction which is symmetric with the mirror plane that bisects b,c. The pertinent orbitals are correlated in Chart I where the π orbital symmetries were obtained from Hückel calculations on biphenyl and 2,2′-dimethylene-2,2′-dihydrobiphenyl (VIII).

Chart I. Correlation Diagram for Electrocyclic Ring Opening



Dibenzonorcaradiene radical anion (IV)		Dibenzocycloheptatriene radical anion (V)	
Orbital	Symmetry	Symmetry	Orbital
σ^*	A	A	ϕ_{14}
π_{12}	A	S	ϕ_{13}
π_{11}	S	A	ϕ_{12}
π_{10}	A	A	ϕ_{11}
π_9	A	S	ϕ_{10}
π_8	S	S	ϕ_9
π_7 ↑	S	A	ϕ_8
π_6 ↓↑	A	S	ϕ_7
π_5 ↓↑	A	A	ϕ_6
π_4 ↓↑	S	A	ϕ_5
π_3 ↓↑	S	S	ϕ_4
π_2 ↓↑	A	S	ϕ_3
π_1 ↓↑	S	A	ϕ_2
σ ↓↑	S	S	ϕ_1



VIII

It can be seen from Chart I that the disrotatory anion radical reaction[15] leads to an excited state of the ring opened anion radical V. The observation of product, II, from b,c cleavage is, therefore, *an apparent violation of the orbital symmetry prediction.*

Although this correlation diagram gives the same prediction that would be arrived at by consideration of the related cyclohexadiene–hexatriene pair, it is of some concern to verify that the orbitals ϕ_8 and ϕ_9 are properly ordered and to evaluate the magnitude of the energy gap between them. It is conceivable that an aromatic system of the type under consideration would have closely spaced energy levels and if the symmetric orbital ϕ_9 was relatively low lying it could provide a pathway for direct electrocyclic cleavage. Self-consistent field calculations were, therefore, utilized to estimate the relative energies of ϕ_8 and ϕ_9. Although these calculations explicitly take into account electron repulsion which is often important in assessing the properties of ions, it was necessary to use VIII as a model system. Various geometries were generated by varying (116–120°) the bond angles external to the benzo rings and the bond distance joining these rings. These variations produced bond distances between the *exo*-methylene carbons of 1.5 to 1.9 Å. In all cases the symmetric ϕ_9 was more than 2 eV higher in energy than ϕ_8 indicating that it will not be available at room temperature. It should be noted, however, that a strictly planar model compound was employed and that the calculations involve the usual assumptions about π separability, etc. As might be expected from the bond distances involved, the calculations suggest that homoconjugation in the anion radical V would be unimportant. This is supported by the work of Levy and Myers[16] who found no

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[13] K. W. Bowers, G. J. Nolfi, T. H. Lowry, and F. D. Greene, *Tetrahedron Letters*, 4063 (1966); F. Gerson, E. Heilbronner, and J. Heinzer, *ibid.*, 2095 (1966).

[14] R. B. Woodward and R. Hoffman, *J. Am. Chem. Soc.*, **87**, 395 (1965).

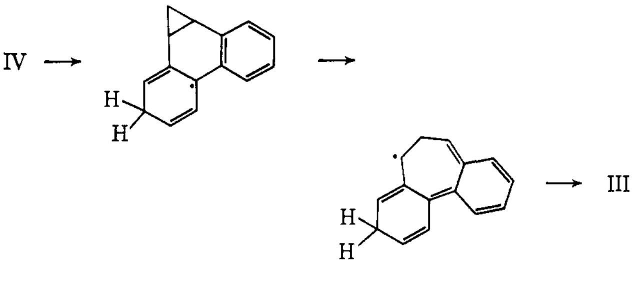
[15] In any electron transfer redox reaction there is the possibility that reaction occurs not *via* the radical ion, but from a more difficultly formed but more reactive diion. For the present consideration, it may be noted, however, that both mono- and diions have the same highest occupied orbital.

[16] D. H. Levy and R. J. Myers, *J. Chem. Phys.*, **43**, 3063 (1965).

evidence for homoconjugation in the esr spectrum of the cycloheptatriene anion radical.

The use of biphenyl π orbitals plus a σ orbital as a model for ion radical IV also needs to be examined since the orbitals of cyclopropane are probably not localized. This problem can be approached by mixing cyclopropane orbitals with the π orbitals of biphenyl. If this interaction is not large, a correlation diagram using Walsh[17] orbitals for cyclopropane indicates no change in the orbital symmetry prediction. Although further studies will investigate this problem more extensively, it may be noted that the closely related bicyclononane radical anion reactions[6–8] are predicted by the sort of model used here.

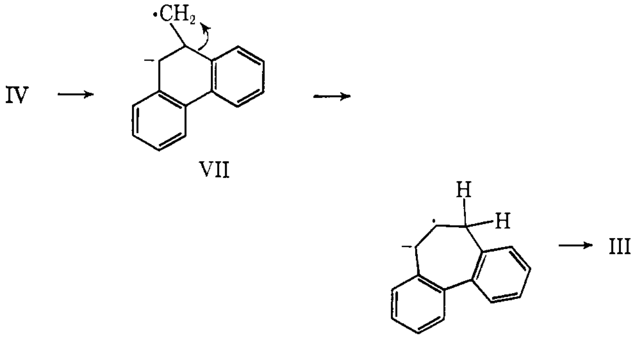
The novelty of an electrocyclic ion radical reaction, especially one which apparently violates the orbital symmetry rules, led us to test several other mechanisms which could lead to product III. A trivial possibility which avoids the orbital symmetry problem is one in which ring protonation precedes rearrangement. Such a ring protonation, however, seems improbable under these reaction conditions where the biphenyl radical anion is stable and, indeed, no cyclohexadiene-type products are formed. The immediate and continued presence of radical anions during the reaction negates any possibility of forming II *via* adventitious water since it is known that this product is not all formed at the beginning of the reaction. Furthermore, quenching with D_2O gives less than 2% deuterium incorporation in III. This demands that III be formed before quenching, presumably by proton abstraction from glyme. It has also been established that 9-methylphenanthrene or 9-methyl-9,10-dihydrophenanthrene under the usual reaction conditions does not give III. 9-Methylphenanthrene reduction followed by D_2O quenching gave 9-methyl-9,10-dideuteriophenanthrene.



Another *a priori* possibility is that we are dealing with a heterogeneous reaction. If bond cleavage took place on the sodium surface, orbital symmetry considerations could be meaningless. This possibility has been eliminated by carrying out the reduction homogeneously with an excess of sodium naphthalenide. Usual work-up and analysis revealed that the product ratios were essentially unchanged from those found for direct sodium reduction. In fact, it seems that cleavage of the cyclopropane ring occurs in solution soon after electron transfer and that the barrier imposed by orbital symmetry is surpassed or circumvented in this case because of the unique nature of the species involved.

An important possibility for bypassing the symmetry unallowed reaction would involve a concerted protonation and b,c bond cleavage, *i.e.*, direct conversion of IV to VI. Attack by the very weak acid, glyme, on the radical anion IV could conceivably take place at either position a or b and from the latter lead to the desired product III. It will be noted, however, that the stereoelectronics strongly favor overlap of the external bonds with the π system, but not the internal cyclopropane bond. Negative charge is, therefore, preferentially delocalized into the a,b and a,c bonds rather than b,c. This indicates the protonation should be favored at position a *via* attack on the electron-rich external bonds. In fact, if the reduction is conducted in the presence of 1 equiv of *t*-butyl alcohol 9-methylphenanthrene and 9-methyl-9,10-dihydrophenanthrene are formed exclusively. This amount of *t*-butyl alcohol is too small to cause a bulk solvent effect, and it is clear that the ion radicals are quenched very rapidly under these conditions since only the surface of the sodium becomes green. There is no doubt, therefore, that protonation at a can interfere with the "normal" competition in glyme. This result does not, however, unequivocally differentiate between direct and acid-promoted b,c bond cleavage. It is certainly quite consistent with a picture in which there is a competition between unassisted cleavage at a,b or b,c in dry glyme, but direct protonation at a in the presence of acids. In fact, if glyme assisted the b,c cleavage it would require this less reactive acid to be unexpectedly less selective than *t*-butyl alcohol.

It is interesting that several other apparent violations of the conservation of orbital symmetry in three-membered ring reactions have been discovered.[18,19] In each of these examples, however, direct electrocyclic cleavage may be mechanistically circumvented. Bordwell[19] has recently shown, for example, that the stereospecific, symmetry unallowed, episulfone decomposition is very likely a two-step process with some charge separation in the intermediate. More exotic possibilities for formation of III without electrocyclic cleavage can also be imagined. These processes have the common property of an unsymmetrical transition state for b,c bond cleavage and are exemplified by the following.



Other schemes are generated by transposition of protonation and electron-transfer steps. Each of these, however, has one or more steps which lack close analogy in the literature or which would be expected not to compete kinetically with some other possible reaction, *e.g.*, protonation at a benzylic rather than a primary alkyl position. These alternatives will be

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[17] A. D. Walsh, *Trans. Faraday Soc.*, **45**, 179 (1949).

[18] J. P. Freeman and W. H. Graham, *J. Am. Chem. Soc.*, **89**, 1761 (1967).

[19] F. G. Bordwell, *et al.*, *ibid.*, **90**, 429 (1968).

tested in future studies in order to gain further insight into the reasons for apparent violations of orbital symmetry conservation in cyclopropane compounds.

Experimental Section

Dibenzonorcaradiene. Zinc dust (Mallinckrodt AR) was washed successively with four 25-ml portions of 3% HCl, four 30-ml portions of water, four 30-ml portions of absolute ethanol, and five 25-ml portions of absolute ether. The ethanol and ether washings were decanted directly into a Büchner funnel to prevent loss of the zinc. The zinc dust was finally transferred with more absolute ether and suction dried. This freshly prepared zinc dust (6.54 g, 0.1 mol) and a stirring bar were placed in a dry 250-ml, three-necked flask fitted with a reflux condenser leading to a mercury trap and with a gas inlet. Dry glyme (125 ml) was then distilled from lithium aluminum hydride, under nitrogen, directly into the flask and 8.1 ml (26.8 g, 0.1 mol) of methylene iodide was added with stirring. The ensuing exothermic reaction was controlled by immersing the reaction flask in an ice bath. After the initial reaction subsided (about 30 min) the ice bath was removed. While blowing nitrogen through the flask, 12.5 g (0.07 mol) of phenanthrene, mp 97–99°, was added. The reaction was warmed to about 30° for 5 days with stirring, then heated to reflux for 1 additional day.

This mixture was cooled to room temperature and filtered through a Supercell pad on a Büchner funnel and the precipitate was then washed thoroughly with ether. The filtrate was then washed successively with 5% HCl (three 50-ml portions), 5% $NaHCO_3$ (three 50-ml portions), and water (three 50-ml portions). The aqueous washings were extracted with ether, combined with the ethereal reaction mixture, and dried over magnesium sulfate, and the solvent was removed. Oxidation with hot, aqueous, alkaline potassium permanganate[20] was utilized to remove unreacted phenanthrene. Neutralization of the aqueous mixture was followed by extraction with ether and chloroform until the extract was colorless. The organic layers were washed with base to remove any diphenic acid formed in the oxidation, dried over anhydrous magnesium sulfate, and filtered, and the solvent was removed. The product was dissolved in the smallest amount of Skellysolve H (bp 60–70°) and chromatographed on an alumina column (40 × 2 cm) developed with Skellysolve. The initial 200 ml of eluent was discarded, the next 1 l. collected, and the solvent evaporated. The resulting product was recrystallized four times from 95% ethanol. The pure dibenzonorcaradiene, mp 66–68° (lit.[10] 69–70°), was produced in 5% yield and characterized by its nmr[10] and mass spectra.

Alkali Metal Reduction of Dibenzonorcaradiene. Dibenzonorcaradiene (150 mg) and a glass-covered stirring bar were placed in a dry 50-ml, three-necked flask fitted with a mercury trap, a gas inlet, and a distillation set-up. The system was swept through with dry nitrogen and approximately 20 ml of glyme was distilled from lithium aluminum hydride into the flask. The distillation apparatus was removed while blowing in dry nitrogen and approximately 2 equiv of cut and dried sodium metal was added to the reaction. The third neck was then stoppered with a rubber septum and usually within 2 min the solution had turned from colorless to green. After an appropriate time interval the reaction was quenched by adding water with a syringe through the rubber septum (color disappears). This solution was dried with anhydrous magnesium sulfate and filtered and the solvent removed.

The product mixture was dissolved in carbon tetrachloride and its nmr spectrum recorded. The product mixture was also assayed gas chromatographically (10% silicone rubber, UC-W98 on 80–100 mesh Diatoports, 6 ft × $^1/_8$ in.). All chromatograms showed only three major products in addition to any unreacted dibenzonorcaradiene: 6,7-dihydro-5H-dibenzo[*a*,*c*]cycloheptene (III), 9-methylphenanthrene, and 9-methyl-9,10-dihydrophenanthrene. These were isolated by preparative gas chromatography (15% Apiezon Q on Chromosorb P, 6 ft × $^1/_4$ in.). 9-Methylphenanthrene and 9-methyl-9,10-dihydrophenanthrene were identified by comparison of their ir, nmr, and mass spectra and gas chromatographic retention times with those of independently synthesized samples.[21] Dibenzo[*a*,*c*]cycloheptene, III, had intense mass spectral peaks at *m/e* of 194, 179, 187, and 165. Its nmr spectrum had multiplets at τ 2.6–2.9 (8 H) and 7.5–7.9 (6 H) and the uv and ir spectra corresponded exactly to literature values.[12]

Acknowledgment. We wish to thank the Research Corporation for support of this investigation, and John D. Vaughan and Jerold C. Robertson for help with the calculations.

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(20) R. B. Randell, M. Benger, and C. M. Groocock, *Proc. Roy. Soc.* (London), **A165**, 432 (1938).

(21) W. E. Bachman, *J. Am. Chem. Soc.*, **56**, 1363 (1934).