Photoadditions of 1- and 2-Naphthols and Derivatives to Acrylonitrile. Conversion of the Cyclobutane Adducts to Cyanoethylnaphthols

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The photoreactions of 1- and 2-naphthol, their trimethylsilyl (Me_3Si) ethers, and 1-methoxynaphthalene with acrylonitrile in a 1:1 isopropyl alcohol–*tert*-butyl alcohol mixture have been investigated. Irradiation of 2-naphthol and acrylonitrile gives 7-cyano-2,3-benzobicyclo[4.2.0]octa-2,4-dien-6-ol (**3**) while 2-naphthol trimethylsilyl ether gives the trimethylsilyl ether of **3**. Base treatment of **3** or **5** trimethylsilyl ether gave 1-(2-cyanoethyl)-2-naphthol. Photoaddition of 1-naphthol trimethylsilyl ether and acrylonitrile gives 8-cyano-2,3-benzobicyclo[4.2.0]octa-2,4-dien-1-ol trimethylsilyl ether, which is converted to the parent alcohol (**6**) by acid or to 2-(2-cyanoethyl)-1-naphthol (**7**) by base. The latter was also isolated in poor yield from the photolysis of 1-naphthol and acrylonitrile. Photoaddition of 1-methoxynaphthalene and acrylonitrile affords 1-methoxy-8-cyano-2,3-benzobicyclo[4.2.0]-octa-2,4-diene (**8**) and *endo*-4-methoxy-7-cyano-2,3-benzobicyclo[4.2.0]octa-2,4-diene (**9**), in the ratio 1:1. 2,6-Dimethoxynaphthalene adds to acrylonitrile, giving the 7-cyano-6-methoxy-2,3-(2′-methoxy)benzobicyclo-[4.2.0]octa-2,4-diene (**16**). These photoadditions are of possible synthetic utility for the ortho cyanoethylation of phenols.

For many years, we have been interested in the photoadditions of substituted naphthalenes with ethylene derivatives. We have investigated the addition of naphthalene[1,2] and 2-methoxynaphthalene[3] with acrylonitrile, 2-cyanonaphthalene with methyl vinyl ether,[3] and 1- and 2-cyanonaphthalenes with tetramethylethylene.[4,5] Related reactions reported by other groups include the addition of benzene[6] and anisole[7] to acrylonitrile and of benzonitrile[8] and the naphthonitriles[9,10] with olefins and vinyl ethers.

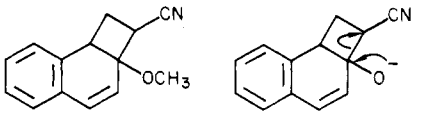
Similar reactions have also been reported in the photochemistry of heterocyclic compounds. For example, the naphthonitriles react with furan on irradiation, giving interesting cage-type adducts.[11] Also, imidazoles[12] and indoles[13] react with acrylonitrile in a way similar to indene and naphthalene.[2]

We have two objectives in continuing this line of work: (i) to understand the mechanism of singlet photoadditions[2,5,14] and (ii) to develop these additions as synthetically useful processes. In the present paper we describe some work in the latter area.

In earlier work, de Mayo[15] and Pac, Sakurai, and coworkers[16] showed that (2 + 2) photoaddition of enols[15] or enol trimethylsilyl ethers[16] to alkenes gave cyclobutanol derivatives which would undergo retroaldol reactions on hydrolysis.[17]

We have already found that the addition of 2-methoxynaphthalene[3] and acrylonitrile affords the epimers of **1**.

It was clear that similar addition of the free naphthol or a hydrolyzable derivative could be converted to the anion **2** which should undergo retroaldol reaction. In this paper we report photoadditions of 1- and 2-naphthol and their trimethylsilyl ethers to acrylonitrile and subsequent hydrolysis of the adducts. Addition of 1-methoxynaphthalene and acrylonitrile gives an unusual adduct whose characterization is also described.

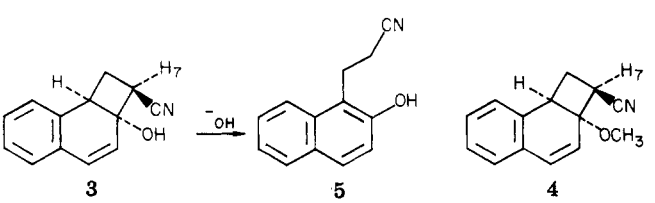


1 2

Results

To our knowledge, the only reported photoadditions of phenols have utilized their methyl ethers.[3,7,18] In the case of free phenols, we expected that the ring cycloaddition might not occur because of the acidic hydroxyl group. However, irradiation of 2-naphthol and acrylonitrile in isopropyl alcohol–*tert*-butyl alcohol mixture gave the readily isolable cyclobutanol **3**.

From the proton NMR spectrum, this alcohol appeared to be related to the major adduct from 2-methoxynaphthalene and acrylonitrile, which was assigned the endo configuration (**4**).[3] The multiplets due to the methylene and methine protons in the NMR spectrum were very similar for **3** and **4**. In particular, H_7 is a doublet of doublets, J = 9.0 and 10.5 Hz, in both compounds. Both must have the same stereochemistry, probably endo.[3]



3 5 4

(1) R. M. Bowman, C. Calvo, J. J. McCullough, R. C. Miller, and I. Singh, *Can. J. Chem.*, **51**, 1060 (1973).
(2) R. M. Bowman, T. R. Chamberlain, C. W. Huang, and J. J. McCullough, *J. Am. Chem. Soc.*, **96**, 692 (1974).
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(4) J. J. McCullough, R. C. Miller, and W. S. Wu, *Can. J. Chem.*, **55**, 2909 (1977).
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(14) A mechanistic picture of singlet photoadditions has now emerged, due to the work of several groups: (a) F. D. Lewis, *Acc. Chem. Res.*, **12**, 152 (1979); (b) R. A. Caldwell and D. Creed, *ibid.*, **13**, 45 (1980).
(15) P. de Mayo, *Pure Appl. Chem.*, **9**, 597 (1964), and references therein.
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(17) See also B. A. Pearlman, *J. Am. Chem. Soc.*, **101**, 6398 (1979).
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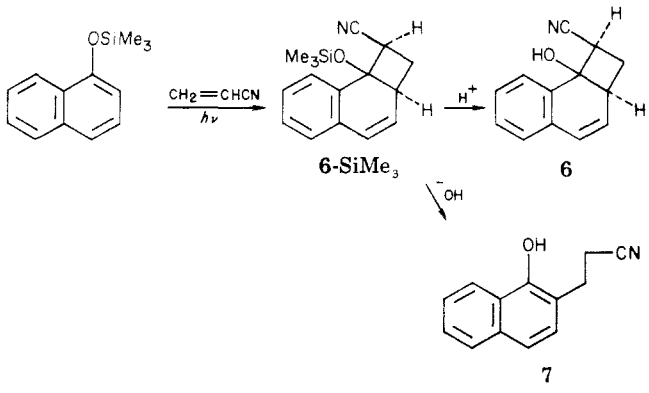
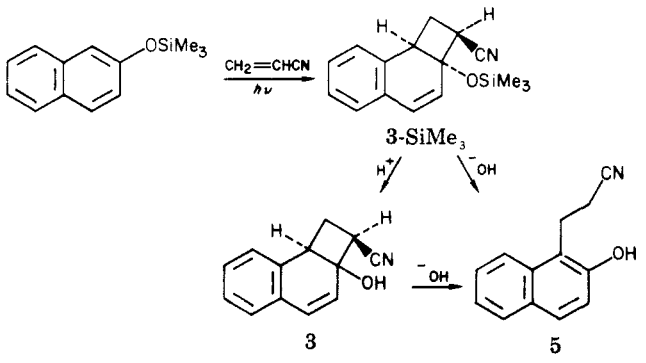
Scheme I



Scheme II



Treatment of 3, or its trimethylsilyl ether, with 2 N NaOH gave 1-(2-cyanoethyl)-2-naphthol (5)[19] in 76% yield, via the expected retroaldol reaction.

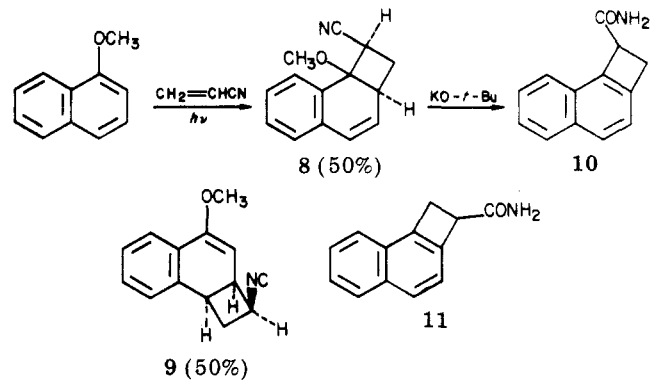
Attempted photoaddition of 1-naphthol and acrylonitrile gave a colored, intractable mixture, from which 2-(2-cyanoethyl)-1-naphthol was isolated in poor yield. Reasons for the failure of this reaction will be considered later.

Since addition of phenol methyl ethers to acrylonitrile occurs readily,[3,7] we considered using trimethylsilyl ethers of phenols in this reaction. The (trimethylsilyl)oxy and methoxy groups should have similar electronic effects, but the trimethylsilyl protecting groups could be readily hydrolyzed in the adducts formed.

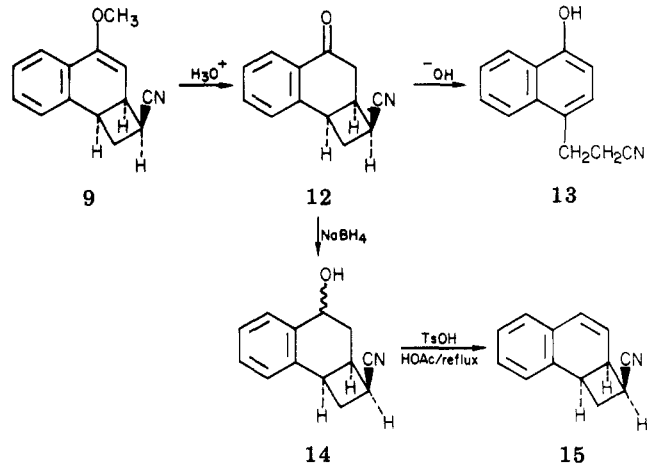
Irradiation of 1-naphthol trimethylsilyl ether[20] or 2-naphthol trimethylsilyl ether with acrylonitrile gave the trimethylsilyl ethers of the cyanobutanols 6 and 3, respectively (Schemes I and II). Hydrolysis of the silylated adducts gave the parent cyclobutanols while treatment with base gave naphthols 7 and 5 by retroaldol reaction.

The unexpected difference between above reactions of 1- and 2-naphthol prompted us to study the photoaddition of 1-methoxynaphthalene and acrylonitrile. The latter reaction also proved to be different from addition of 2-methoxynaphthalene and acrylonitrile.[3] The products are shown in Scheme III. Cyclobutane 8 is formed by addition to the substituted double bond of 1-methoxynaphthalene, which is the normal course of these additions.[3-5,7,8] The spectra (see Experimental Section) were consistent with structure 8, but the regiochemistry of the acrylonitrile fragment was confirmed by treatment with *tert*-butoxide in *tert*-butyl alcohol. These conditions have been found to aromatize the aromatic ring and hydrolyze the nitrile to amide.[3,7] The amide 10 formed from 8 had mp 183 °C

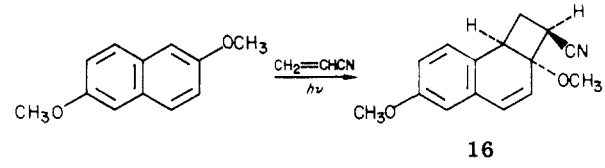
Scheme III



Scheme IV



Scheme V



and was different from 11,[3] mp 208–210 °C, obtained from the 2-methoxynaphthalene adduct (4).

The second product, assigned structure 9, was first thought to be a vinyl ether from the vinylic proton doublet, J = 3.0 Hz, at δ 4.94. Hydrolysis with 1.5 N HCl in 50:50 methanol/water afforded a cyano ketone, assigned structure 12 (Scheme IV). The structure of this ketone was established by the reactions shown in Scheme IV. Treatment with aqueous NaOH gave 4-(2-cyanoethyl)-1-naphthol (13), which confirms the regiochemistry of 12.

It was also possible to assign the stereochemistry of the nitrile by converting the cyanoketone to nitrile 15. The latter is the adduct of naphthalene and acrylonitrile, whose complete structure is known from X-ray work.[1] Borohydride reduction of the ketone gave a mixture of epimeric alcohols 14, which on dehydration gave the ethylenic nitrile 15, mp 97–99 °C (lit.[1] mp 97–98 °C). This shows that the stereochemistry of the nitrile group in adduct 9 is also endo.

As a final part of this series of experiments, the photoaddition of 2,6-dimethoxynaphthalene with acrylonitrile was investigated. This is of interest, as it is one of the few cases of addition of a naphthalene derivative substituted in both rings, and also, because the oxygen substituent in the second ring is in the correct position to allow conversion to steroid analogues.

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Irradiation of 2,6-dimethoxynaphthalene and acrylonitrile in the usual way, resulted in reasonable yield (based on reacted dimethoxynaphthalene) of the dimethoxy adduct **16** (see Scheme V). This was isolated by chromatography and had mp 85–87 °C. The multiplet structure of the methylene and methine proton resonances in the NMR spectrum indicates that this adduct has the same stereochemistry as the major epimer from 2-methoxynaphthalene and acrylonitrile,[3] probably endo.

Discussion

From the reactions described in the above results section, photoadditions of naphthol derivatives with acrylonitrile are clearly useful synthetically. The adducts from free naphthols, or from their readily prepared trimethylsilyl ethers, undergo retroaldol reaction with base to give (2-cyanoethyl)naphthols. This extends the scope of the "photo-Michael reaction", used earlier by de Mayo[15] and Pac, Sakurai, and co-workers,[16] to include addition of phenol derivatives. Addition of methoxynaphthalenes also occurs readily, and the "normal" adducts **1** and **8** aromatize in strong base to give naphthocyclobutene derivatives **11**[3] and **10**. Further reactions of **10** and **11** via opening of the cyclobutene ring should be feasible.

Addition of 1-methoxynaphthalene gives a significant yield of an "abnormal" adduct **9** (addition of ethylene derivatives usually occurs at the substituted double bond of the naphthalene[3-5,7,8]). Interestingly, the adduct corresponding to **9** was not obtained from 1-naphthol trimethylsilyl ether, indicating that the (trimethylsilyl)oxy group is more strongly directing than methoxyl.

However, if addition of the acrylonitrile to 1-naphthol gave some adduct corresponding to **9**, this could account for the variable nature of 1-naphthol reaction. The enol of **9** would ketonize to give ketone **12**, which would absorb light and undergo complex ketone chemistry in the isopropyl alcohol used as solvent.

It is possible that the above reactions are applicable to other phenol derivatives as well as to the naphthols. However, although the addition of anisole and derivatives with acrylonitrile have been described,[7] our initial experiments with other simple (benzenoid) phenols were not encouraging. The range of derivatives studied was not large, and the above naphthol reactions may occur in some other cases.

Experimental Section

Materials. The 1- and 2-naphthols were from BDH, Analar grade, and were crystallized from ether–petroleum ether. Trimethylchlorosilane was from BDH or Aldrich. 1-Methoxynaphthalene was from Aldrich and was distilled. Acrylonitrile was purified by the method of Bevington and Eaves.[21] Column chromatography was by the method of Still et al.,[22] using silica gel (E. Merck no. 9385, 40–60 μm) eluted with ethyl acetate–hexane and using E. Merck TLC sheet no. 60 (silica gel) to monitor.

Instrumentation. Infrared absorption spectra were recorded on a Perkin-Elmer Model 283 spectrometer in chloroform solution. NMR spectra were run at 90 MHz on a Varian EM-390 instrument in $CDCl_3$. Chemical shifts are given in parts per million (δ) downfield from tetramethylsilane as internal standard. Mass spectra were recorded on a Micromass VG-7070 spectrometer. Gas chromatography (GLC) was on 5 ft × 0.25 in. of 3% OV-1 on Chromosorb W, 80–100 mesh, at 170 °C, using a Tracor 560 instrument. Melting points were taken on a Kofler hot stage and are uncorrected. Microanalyses were by Galbraith Laboratories, Knoxville, TN.

Trimethylsilyl Ether of 2-Naphthol. The following modification of literature procedures[20] was used. To 2-naphthol (6.0 g, 0.0416 mol) in benzene (50 mL) and triethylamine (10 mL, 0.08 mol) was added trimethylchlorosilane (5.5 g, 0.0506 mol) dropwise with stirring. After 1 h at reflux, the solution was cooled and the triethylamine hydrochloride filtered. The residue on evaporation of solvent was distilled twice: bp 130–135 °C (20 mm); 6.0 g, 67%; IR ν_{max} 1630, 1600 cm^{-1}; ^1H NMR δ 7.4 (m, 7 H, aromatics), 0.3 (s, 9 H, $Si(CH_3)_3$). The trimethylsilyl ether of 1-naphthol[20] was prepared similarly.

Photoaddition of 2-Naphthol Trimethylsilyl Ether and Acrylonitrile. The trimethylsilyl ether of 2-naphthol (1.736 g, 0.008 mol) and acrylonitrile (20.0 g, 0.377 mol) in 400 mL of *tert*-butyl alcohol–isopropyl alcohol (1:1) mixture were irradiated with the 450-W Hanovia lamp as described previously.[1] After 3 h, GLC analysis showed ~90% conversion of reactant, and the irradiation was stopped. The solution was filtered through Celite and evaporated under vacuum. The residual oil (2.2 g) was distilled to afford the trimethylsilyl ether of 7-cyano-2,3-benzobicyclo[4.2.0]octa-2,4-dien-6-ol, **3**-$SiMe_3$ bp 95–98 °C; IR ν_{max} 2245 cm^{-1} (C≡N); ^1H NMR δ 0.15 (s, 9 H, $Si(CH_3)_3$), 1.6 and 2.25 (each 1 H, methylenes), 3.45 (2 H, methines), 5.7 and 6.57 (d, J = 10.0 Hz, each 1 H, vinylic), and 7.05 (4 H, m, aromatics).

Photoaddition of 1-Naphthol Trimethylsilyl Ether and Acrylonitrile. Similar irradiation of 1-naphthol trimethylsilyl ether (2.0 g) and acrylonitrile (20 g) for 5 h gave 50% reaction of the 1-naphthol trimethylsilyl ether. Chromatography of the crude mixture separated the adduct 8-cyano-2,3-benzobicyclo-[4.2.0]octa-2,4-dien-1-ol trimethylsilyl ether: 24%; mass spectrum, m/e 269 (parent ion); IR ν_{max} 2245 cm^{-1} (CN); ^1H NMR δ −0.2 (9 H, s, $Si(CH_3)_3$), 1.65 and 2.25 (each 1 H, m, methylenes), 3.25 (2 H, m, methines) 5.75 (dd, J = 10.0, 6.0 Hz, 1 H, vinylic), 6.3 (d, J = 10.0 Hz, 1 H, vinylic) 7.1 (m, 4 H, aromatics).

Photoaddition of 2-Naphthol and Acrylonitrile. Irradiation of 2-naphthol (1.2 g, 0.0083 mol) and acrylonitrile (20.0 g, 0.377 mol) as ahbove resulted in rapid reaction, since only traces of naphthol remained after 2 h (TLC). Chromatography of the mixture afforded *endo*-7-cyano-2,3-benzobicyclo[4.2.0]octa-2,4-dien-6-ol (**3**), which was crystallized from ether–petroleum ether: mp 94–95 °C; 36%; IR ν_{max} 3580, 3370 (OH), 2245 cm^{-1} (CN); ^1H NMR δ 1.6 and 2.35 (each 1 H, m, methylenes), 2.8 (1 H, br s, OH), 3.4 (2 H, m, methines), 5.85 and 6.7 (each 1 H, d, J = 10.0 Hz, vinylic), 7.05 (4 H, m, aromatics). An NMR spectrum of the crude mixture showed that the exo epimer of **3** was present, but it was not characterized. Anal. Calcd for $C_{13}H_{11}NO$: C, 79.17; H, 5.62; N, 7.1. Found: C, 78.95; H, 5.80; N, 7.1.

Photoaddition of 1-Naphthol and Acrylonitrile. Irradiation of 1-naphthol and acrylonitrile as described above resulted in reaction with variable results. Colored material was formed, and spectra showed that the cyclobutanol adduct (**6**) was sometimes present in the crude product. In other runs, the (cyanoethyl)-naphthol (**7**) was obtained. The reaction is apparently not useful as carried out for preparative purposes.

Preparation of 8-Cyano-2,3-benzobicyclo[4.2.0]octa-2,4-dien-1-ol (6) by Hydrolysis of the Trimethylsilyl Ether. The trimethylsilyl ether of **6** (1.0 g, 0.0037 mol) was suspended in 3 N HCl (25 mL) and stirred for 1 h at 20 °C. Ether extraction gave 0.92 g of oil, which after chromatography gave 0.4 g which crystallized in cooling in the refrigerator. Recrystallization from petroleum ether gave plates: mp 69–71 °C[; 100 mg; mass spectrum, m/e 197 (parent ion); IR ν_{max} 2245 (CN), 3580, 3350 cm^{-1} (OH); ^1H NMR δ 1.95 and 2.6 (each 1 H, m, methylenes), 3.35 (2 H, m, methines), 4.7 (1 H, br s, OH), 5.85 (1 H, dd, J = 10.0, 6.0 Hz, vinylic), 6.45 (1 H, d, J = 10.0 Hz, vinylic), 7.35 (4 H, m, aromatics). Anal. Calcd for $C_{13}H_{11}NO$: C, 79.17; H, 5.62; N, 7.10. Found: C, 79.49; H, 5.82; N, 6.96.

Similar hydrolysis of the trimethylsilyl derivative of **3** gave the alcohol identical with the photoadduct of 2-naphthol and acrylonitrile.

Base-Catalyzed Retroaldol Reaction of the Trimethylsilyl Ether of the 2-Naphthol–Acrylonitrile Adduct (3). The trimethylsilyl ether of **3** (2.2 g) was suspended in 1 N NaOH (100 mL) and kept for 12 h at 20 °C. Extraction with ether after acidification and evaporation gave a solid release (1.2 g). The product was separated by chromatography, using 25% ethyl acetate–petroleum ether as eluant. 1-(2-Cyanoethyl)-2-naphthol

(21) J. C. Bevington and D. E. Eaves, *Trans. Faraday Soc.*, **55**, 1777 (1957).
(22) W. C. Still, M. Kahn, and A. Mitra, *J. Org. Chem.*, **43**, 2923 (1978).

(5) was obtained: mp 141–143 °C (from chloroform) (lit.[19] mp 142 °C); 76%; IR ν_{max} 3600, 3310 (OH), 2255 cm^{-1} (CN); ^{1}H NMR δ 2.8 and 3.6 (each 2 H, A_2B_2 system, J = 8.0 Hz, side-chain methylenes), 5.8 (br, 1 H, OH), 7.9 (6 H, m, aromatics).

Treatment of the 2-naphthol–acrylonitrile adduct (3) with 1 N NaOH in the same way also gave 1-(2-cyanoethyl)-2-naphthol (5) in quantitative yield.

Base-Catalyzed Retroaldol Reaction of the Trimethylsilyl Ether of the 1-Naphthol–Acrylonitrile Adduct (6). Treatment of the trimethylsilyl ether of the 1-naphthol–acrylonitrile adduct (6) (200 mg) with 1 N NaOH as described above gave 2-(2-cyanoethyl)-1-naphthol (7): mp 87–88 °C (from ether–petroleum ether); yield 25%; IR ν_{max} 3590, 3350 (OH)8 2250 cm^{-1} (CN); ^{1}H NMR δ 2.6 and 3.1 (each 2 H, A_2B_2 system, J = 8.0 Hz, side-chain methylenes), 5.9 (1 H, s, OH), 7.6 (6 H, m, aromatics). Anal. Calcd for $C_{13}H_{11}NO$: C, 79.17; H, 5.62; N, 7.10. Found: C, 79.32; H, 5.80; N, 7.10.

Photoaddition of 1-Methoxynaphthalene and Acrylonitrile. Irradiation of 1-methoxynaphthalene (2.1 g) and acrylonitrile (20.0 g) in *tert*-butyl alcohol–isopropyl alcohol (400 mL), as described above, for 5 h resulted in 70% reaction of the 1-methoxynaphthalene, shown by GLC. Chromatography of the reaction mixture separated two products. Eluted first was 1-methoxy-8-cyano-2,3-benzobicyclo[4.2.0]octa-2,4-diene, 8: bp 132–135 °C (0.5 mm); 32%; IR ν_{max} 2245 (CN); ^{1}H NMR δ 1.95 and 2.57 (each 1 H, m, methylene protons), 3.05 (3 H, s, OCH_3)8 3.4 (2 H, m, methines), 6.0 (1 H, dd, J = 10.0, 6.0 Hz, vinylic), 6.42 (1 H, d, J = 10.0 Hz, vinylic), 7.3 (4 H, m, aromatics). Anal. Calcd for $C_{14}H_{13}NO$: C, 79.60; H, 6.20; N, 6.63. Found: C, 79.56; H, 6.30; N, 6.80.

Next eluted was *endo*-4-methoxy-7-cyano-2,3-benzobicyclo-[4.2.0]octa-2,4-diene (9): mp 86–88 °C (from ether); 43%; IR ν_{max} 2245 (CN)8 1645 cm^{-1} (C=C); ^{1}H NMR δ 2.55 (2 H, m, methylenes), 3.50 (2 H, m, methines), 3.75 (3 H, s, OCH_3), 4.94 (1 H, d, J = 3.0 Hz, vinylic), 6.85, 7.18, and 7.60 (total 4 H, m, aromatics). Anal. Calcd for $C_{14}H_{13}NO$: C, 79.60; H, 6.20; N, 6.63. Found: C, 79.61; H, 6.32; N, 6.57. The structures of these adducts were determined chemically, as described below.

Base-Catalyzed Aromatization of 1-Methoxy-8-cyano-2,3-benzobicyclo[4.2.0]octa-2,4-diene (8). The above oily adduct (8) of 1-methoxynaphthalene and acrylonitrile (0.3 g, 0.0014 mol) in *tert*-butyl alcohol (20 mL) was added to potassium *tert*-butoxide (from 0.6 g of potassium) in *tert*-butyl alcohol (80 mL). The mixture was heated under reflux for 2 h. The cooled solution was acidified (15 mL of 1 N HCl), washed with aqueous NaCl–$NaHCO_3$, fried ($MgSO_4$), and evaporated. The residue (0.30 g), mp 150–160 °C, gave white plates, mp 181–183 °C, from ethanol. (The corresponding product (11) from the adduct of 2-methoxynaphthalene and acrylonitrile[3] had mp 210 °C.) This amide is identified as 1,2-naphtho[*a*]cyclobutene-1-carboxamide, 10: IR 3630, 3415 (NH_2), 1675 cm^{-1} (C=O); UV (ethanol) λ_{max} 225 nm (log ϵ 4.85); ^{1}H NMR δ 3.40 (1 H, dd, J = 13.5, 2.7 Hz, methylene), 3.75 (1 H, dd, J = 13.5, 5.5 Hz, methylene), 4.42 (1 H, dd, J = 5.5, 2.7 Hz, methine), 5.8 (br, NH_2), 7.7 (6 H, m, aromatics). Anal. Calcd for $C_{13}H_{11}NO$: C, 79.21; H, 5.58; N, 7.10. Found: C, 78.95; H, 5.76; N, 7.04.

Acid Hydrolysis of Enol 9 to Corresponding Ketone, 7-Cyano-2,3-benzobicyclo[4.2.0]oct-2-en-4-one (12). The enol ether adduct 9 (1.5 g, 0.0071 mol) in methanol (50 mL) and 3 N HCl (50 mL) was heated under reflux for 1 h. The solution was cooled and ether extracted, and the extracts were washed with saturated $NaHCO_3$ and dried. Evaporation gave 1.4 g (100%), mp 93–95 °C, which was recrystallized from ether to give an analytical sample: mp 97–98 °C; IR ν_{max} 2250 (CN), 1690 cm^{-1} (C=O); ^{1}H NMR δ 3.0 (6 H, complex m, methylene and methines), 7.14 (1 H, dd, J = 7.0, 2.0 Hz), 7.95 (1 H, dd, J = 7.0, 2.0 Hz, aromatics), 7.45 (2 H, m, aromatics). Anal. Calcd for $C_{13}H_{11}NO$: C, 79.17; H, 5.62; N, 7.10. Found: C, 79.34; H, 5.73; N, 7.09.

Base-Catalyzed Retro-Michael Reaction of Ketone 12 to give 4-(2-Cyanoethyl)-1-naphthol (13). The cyano ketone 12 (250 mg) was suspended in 2 N NaOH (25 mL) for 48 h. The solution was acidified, extracted with ether, and evaporated. Chromatography of residue (20% ethyl acetate–hexane) afforded 76 mg of 4-(2-cyanoethyl)-1-naphthol (13): mp 126–128 °C (from ether–hexane); IR ν_{max} 3595, 3320 (OH)8 2255 cm^{-1} (CN); ^{1}H NMR δ 2.65 and 3.38 (each 2 H, A_2B_2 system, J = 8.0 Hz, side-chain methylenes), 6.65 and 7.15 (each 1 H, AB system, J = 7.0 Hz, substituted ring protons), 7.45, 7.75, 7.25 (total 4 H, m, aromatics). Anal. Calcd for $C_{13}H_{11}NO$: C, 79.17; H, 7.62; N, 7.1. Found: C, 79.32; H, 5.80; N, 7.09.

Conversion of Cyano Ketone 12 to *endo*-7-Cyano-2,3-benzobicyclo[4.2.0]octa-2,4-diene (15). The cyano ketone 12 (0.30 g, 0.0015 mol) was stirred with sodium borohydride (0.55 g, 0.0015 mol) in 95% ethanol (20 mL) for 48 h. A further 0.1 g of $NaBH_4$ was added, and stirring continued for 4 h. The solution was poured in 25% v/v H_2SO_4–water, cooled to 0 °C, and extracted with CH_2Cl_2. The extracts were dried ($MgSO_4$) and evaporated to give 0.3 g of oil. Infrared showed no C=O, but CN and OH bands were observed. The oil did not crystallize and was used in the next step without further characterization. The reduction product (0.30 g) was heated under reflux with *p*-toluenesulfonic acid (0.05 g) in acetic acid (25 mL) for 0.5 h. The cooled mixture was poured into ice–water and extracted with CH_2Cl_2, and the extracts were washed with $NaHCO_3$ solution and then water and finally dried ($MgSO_4$). Evaporation gave ~100 mg of gum whose infrared showed a ketonic impurity. Chromatography on silica gel gave 100 mg of *endo*-7-cyano-2,3-benzobicyclo[4.2.0]octa-2,4-diene (15), mp 97–99 °C, undepressed on mixing with authentic material.[1] Also, infrared and ^{1}H NMR were identical with those of an authentic sample.[1]

Photoaddition of 2,6-Dimethoxynaphthalene and Acrylonitrile. 2,6-Dimethoxynaphthalene (Aldrich, 1.88 g, 0.01 mol) and acrylonitrile (11.7 g, 0.22 mol) in *tert*-butyl alcohol–isopropyl alcohol (1:1; 400 mL) were irradiated with a 450-W Hanonia lamp for 4.5 h. TLC suggested 30% reaction of the dimethoxynaphthalene, and NMR showed an adduct was present. Filtration and evaporation gave a mixture from which only 2,6-dimethoxynaphthalene could be obtained on crystallization. Chromatography (20% ethyl acetate–hexane) gave 2,6-dimethoxynaphthalene (1.2 g) eluted first, followed by the adduct (0.55 g) as an oil which solidified on cooling at −20 °C. Recrystallization from ether at −5 °C gave *endo*-7-cyano-6-methoxy-(2′-methoxy)benzobicyclo[4.2.0]octa-2,4-diene (16): mp 85–87 °C (20%); IR 2840 (CH), 1607 (C=C), 2245 cm^{-1} (CN); ^{1}H NMR δ 1.72 and 2.45 (each 1 H, m, methylenes) 3.5 (2 H, m, methines), 3.1 and 3.8 (each 3 H, s, OCH_3), 5.82 (1 H, dd, J = 10.0, 2.0 Hz, vinylic), 6.9 (4 H, m, vinlic plus aromatics). Anal. Calcd for $C_{15}H_{15}NO_2$: C, 74.67; H, 6.27; N, 5.80. Found: C, 74.86; H, 6.27; N, 5.70.

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Registry No. 3, 76466-81-4; 3 TMS, 76466-82-5; 4, 43215-71-0; 5, 14233-73-9; 6, 76466-83-6; 6 TMS, 76466-84-7; 7, 76466-85-8; 8, 76466-86-9; 9, 76466-87-0; 10, 76466-88-1; 11, 43215-78-7; 12, 76466-89-2; 13, 10441-54-0; 15, 42049-78-5; 16, 76466-90-5; 2-naphthol, 135-19-3; 2-naphthol TMS, 18081-08-8; acrylonitrile, 107-13-1; 1-naphthol, 90-15-3; 1-methoxynaphthalene, 2216-69-5; 2,6-dimethoxynaphthalene, 5486-55-5.