Thermal Decomposition of Some 5-Substituted 5-Azido-5*H*-dibenzo[*a*,*d*]cycloheptenes. A Transannular Nitrene Addition

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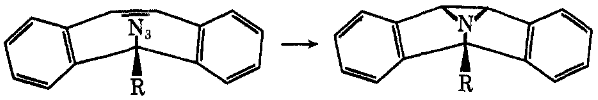
Received September 28, 1970

Thermal decomposition of 5-(1-naphthyl)-5-azido-5*H*-dibenzo[*a*,*d*]cycloheptene yields 9-(1-naphthyl)anthracene, probably *via* an unstable azasemibulvalene. When the substituent group is smaller than naphthyl, ring contraction is not favored. When the naphthyl ring of the azide has a 4-dimethylamino substituent, the latter is readily replaced by nucleophiles, providing a novel method for the preparation of 9-(4-substituted 1-naphthyl)-anthracenes.

The preparation of one azasemibulvalene system, **1**, has been reported.[1] The sandwich structure[2] proposed for the product formed by photolysis of tropylium azide suggests that transannular nitrene addition can occur in cycloheptatrienes. A variety of transannular reactions do occur in the 5*H*-dibenzo[*a*,*d*]cycloheptene system,[3] and azasemibulvalene (**2**) might result from decomposition of the proper azide, **3**, if the nitrene undergoes intramolecular addition to the double bond. The preparation and thermal decomposition of some azides of this type have been undertaken in order to test this possibility.

1

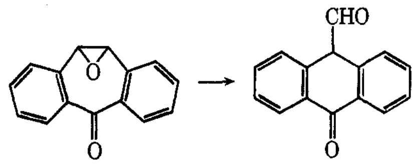


3a, R = 1-naphthyl
b, R = hydrogen
c, R = phenyl

2

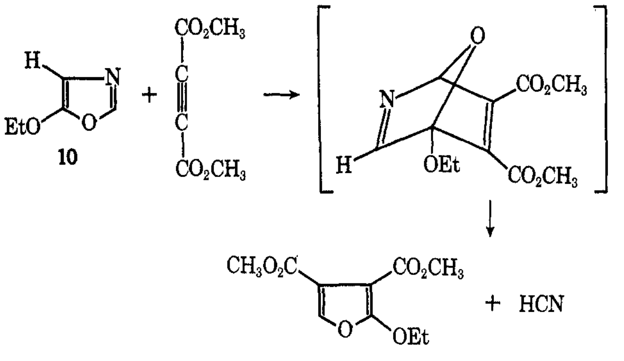
The naphthyl-substituted azide **3a** is readily prepared and thermally decomposed smoothly in refluxing *o*-dichlorobenzene with evolution of nitrogen to yield the nitrogen-free product 9-(1-naphthyl)anthracene (**7**) in good yield (88%). If the gas evolved is passed through water, a solution is obtained from which, after addition of silver nitrate, silver cyanide can be precipitated in 75% yield. Thus, the carbon atom is lost as hydrogen cyanide. The mechanism suggested for this reaction is presented in Scheme I. The azide **3a**, upon loss of nitrogen, forms nitrene **4** which adds to the double bond, generating azasemibulvalene **5**. Aryl group migration and opening of the aziridine ring gives imine **6**. The imine, a Diels–Alder adduct of hydrogen cyanide and anthracene, thermally reverses to its components, the observed products. It is also possible that the triazoline, formed by addition of the azide to the double bond, is an intermediate leading to aziridine **5** or imine **6**.

There are precedents for the proposed phenyl migration and ring opening (**5** → **6**) which occur under thermal,[4] acidic,[4,5] and basic[6] conditions. Epoxide **8**, for example, rearranges thermally[4] to the anthrone **9**.



8 **9**

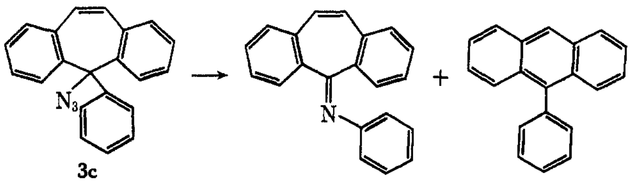
The first example of hydrogen cyanide elimination in retrodiene reactions has recently been reported for heterocyclic systems;[7] furan **11** is formed from oxazole **10** and dimethyl acetylenedicarboxylate.



10

11

Smaller substituents on position 5 of the azide **3** are less effective promoters of the thermal ring contraction. When R is hydrogen (azide **3b**) no product is isolated, and only a trace of hydrogen cyanide is evolved. The phenyl-substituted azide **3c** gives two products: imine **12** (58%) is the major, and 9-phenylanthracene **13** (11%) the minor. Formation of imine **12**, identified by hydrolysis to the corresponding ketone, is analogous to the thermal behavior of the triphenylmethyl azides.[8]



3c **12** **13**

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[1] L. A. Paquette, *Tetrahedron Lett.*, 2133 (1968).

[2] D. S. Wulfman and J. J. Ward, *Chem. Commun.*, 276 (1967).

[3] T. Dobson, M. A. Davis, A. M. Hartung, and J. M. Manson, *Can. J. Chem.*, **46**, 2843 (1968).

[4] J. Rigaudy and L. Nédélec, *Bull. Soc. Chim. Fr.*, 400 (1960).

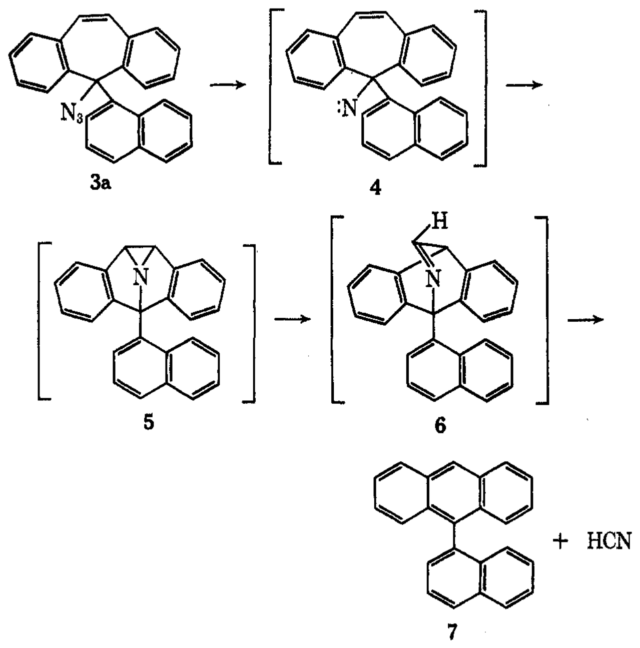
[5] G. Buchanan and D. Jhaveri, *J. Org. Chem.*, **26**, 4295 (1961).

[6] T. Dobson, M. A. Davis, and A. M. Hartung, *Can. J. Chem.*, **46**, 3391 (1968).

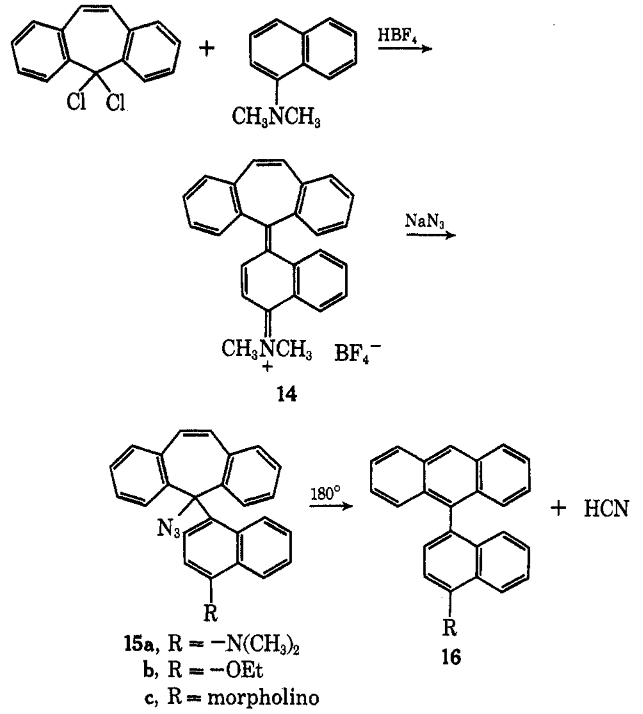
[7] R. Grigg, R. Hayes, and J. Jackson, *Chem. Commun.*, 1167 (1969).

[8] W. Saunders, Jr., and J. Ware, *J. Amer. Chem. Soc.*, **80**, 3328 (1958).

SCHEME I



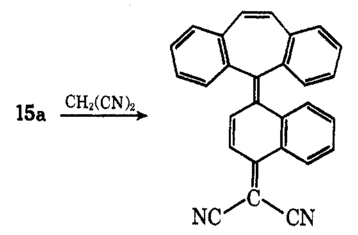
SCHEME II



These lower yields of transannular products (anthracenes) may mean that the larger naphthyl group crowds the molecule into a conformation more favorable for the intramolecular nitrene addition.

The 4-dimethylamino-1-naphthyl azide **15a** was prepared (Scheme II) from iminium salt **14** to expand the scope of the reaction. Not only does it give anthracene **16a** in good yield (67%), but it possesses a readily replaceable dimethylamino group; heating azide **15a** with ethanol gives ethoxy azide **15b**, and with morpholine, azide **15c** is obtained. These azides decompose smoothly and in good yield to the corresponding naphthylanthracenes **16b** and **16c** with loss of hydrogen cyanide.

When an active methylene group, malononitrile, is used as a potential displacing group, dicyanomethylene compound **17** is obtained.



17

Experimental Section

5-Azido-5-(1-naphthyl)-5*H*-dibenzo[*a,d*]cycloheptene (3a).—The reaction of 1-naphthylmagnesium bromide with 5*H*-dibenzo[*a,d*]cyclohepten-5-one (0.1 mol scale) gave 19 g (57%) of 5-hydroxy-5-(1-naphthyl)-5*H*-dibenzo[*a,d*]cycloheptene: mp 191–192° (from acetonitrile); nmr $\tau_{\mathrm{TMS}}^{\mathrm{DCCl_3}}$ 7.23 (s, 1, OH, exchangeable with D_2O), 3.26 (s, 2, vinyl), 2.0–3.0 (m, 13, aromatic), 1.4–1.6 (m, 2, aromatic).

Anal. Calcd for $C_{25}H_{18}O$: C, 89.8; H, 5.4. Found: C, 90.1; H, 5.6.

A solution of 2.0 g (0.006 mol) of this alcohol in 40 ml of propionic anhydride was kept below 25° while 2 g of 37% fluoroboric acid was added dropwise. The mixture was stirred for 30 min after completion of the addition and the precipitation was completed with 100 ml of anhydrous ether. The red solid was collected, washed with ether, and dissolved in 75 ml of anhydrous acetonitrile. Excess sodium azide was added, and the mixture was stirred and heated gently until the solution was colorless. The solvent was removed and the residue extracted with benzene. Chromatography of the extract on Florisil with 10% benzene–ligroin (bp 63–75°) gave 1.7 g (79%) of azide **3a**: mp 134–135° (from ligroin bp 63–75°); ir $\nu_{\mathrm{max}}^{\mathrm{KBr}}$ 2090 cm^{-1} (azide); nmr $\tau_{\mathrm{TMS}}^{\mathrm{DCCl_3}}$ 3.50 (s, 2, olefinic), 2.2–3.3 (m, 13, aromatic), 1.70–1.85 (m, 2, aromatic).

Anal. Calcd for $C_{25}H_{17}N_3$: C, 83.5; H, 4.7; N, 11.8. Found: C, 83.5; H, 4.5; N, 12.0.

9-(1-Naphthyl)anthracene (7).—A solution of 0.90 g (0.0025 mol) of 5-azido-5-(1-naphthyl)-5*H*-dibenzo[*a,d*]cycloheptene (**3a**) in 20 ml of *o*-dichlorobenzene was heated at reflux until gas evolution stopped (5 min). The evolved gas was collected over water. Addition of a silver nitrate solution to the water caused separation of 0.25 g (75%) of silver cyanide, which was identified by comparison of its infrared spectrum with that of a known sample. The solvent was removed from the organic solution and the solid residue was recrystallized from benzene–ligroin (bp 63–75°) to give 0.67 g (88%) of **7**: mp 162–163° (reported[9] mp 160–161°); nmr $\tau_{\mathrm{TMS}}^{\mathrm{DCCl_3}}$ 1.9–3.0 (m, 15, aromatic), 1.50 (s, 1, 10 H of anthracene).

5-Azido-5*H*-dibenzo[*a,d*]cycloheptene (3b).—5-Chloro-5*H*-dibenzo[*a,d*]cycloheptene was prepared by heating the corresponding alcohol in thionyl chloride as described.[10] The chloride melted at 130–132° after recrystallization from ligroin (bp 63–75°) (reported[10] mp 122–124 and 123–125°).

A mixture of 14.5 g (0.064 mol) of the chloride, 7.5 g of sodium azide, and 150 ml of anhydrous *N,N*-dimethylformamide was stirred for 15 hr and diluted with water. The solution was extracted with ligroin (bp 63–75°) and the extract passed through a small amount of Florisil. Removal of the solvent left an oil, which crystallized on cooling and scratching to give 13 g (87%) of azide **3b**: mp 55–56°; recrystallized from ligroin (bp 63–75°); ir $\nu_{\mathrm{max}}^{\mathrm{KBr}}$ 2100 cm^{-1} (azide); nmr $\tau_{\mathrm{TMS}}^{\mathrm{DCCl_3}}$ 4.70 (s, 1, benzyl), 3.00 (s, 2, vinyl), 2.5–2.8 (m, 8, aromatic).

Anal. Calcd for $C_{15}H_{11}N_3$: C, 77.3; H, 4.7; N, 18.0. Found: C, 77.3; H, 5.0; N, 17.8.

Thermal decomposition of this azide in *o*-dichlorobenzene occurred slowly. Concentration of the solution after complete decomposition and chromatography of the residue afforded no identifiable products. Decomposition occurred much faster in 1,2,4-trichlorobenzene (bp 210°), but no material was isolated

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[9] F. Vingiello, A. Bórkovec, and W. Zajac, Jr., *J. Amer. Chem. Soc.*, **80**, 1714 (1958).

[10] G. Berti, *J. Org. Chem.*, **22**, 230 (1957); *Gazz. Chim. Ital.*, **87**, 293 (1957).

from the residue. When the evolved gas was collected over water and silver nitrate solution added to the water, only a faint cloudiness was produced.

5-Phenyl-5-azido-5*H*-dibenzo[*a,d*]cycloheptene (3c).—A solution of 5.0 g (0.018 mol) of 5-phenyl-5-hydroxy-5*H*-dibenzo-[*a,d*]cycloheptene[11] in 50 ml of propionic anhydride was cooled to 10° and 6 g of 37% fluoroboric acid was added dropwise with cooling and stirring at such a rate as to keep the temperature below 25°. The red mixture was cooled to 5° for 3 hr. The solid was collected, washed with benzene, and added to a suspension of excess sodium azide in 100 ml of anhydrous acetonitrile. The mixture was stirred and heated gently until the red color disappeared. The solvent was removed and the residue washed with water and recrystallized from acetonitrile to give 5.0 g (92%) of azide **3c**: mp 157–158°; ir $\nu_{\max}^{\mathrm{KBr}}$ 2100 cm^{-1} (azide); nmr $\tau_{\mathrm{TMS}}^{\mathrm{DCCl_3}}$ 3.3–3.5 (m, 4, 2 aromatic and 2 vinyl), 2.4–3.0 (m, 9, aromatic), 1.8–2.0 (m, 2, aromatic).

Anal. Calcd for $C_{21}H_{15}N_3$: C, 81.5; H, 4.9; N, 13.6. Found: C, 81.4; H, 5.0; N, 13.7.

Pyrolysis of 5-Phenyl-5-azido-5*H*-dibenzo[*a,d*]cycloheptene (3c).—A mixture of 0.50 g (0.0016 mol) of azide **3c** and 10 ml of 1,2,4-trichlorobenzene was heated at reflux for 30 min. The solvent was removed and the residue chromatographed on Florisil. The 1:1 benzene–ligroin (bp 63–75°) fraction gave a solid which was recrystallized from ethanol, 0.045 g (11%), mp 153–154°. A mixture melting point with 9-phenylanthracene (**13**) was not depressed, and the nmr spectra were identical.

The methylene chloride fraction gave anil **12**, which was recrystallized from methylcyclohexane: 0.26 g (58%); ir $\nu_{\max}^{\mathrm{KBr}}$ 1620 cm^{-1} (C=N); nmr $\tau_{\mathrm{TMS}}^{\mathrm{DCCl_3}}$ 2.4–3.4 (m, 14, 12 aromatic and 2 vinyl), 2.0–2.15 (m, 1, aromatic).

Anal. Calcd for $C_{21}H_{15}N$: C, 89.6; H, 5.4; N, 5.0. Found: C, 89.5; H, 5.3; N, 5.2.

Upon heating with dilute hydrochloric acid the anil was readily hydrolyzed in good yield (95%) to 5*H*-dibenzo[*a,d*]cyclohepten-5-one, mp 87–88°. The ketone was identified by a mixture melting point determination and comparison of spectral properties.

5-[4-Dimethyliminium-1(4*H*)-naphthylidene]-5*H*-dibenzo-[*a,d*]cycloheptene Fluoroborate (14).—To a solution of 5,5-dichloro-5*H*-dibenzo[*a,d*]cycloheptene,[12] prepared from 10 g (0.048 mol) of 5*H*-dibenzo[*a,d*]cyclohepten-5-one, in 100 ml of anhydrous acetonitrile was added 17 g (0.10 mol) of 1-dimethylaminonaphthalene. After 20 hr the solid was collected. Concentration of the filtrate gave additional yellow solid, which was combined with the first crop and stirred with 50 ml of 50% fluoroboric acid for 15 min, before recrystallization from acetonitrile: 9.5 g (44%) of iminium salt **14**; mp 283–285°; nmr $\tau_{\mathrm{TMS}}^{\mathrm{DMSO}\text{-}d_6}$ 6.19 (s, 3, methyl), 6.03 (s, 3, methyl), 3.30–3.45 (m, 1, aromatic), 2.4–2.8 (m, 14, aromatic and vinyl), 1.9–2.1 (m, 1, aromatic).

Anal. Calcd for $C_{27}H_{22}BF_4N$: C, 72.5; H, 5.0; N, 3.1. Found: C, 72.3; H, 5.3; N, 3.1.

5-Azido-5-(4-dimethylamino-1-naphthyl)-5*H*-dibenzo[*a,d*]-cycloheptene (15a).—A mixture of 3.0 g (0.067 mol) of iminium salt **14**, excess sodium azide, and 100 ml of anhydrous acetonitrile was heated gently and stirred until the orange-yellow color of the salt disappeared. The solvent was removed and the residue extracted with benzene. The inorganic material was removed by filtration, and the filtrate concentrated to give 2.7 g (100%) of azide **15a**: mp ~137° dec; nmr $\tau_{\mathrm{TMS}}^{\mathrm{DCCl_3}}$ 7.10 (s, 6, methyl), 3.27 (s, 2, vinyl or aromatic of dimethylamino ring), 3.20 (s, 2, vinyl or aromatic of dimethylamino ring), 2.2–3.0 (m, 9, aromatic), 1.6–1.8 (m, 3, aromatic).

Anal. Calcd for $C_{27}H_{22}N_4$: C, 80.6; H, 5.5; N, 13.9. Found: C, 80.8; H, 5.4; N, 14.0.

9-(4-Dimethylamino-1-naphthyl)anthracene (16a).—A mixture of 1.0 g (0.0025 mol) of azide **15a** and 20 ml of *o*-dichlorobenzene was heated at reflux for 10 min. The solvent was removed in a stream of nitrogen and the residue dissolved in benzene. After the solution had been passed through a small amount of Florisil, the solvent was removed and the residue recrystallized from methylcyclohexane to give 0.52 g (60%) of anthracene **16a**: mp 214–215°; nmr $\tau_{\mathrm{TMS}}^{\mathrm{DCCl_3}}$ 6.87 (s, 6, methyls), 1.2–2.8 (m, 15, aromatic); mass spectrum *m/e* 347.

Anal. Calcd for $C_{26}H_{21}N$: C, 89.9; H, 6.1; N, 4.0. Found: C, 89.6; H, 6.1; N, 3.8.

5-Azido-5-(4-ethoxy-1-naphthyl)-5*H*-dibenzo[*a,d*]cycloheptene (15b).—A mixture of 0.50 g (0.0012 mol) of azide **15a** and 50 ml of ethanol was heated at reflux for 1 hr. Concentration gave 0.47 g (94%) of ethoxy azide **15b**: mp 171° dec; nmr $\tau_{\mathrm{TMS}}^{\mathrm{DMSO}\text{-}d_6}$ 8.95 (t, J = 8.0 Hz, 3, methyl), 6.21 (q, J = 8.0 Hz, 2, methylene), 3.65 and 3.72 (2 s, 4, vinyl and aromatic of ethoxynaphthyl ring), 2.1–3.3 (m, 12, aromatic).

Anal. Calcd for $C_{27}H_{21}N_3O$: C, 80.4; H, 5.3; N, 10.4. Found: C, 80.7; H, 5.2; N, 10.3.

9-(4-Ethoxy-1-naphthyl)anthracene (16b).—A mixture of 1.0 g (0.0025 mol) of azide **15b** and 10 ml of *o*-dichlorobenzene was heated at reflux for 15 min. The solvent was removed in a stream of nitrogen and the residue recrystallized from methylcyclohexane: 0.55 g (64%); mp 216–218° (sometimes melted at 208–210° but resolidified if kept at 200°, then melted at 216–218°); nmr $\tau_{\mathrm{TMS}}^{\mathrm{DMSO}\text{-}d_6}$ 9.22 (t, J = 7.0 Hz, 3, methyl), 6.42 (q, J = 7.0 Hz, 2, methylene), 2.3–4.1 (m, 14, aromatic), 2.06 (s, 1, 10 position of anthracene); mass spectrum *m/e* 348.

Anal. Calcd for $C_{26}H_{20}O$: C, 89.6; H, 5.8. Found: C, 89.9; H, 5.8.

5-Azido-5-(4-morpholino-1-naphthyl)-5*H*-dibenzo[*a,d*]cycloheptene (15c).—A solution of 7.3 g (0.018 mol) of 5-azido-5-(4-dimethylamino-1-naphthyl)-5*H*-dibenzo[*a,d*]cycloheptene (**15a**) in 50 ml of morpholine was heated on a steam bath (90°) for 2 hr. The solvent was removed in a stream of nitrogen and the solid washed with ligroin (bp 63–75°) and acetonitrile leaving 6.5 g (81%) of azide **15c**: mp 196° dec; ir $\nu_{\max}^{\mathrm{KBr}}$ 2100 cm^{-1} (N_3); nmr $\tau_{\mathrm{TMS}}^{\mathrm{DCCl_3}}$ 6.83–7.00 (m, 4, morpholine), 5.93–6.07 (m, 4, morpholine), 3.27 (s, 2, vinyl or aromatic), 3.13 (s, 2, vinyl or aromatic), 2.1–3.0 (m, 10, aromatic), 1.70 (broad s, 1, aromatic), 1.60 (broad s, 1, aromatic); mass spectrum *m/e* 444.

Anal. Calcd for $C_{29}H_{24}N_4O$: C, 78.3; H, 5.4; N, 12.6. Found: C, 78.0; H, 5.4; N, 12.6.

9-[4-(Morpholino)-1-naphthyl]anthracene (16c).—A mixture of 6.3 g (0.014 mol) of azide **15c** and 150 ml of *o*-dichlorobenzene was heated at reflux for 20 min. The solvent was removed in a stream of nitrogen and the residue treated with ethanol. The solid obtained was purified by recrystallization from ethanol–chloroform to give 3.5 g (64%) of anthracene **16c**. Other solvents, such as benzene or methylcyclohexane, were tightly held by this material: nmr $\tau_{\mathrm{TMS}}^{\mathrm{DCCl_3}}$ 6.63–6.80 (m, 4, morpholine), 5.80–5.97 (m, 4, morpholine), 1.0–2.8 (m, 15, aromatic); mass spectrum *m/e* 389.

Anal. Calcd for $C_{28}H_{23}NO$: C, 86.3; H, 6.0; N, 3.6. Found: C, 85.9; H, 6.0; N, 3.6.

5-[4-Dicyanomethylene-1(4*H*)-naphthylidene]-5*H*-dibenzo-[*a,d*]cycloheptene (17).—A mixture of 9.25 g (0.021 mol) of iminium salt **14**, excess sodium azide, and 200 ml of anhydrous acetonitrile was stirred and heated gently until the orange-yellow color of the salt disappeared. Solvent was removed and the residue extracted into benzene, filtered, and concentrated. The resulting azide was dissolved in a solution of 2 g (0.03 mol) of malononitrile in 200 ml of dry 1,2-dimethoxyethane and heated at reflux for 2 hr. The solvent was removed and the orange residue washed with ethanol and recrystallized from toluene leaving 5.6 g (70%) of dinitrile **17**: mp 287–289°; ir $\nu_{\max}^{\mathrm{KBr}}$ 2200 cm^{-1} (CN); nmr $\tau_{\mathrm{TMS}}^{\mathrm{DCCl_3}}$ 3.1–3.3 (m, 1, aromatic), 2.3–2.9 (m, 14, aromatic), 1.1–1.2 (m, 1, aromatic).

Anal. Calcd for $C_{28}H_{16}N_2$: C, 88.4; H, 4.2; N, 7.4. Found: C, 88.8; H, 4.1; N, 7.6.

Registry No.—**3a**, 27915-25-9; **3b**, 27915-26-0; **3c**, 27915-27-1; **7**, 7424-70-6; **12**, 27971-66-0; **14**, 27909-07-5; **15a**, 27971-67-1; **15b**, 27915-29-3; **15c**, 27971-68-2; **16a**, 27915-30-6; **16b**, 27915-31-7; **16c**, 27915-32-8; **17**, 27915-33-9; 5-hydroxy-5-(1-naphthyl)-5*H*-dibenzo[*a,d*]cycloheptene, 27915-34-0.

Acknowledgment.—The author is grateful to Mr. D. P. Maier for the mass spectra and Dr. T. H. Regan for the nmr spectra.

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[11] W. Treibs and H. Klinkhammer, *Ber.*, **84**, 671 (1951).

[12] J. J. Looker, *J. Org. Chem.*, **31**, 3599 (1966).