were added 1.54 mL (11 mmol) of diisopropylamine and 50 mL of THF. To the addition funnel was added 1.38 g (5 mmol) of the amine **30** in 20 mL of THF via cannula. To the diisopropylamine solution at 0 °C was added 4.5 mL (11 mmol) of *n*-butyllithium. After 5 min, the solution was cooled to −45 °C (acetonitrile–dry ice), and **30** was added over 30 min. After being stirred 17 h, the cold mixture was quenched with 5 mL of water, permitted to warm to room temperature, extracted with ether, washed with brine, dried (Na_2SO_4), and concentrated under vacuum to give 1.19 g of crude product. Preparative layer chromatography using ethyl acetate–hexane (1:1) gave 590 mg (48%) of an oil which crystallized after the sides of the flask were scratched. recrystallization from ethanol–water gave a white solid: mp 44.5–45 °C; ^{1}H NMR (CCl_4) δ 8.28 (br s, 1), 7.53 (dd, 1), 7.03 (br d, 1), 6.53 (t, 1), 3.92 (s, 2), 3.18 (m, 2), 2.78 (m, 2), 1.8 (m, 4), 1.37 (s, 6); IR (KBr) 1622 cm^{-1}.

Anal. Calcd for $C_{15}H_{20}N_2O$: C, 73.78; H, 8.25. Found: C, 73.78; H, 8.08.

Benzazepin-9-carboxylic Acid (36). A solution of 50.8 mg of **35** in 1 mL of 4.5 N HCl was heated to reflux for 25 h, cooled, and adjusted to pH 4.5 with 5 M NaOH. The mixture was extracted with dichloromethane, and the extracts were washed with brine, dried (Na_2SO_4), filtered, and concentrated to give 17.9 mg (45%) of **36** as a colorless solid. Recrystallization from ethanol–water gave purified product: mp 160–163 °C dec; ^{1}H NMR ($CDCl_3$) δ 9.03 (br s, 2), 7.88 (d, 1), 7.3–6.6 (m, 2), 3.4–3.0 (m, 2), 3.0–2.75 (m, 2), 2.17–1.67 (m, 4).

Anal. Calcd for $C_{13}H_{13}NO_2$: C, 69.09; H, 6.85. Found: C, 69.13; H, 6.77.

Acknowledgment. The authors express their gratitude to the Army Research Office (Durham) for financial support of this work.

Registry No. **4**, 6282-42-4; **5**, 31456-98-1; **6a**, 75934-00-8; **6b**, 75934-01-9; **7**, 75934-02-0; **8**, 75934-03-1; **9**, 63667-83-4; **10**, 75934-04-2; **11**, 75934-05-3; **12**, 75961-46-5; **12** phthalimide derivative, 75934-06-4; **13**, 75934-07-5; **14**, 75934-08-6; **15**, 75948-75-3; **16**, 31457-16-6; **17**, 75934-09-7; **18**, 4044-54-6; **19**, 75934-10-0; **20**, 635-46-1; **21**, 75934-11-1; **21** mesylate, 75934-12-2; **21** phthalimide derivative, 75934-13-3; **22**, 75934-14-4; **23**, 75934-15-5; **24**, 35700-40-4; **25**, 75934-16-6; **26**, 15861-40-2; **27**, 75934-17-7; **28**, 75948-76-4; **28** phthalimide derivative, 75934-18-8; **29**, 75934-19-9; **30**, 75934-20-2; **31**, 75934-21-3; **32**, 31457-17-7; **33**, 75934-22-4; **34**, 4242-18-6; **35**, 75934-23-5; **36**, 34967-95-8; methyl salicylate, 119-36-8; allyl bromide, 106-95-6; 2-amino-2-methyl-1-propanol, 124-68-5; 1,4-diiodobutane, 628-21-7; (4-iodobutyl)anisole, 75934-24-6; 3-(3-butenyl)anisic acid, 75934-25-7.

Photochemical Reactions of Aromatic Compounds. 35.[1] Photo-Birch Reduction of Arenes with Sodium Borohydride in the Presence of Dicyanobenzene

Masahide Yasuda, Chyongjin Pac,* and Hiroshi Sakurai

The Institute of Scientific and Industrial Research, Osaka University, Suita, Osaka 565, Japan

Received August 13, 1980

Birch-type reduction of phenanthrene, anthracene, naphthalene, and several substituted naphthalenes efficiently occurs upon irradiation of 9:1 acetonitrile–water solutions in the presence of sodium borohydride and *m*- or *p*-dicyanobenzene. The reduction products of phenanthrene and anthracene are the respective 9,10-dihydroarenes, whereas naphthalene, 2,6-dimethylnaphthalene, acenaphthene, and 2-methoxynaphthalene are exclusively photoreduced at C_1 and C_4. With the naphthalenes having alkyl groups on the one ring, the photoreduction gives both the 1,4- and 5,8-dihydronaphthalenes. The exception is the photoreduction of 1-methoxynaphthalene that gives both the 1,2- and 1,4-dihydronaphthalenes. The reaction mechanism has been discussed in terms of electron transfer from the excited singlet state of arenes to the dicyanobenzenes followed by the nucleophilic attack of borohydride anion on the cation radicals of the arenes.

The Birch reduction, one of the most useful synthetic reactions, has now been firmly established to proceed via anion radicals and dianions of substrates;[2] the electron sources are usually alkaline metals in liquid ammonia or amine solvents. For convenience, however, it is desirable that stable electron sources can be used in usual solvents at room temperature. Photochemical electron-transfer reactions of electron donor–acceptor pairs in polar solvents[3] can provide a convenient, elegant method for generation of anion radicals; photoreduction of arenes by amines has been investigated.[4] However, yields of reduction products are usually low because of formation of adducts with amines.[4,5] Sodium borohydride[4,6-8] and sodium sulfite[8] are other candidates as reductants for photoreduction of arenes, though the yields are again low.

Scheme I

$$\mathrm{ArH} + \mathrm{H^-(BH_4^-)} + \mathrm{H^+(H_2O)} \xrightarrow[\mathrm{CH_3CN\text{-}H_2O}]{h\nu/\mathrm{DCNB}} \mathrm{H\text{-}ArH\text{-}H}$$

$$\mathrm{ArH} \xrightarrow{h\nu} {}^1\mathrm{ArH}^* \xrightarrow[\mathrm{DCNB\ DCNB^{-\cdot}}]{} {}^-\mathrm{ArH\text{-}H} \xrightarrow{\mathrm{H^+}} \mathrm{H\text{-}ArH\text{-}H}$$

$$\cdot\mathrm{ArH\text{-}H} \xrightarrow[\mathrm{DCNB\ DCNB}]{} {}^-\mathrm{ArH\text{-}H} \xrightarrow{\mathrm{H^+}} \mathrm{H\text{-}ArH\text{-}H}$$

$$2\cdot\mathrm{ArH\text{-}H} \longrightarrow \mathrm{H\text{-}ArH\text{-}H} + \mathrm{ArH}$$

In a previous paper,[9] we reported that efficient photoreduction of some aromatic hydrocarbons can be accomplished by the use of sodium borohydride and *p*-di-

(1) Part 34: Yasuda, M.; Pac, C; Sakurai, H. *J. Chem. Soc., Perkin Trans. 1*, in press.
(2) Birch, A. J. *Q. Rev., Chem. Soc.* **1950**, *4*, 69. Holy, A. *J. Chem. Rev.* **1974**, *74*, 244.
(3) Mataga, N.; Ottolenghi, M. In "Molecular Associations"; Foster, R., Ed.; Academic Press: London, 1979; Vol. 1, p 1. Froehlich, P.; Wehry, E. L. In "Modern Fluorescence Spectroscopy"; Wehry, E. L., Ed.; Plenum: New York, 1976; Vol. 2, p 381.
(4) Barltrop, J. A. *Pure Appl. Chem.* **1973**, *33*, 179.
(5) Pac, C.; Sakurai, H. *Tetrahedron Lett.* **1969**, 3829.
(6) Yonemitsu, O.; Cerutti, P.; Witkop, B. *J. Am. Chem. Soc.* **1966**, *88*, 3941. Balle, G.; Cerutti, P.; Witkop, B. *Ibid.* **1966**, *88*, 3946.
(7) Paskovich, D. H.; Reddoch, A. H.; Williams, D. F. *J. Chem. Soc., Chem. Commun.* **1972**, 1195.
(8) Tokuyama T.; Senoh, S.; Sakan, T.; Brown, K. S. Jr.; Witkop, B. *J. Am. Chem. Soc.* **1967**, *89*, 1017.
(9) Mizuno, K.; Okamoto, H.; Pac, C.; Sakurai, H. *J. Chem. Soc., Chem. Commun.* **1975**, 839.

0022-3263/81/1946-0788$01.00/0

Table I. Photo-Birch Reduction of Arenes by $NaBH_4$ and DCNB[a]

arenes	DCNB	irradn time, h	products (isomer ratios)	yield,[b] %
phenanthrene (1a)	*p*-DCNB	8	**2a**	71
anthracene (1b)	*p*-DCNB	7	**2b**	70
naphthalene (1c)	*p*-DCNB	18	**2c**	50
	m-DCNB	16	**2c**	59
1-methylnaphthalene (1d)	*m*-DCNB	6	**2d**, **2d'** (1.3:1)	75
2-methylnaphthalene (1e)	*p*-DCNB	5	**2e**, **2e'** (2.0:1)	66
	m-DCNB	5	**2e**, **2e'** (2.0:1)	70
2-acetonaphthone ethylene glycol acetal (1f)	*m*-DCNB	7	**2f**, **2f'** (1:1.5)	85
2,3-dimethylnaphthalene (1g)	*m*-DCNB	4	**2g**, **2g'** (5:1)	88
2,6-dimethylnaphthalene (1h)	*m*-DCNB	7	**2h**	81
acenaphthene (1i)	*m*-DCNB	8	**2i**	76
1-methoxynaphthalene (1j)	*m*-DCNB	7	**2j**, **2j'** (1:1)	88
2-methoxynaphthalene (1k)	*p*-DCNB	15	**2k**	35
			3k	21 (84)[c]
	m-DCNB	17	**2k**	81

[a] For 100 mL of 9:1 acetonitrile–water solutions containing arenes (10 mmol), DCNB (2.5 mmol) and $NaBH_4$ (100 mmol). [b] Isolated yields at 100% conversion. [c] Based on *p*-DCNB used.

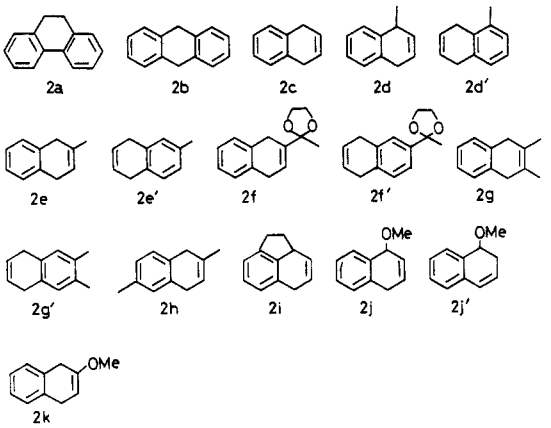
cyanobenzene (*p*-DCNB). Moreover, it was confirmed that the coexistence of both *p*-DCNB and water is indispensable for the efficient photoreduction. The key mechanistic reaction pathways have been explained in terms of electron transfer from the excited singlet state of arenes to *p*-DCNB followed by the nucleophilic attack of borohydride anion on the cation radical of arenes as is shown in Scheme I. This mechanism is very similar to that for the direct photocyanation of arenes with sodium cyanide in the presence of electron acceptors.[1,10] This photoreduction is, therefore, entirely different in mechanism from any Birch-type reductions reported so far. The present paper deals with details of the photoreduction of phenanthrene, anthracene, naphthalene, and the eight substituted naphthalenes and with qualitative aspects of the reaction mechanism that support Scheme I.

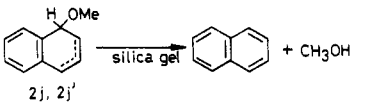
Results and Discussion

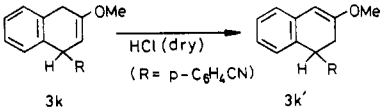
Reaction Products. Irradiation was carried out for 9:1 acetonitrile–water solutions in Pyrex vessels with a high-pressure mercury lamp at room temperature. The results are summarized in Table I. The photoreduction of phenanthrene and anthracene gave the respective 9,10-dihydro compounds **2a** and **2b** (Chart I) as the exclusive products. It was confirmed by GLC and NMR that the 1,4-dihydronaphthalenes are selectively formed by the photoreduction of naphthalene, 2,6-dimethylnaphthalene, acenaphthene, and 2-methoxynaphthalene. The reduction products are known compounds[11] and were unambiguously identified by the physical properties as well as direct comparison with authentic samples which were prepared by the usual Birch reduction.[11]

On the other hand, the photoreduction of the other naphthalenes gave both the 1,4- and 5,8-dihydronaphthalenes except in the case of 1-methoxynaphthalene where the naphthalene ring was photoreduced at both the C_1–C_2 and C_1–C_4 positions. Although the two isomeric products of each pair were not separated, the structures of the products were easily determined by first-order analyses of the NMR spectra of each mixture as well as spin-decoupling experiments. Catalytic hydrogenation of each product mixture from **1d**, **1e**, **1f**, or **1g** over 5% Pd/C gave again a mixture of the corresponding isomeric tetralins, whereas only 1-methoxytetralin was formed upon hydrogenation of the photoproduct from **1j**. When a mixture of **2j** and **2j'** was treated with silica gel, naphthalene was quantitatively obtained. In all the cases, *m*- or *p*-DCNB could not be recovered after the completion of the photoreduction. The nitriles may be consumed by hydrolysis and/or reduction, though no attempts were made for detection and isolation of products arising from the nitriles. However, cyanophenylated product **3k** was formed in substantial amounts by the photoreduction of **1k** with *p*-DCNB. This compound readily isomerized to **3k** upon addition of a catalytic amount of dry hydrogen chloride to a carbon tetrachloride solution, as shown by NMR. Attempts for the photoreduction with 1-cyanonaphthalene and 9-cyanophenanthrene in place of *m*- or *p*-DCNB failed since the aromatic nitriles were readily photoreduced by sodium borohydride.[4]

Chart I







Deuteration Experiments. In a previous communication,[7] we reported that the photoreduction of **1a** and **1b**

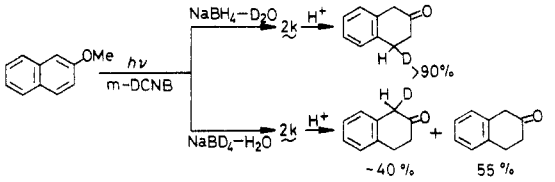
(10) Mizuno, K.; Pac, C.; Sakurai, H. *J. Chem. Soc., Chem. Commun.* **1975**, 553.
(11) Rabideau, P. W.; Harvey, R. G. *J. Org. Chem.* **1970**, *35*, 25. Bass, K. C. "Organic Syntheses"; Wiley: New York, 1973; Collect. Vol. V, p 398. Huckel, W.; Schlee, H. *Chem. Ber.* **1955**, *88*, 346. Arich, G.; Volpe, S. *J. Gas Chromatogr.* **1968**, *6*, 384. Sakane, K; Oda, S.; Haruki, E.; Otuji, Y.; Imoto, E. *Bull. Chem. Soc. Jpn.* **1974**, *47*, 2515. Birch, A. J. *J. Chem. Soc.* **1944**, 430.

Table II. Deuterium Isotopic Distribution in the Photo-Birch Reduction of 2,6-Dimethylnaphthalene (1h) Using Deuteration Reagents[a,b]

reagents	2h	2h-d_1	2h-d_2	2h-d_3
$NaBH_4$-D_2O	8	76	13	3
$NaBD_4$-H_2O	8	57	28	7
$NaBD_4$-D_2O	~1	13	52	34

[a] For 6 mL of acetonitrile-water or deuterium oxide solutions containing 0.4 mmol of the arene, 0.1 mmol of *m*-DCNB, and 2 mmol of $NaBH_4$ or $NaBD_4$. [b] Values at 100% conversion.

Scheme II



in 9:1 CH_3CN–D_2O affords mainly the monodeuterated compounds (70–80%). Therefore, it is concluded that one proton from water is involved in the reduction pathway. However, it is left undetermined whether or not sodium borohydride acts as the hydride source as is shown in Scheme I.

Table II lists the deuterium isotope distributions in the photoreduction products of **1h** with the following couples of deuteration reagents: $NaBH_4$–D_2O, $NaBD_4$–H_2O, $NaBD_4$–D_2O. The values were computed from the relative intensities at *m/e* 158, 159, 160, and 161 in the mass spectra. It is notable that the photoreduction with the $NaBD_4$–H_2O couple resulted in a lower content of **2h**-d_1 but a higher content of **2h**-d_2 compared with that for the $NaBH_4$–D_2O couple (Scheme II).

When **1k** was photoreduced with the $NaBH_4$–D_2O couple, **2k**-d_1 was obtained in >90% of the total **2k** as shown by the mass spectra. The 2-tetralone obtained by hydrolysis of the **2k** with dilute hydrochloric acid was analyzed by NMR; the area ratio of C_1-, C_3-, and C_4-methylene protons of the 2-tetralone at δ 3.46 (s), 2.4 (m), and 3.0 (m) was 18:17:9. Therefore, >90% of the deuterium atoms incorporated were determined to be located at C_4. On the other hand, the photoreduction of **1k** with the $NaBD_4$–H_2O couple gave **2k**, **2k**-d_1, and **2k**-d_2 in a ratio of 55:40:5. Similarly, the reduction products were hydrolyzed, and the NMR spectrum of the 2-tetralone so formed was taken. The area ratio of the C_1-, C_3-, and C_4-methylene protons was 21:25:26, thus indicating that deuterium incorporation mostly occurs at C_1.

Photoreduction with $NaBH_3CN$ or $NaBH(OCH_3)_3$. In order to see the relationships of the nucleophilicity of the reductants with regioselectivity, we carried out the photoreduction of **1d**, **1e**, and **1g** with $NaBH_3CN$ or $NaBH(OCH_3)_3$. The product ratios were determined by GLC and NMR. As is shown in Table III, the photoreduction is more selective with $NaBH_3CN$ than that with $NaBH_4$, while $NaBH(OCH_3)_3$ is a less selective reductant.

Mechanism. All the results obtained support the mechanism shown in Scheme I. An interaction of the excited singlet arenes (^{1}ArH*) with *m*- or *p*-DCNB in the ground state is responsible for the primary process of the photo-Birch reduction, since the fluorescence of some arenes is quenched by *p*-DCNB at diffusion-controlled rates in acetonitrile[12] and since the photoreactions in the absence of *m*- or *p*-DCNB are extremely slow. Table IV lists the calculated free-energy changes (ΔG) for the electron-transfer process from the excited singlet state of some arenes to *m*- or *p*-DCNB found by using eq 1;[13] the

$$\Delta G = 23.06[E(\mathrm{ArH/ArH^{+}\cdot}) - E(\mathrm{DCNB/DCNB^{-}\cdot}) - e^2/\epsilon a] - E_{0\text{-}0}(^1\mathrm{ArH^*}) \quad (1)$$

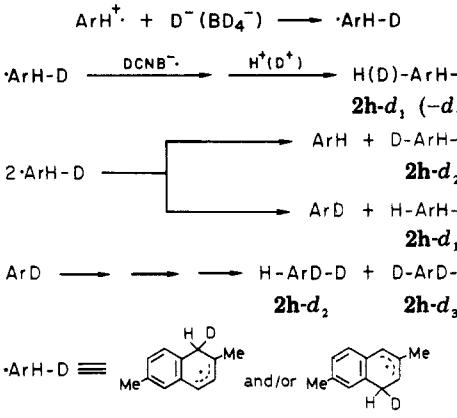
calculated values are substantially negative. Therefore, it is strongly suggested that electron transfer from ^{1}ArH* to the DCNB occurs to give $ArH^{+}\cdot$ and $DCNB^{-}\cdot$.

Table III. Dependence of the Ratios of 1,4- to 5,8-Dihydronaphthalenes on Reductants[a]

reductants	2d/2d′	2e/2e′	2g/2g′
$NaBH_3CN$	4.4	6.0	7.0
$NaBH_4$	1.3	2.0	5.0
$NaBH(OCH_3)_3$		2.0	2.2

[a] For 50 mL of 9:1 acetonitrile-water solutions containing 5 mmol of the arenes, 1.25 mmol of *m*-DCNB, and 25 mmol of reductants.

Scheme III



The nucleophilic attack of borohydride anion on $ArH^{+}\cdot$ is demonstrated by the fact that the photoreduction of **1h** with the $NaBD_4$–H_2O couple gave predominantly **2h**-d_1 along with a considerable amount of **2h**-d_2 (Scheme III). Deuterated radicals, ·ArH–D, formed by deuteride transfer from BD_4^- to $ArH^{+}\cdot$ may be reduced by $DCNB^{-}\cdot$ to give **2h**-d_1 or may disproportionate to give either **2h**-d_1 or **2h**-d_2. The occurrence of disproportionation is further indicated by the formation of **2h**-d_1 from the photoreduction with the $NaBD_4$–D_2O couple.

However, it should be pointed out that the distribution of deuterated products in Table II reveals only a qualitative figure for possible mechanistic pathways, since H–D exchange between $NaBD_4$ and H_2O or $NaBH_4$ and D_2O has been known to occur.[14] The H–D exchange appears to be suggested by the formation of **2h**-d_2 with the $NaBH_4$–D_2O couple and of **2h** with the $NaBD_4$–H_2O couple. Moreover, the reduction products for the mass analyses were isolated after the complete disappearance of the starting arene.

The photoreduction product of **1k** with the $NaBD_4$–H_2O couple indicates that borohydride anion selectively attacks at C_1 of the cation radical of **1k** where the highest positive charge might develop. In the case of **1j**, therefore, the nucleophilic attack of borohydride anion would selectively occur on the methoxylated ring (perhaps C_1) of the cation radical. On the other hand, the positive charge of the cation radicals of the methylated naphthalenes develops

(12) Pac, C.; Nakasone, A.; Sakurai, H. *J. Am. Chem. Soc.* **1977**, *99*, 5806.

(13) Rehm, D.; Weller, A. *Isr. J. Chem.* **1970**, *8*, 259.

(14) Cornforth, R. H. *Tetrahedron* **1970**, *26*, 4635.

Table IV. Calculated Free-Energy Changes for Electron Transfer from Excited Singlet Arenes to DCNB

arenes	E_s,[a] kcal mol^{-1}	$E_{1/2}^{ox}$,[b] V	ΔG,[c] kcal mol^{-1}		k_q,[d] M^{-1} s^{-1}
			p-DCNB	*m*-DCNB	
phenanthrene	82.9	1.17	−13.2	−8.6	2.0×10^{10}
naphthalene	92.0	1.22	−21.1	−16.5	1.2×10^{10}
1-methylnaphthalene	90.0	1.22	−19.1	−14.5	
2-methylnaphthalene	89.5	1.20	−19.1	−14.5	
2,3-dimethylnaphthalene	89.3	0.99	−23.7	−19.1	
1-methoxynaphthalene	89.3	1.01	−22.0	−17.4	

[a] Excitation energy of the excited singlet arenes abstracted from: Murov, S. L. "Handbook of Photochemistry"; Marcel Dekker: New York, 1973. [b] Oxidation potentials of the arenes in acetonitrile vs. Ag/Ag$^+$. [c] Calculated by eq 1; the Coulombic term ($e^2/\epsilon a$) is estimated to be 1.3 kcal mol^{-1}. E(DCNB/DCNB$^{-}\cdot$) = −1.91 V for *p*-DCNB and −2.11 V for *m*-DCNB in acetonitrile vs. Ag/Ag$^+$. [d] In acetonitrile.[12]

Table V. ^{1}H NMR Spectra of Dihydroarenes

dihydro-arenes	mp or bp (mm), °C	NMR, δ
2a	183–184 (25)	2.76 (s, 4 H), 7.0–7.3 (m, 6 H), 7.4–7.6 (m, 2 H)
2b	108–110	3.95 (s, 4 H), 7.20 (br s, 8 H)
2c	53–54 (6–7)	3.26 (br s, 4 H), 5.73 (br s, 2 H), 6.89 (br s, 4 H)
2d		1.24 (d, 3 H), 3.34 (m, 3 H), 5.76 (br s, 2 H), 6.8–7.2 (m, 4 H)
2d′		2.10 (s, 3 H), 3.34 (m, 4 H), 5.76 (br s, 2 H), 6.8–6.9 (m, 3 H)
2e		1.74 (s, 3 H), 3.34 (br s, 4 H), 5.48 (br s, 1 H), 6.94 (s, 4 H)
2e′		2.22 (s, 3 H), 3.22 (br s, 4 H), 5.78 (br s, 2 H), 6.77 (d, 1 H), 6.94 (br s, 2 H)
2f		1.44 (s, 3 H), 3.38 (br s, 4 H), 3.68–3.96 (m, 4 H), 6.00 (br s, 1 H), 7.06 (m, 4 H)
2f′		1.52 (s, 3 H), 3.38 (br s, 4 H), 3.68–3.96 (m, 4 H), 5.86 (br s, 2 H), 7.06 (m, 3 H)
2g		1.69 (s, 6 H), 3.21 (br s, 4 H), 6.86 (br s, 4 H)
2g′		2.13 (s, 6 H), 3.21 (br s, 4 H), 5.66 (br s, 2 H), 6.63 (br s, 2 H)
2h	61.5–62.5	1.78 (s, 3 H), 2.24 (s, 3 H), 3.20 (br s, 4 H), 5.52 (br s, 1 H), 6.82 (br s, 3 H)
2i	57 (0.1)	1.56–1.88 (m, 2 H), 2.32–2.56 (m, 2 H), 3.30 (br s, 3 H), 5.96 (br s, 2 H), 6.8–7.0 (m, 3 H)
2j		3.24 (s, 3 H), 3.36 (m, 2 H), 5.04 (dd, 1 H), 5.8–5.9 (m, 1 H), 6.04–6.28 (m, 1 H), 6.92–7.20 (m, 4 H)
2j′		2.44–2.56 (m, 1 H), 3.00 (s, 3 H), 4.22 (t, 1 H), 5.92–6.00 (m, 1 H), 6.38 (br d, 1 H), 6.92–7.20 (m, 3 H), 7.30–7.40 (m, 1 H)
2k	69 (0.1)	3.26–3.40 (m, 4 H), 3.48 (s, 3 H), 4.64 (br s, 1 H), 6.98 (s, 4 H)

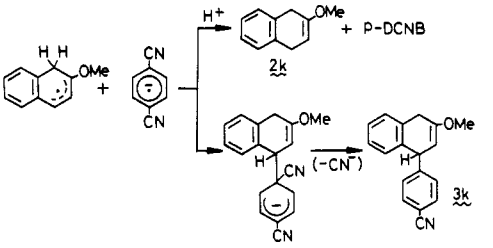
[a] For carbon tetrachloride solutions with tetramethylsilane as internal standard.

on the unsubstituted ring as well, but to a lesser extent.[15] Therefore, the nucleophlic attack of borohydride anion can occur on either the substituted or unsubstituted ring of the cation radicals, depending on the degree of development of the positive charge on the respective rings; both the 1,4- and 5,8-dihydronaphthalenes are thus formed. This is in line with the photocyanation of methylated naphthalenes with sodium cyanide and an electron acceptor.[1,8] Moreover, reactivities of the nucleophiles toward cation radicals may also affect product distribution. The weak nucleophile $NaBH_3CN$ undergoes more selectively the reduction on the substituted ring of the naphthalenes than the stronger nucleophiles $NaBH_4$ and $NaBH(OCH_3)_3$.

The formation of **3k** can be easily interpreted in terms of a coupling reaction between *p*-DCNB$^{-}\cdot$ and ·ArH–H (Scheme IV). Similar reactions have been reported for photochemical electron-transfer systems involving *p*-DCNB as an electron acceptor.[12,16] The coupling reaction which may compete with the reduction of ·ArH–H by *p*-DCNB$^{-}\cdot$ can be readily avoided by the use of *m*-DCNB as the electron acceptor. Since the reduction potential of *m*-DCNB is more negative than that of *p*-DCNB, the reduction of ·ArH–H by *m*-DCNB$^{-}\cdot$ would predominate over other reactions; the chemical yields of the reduction products were thus improved.

In conclusion, the photo-Birch reduction using borohydride anion and *m*-DCNB is relatively efficient and will

Scheme IV



be widely applicable to reduction of arenes which are electron donors in nature. Moreover, no care is required to avoid the formation of higher reduction products, e.g., tetralins and perhydro compounds. It is of interest to note that the Birch reduction via cation radicals is without precedent.

Experimental Section

Melting points were determined with a Yanagimoto hot stage and are uncorrected. ^{1}H NMR spectra were measured on a JEOL JNM-PS-100 spectrometer at 100 MHz or on a JEOL JNM-60 spectrometer at 60 MHz with tetramethyl silane as an internal standard. IR spectra were taken on a Shimadzu IR-400 spectrophotometer and mass spectra on a Hitachi RMU-6E. GLC analyses were carried out on a Shimadzu GC-3BF dual column instrument with flame-ionization detectors and by using 75 cm × 4 mm columns of 5% Ucon oil LB-550X on Celite 545 and 10% PEG-20M on Shimalite W. Oxidation potentials of arenes and reduction potentials of *m*- and *p*-DCNB were measured for N_2-saturated acetonitrile solutions (1×10^{-3} M) vs. an Ag/Ag$^+$ reference electrode by cyclic voltammetry. Tetraethylammonium tetrafluoroborate (0.1 M) was used as the supporting electrolyte.

(15) Yoshida, K.; Nagase, S. *J. Am. Chem. Soc.* **1979**, *101*, 4268.
(16) Tsujimoto, Y.; Hayashi, M.; Nishimura, Y.; Miyamoto, T.; Odaira, Y. *Chem. Lett.* **1977**, 677. Ohashi, M.; Miyake, K.; Tsujimoto, K. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 1683.

Table VI. Mass Spectra of Deuterated 2h[a]

deuteration reagents	relative intensities at m/e			
	158	159	160	161
$NaBH_4$-D_2O	27.0	100	28.5	5.5
$NaBD_4$-H_2O	30.8	100	56.6	16.8
$NaBD_4$-D_2O	11.3	40.3	100	70.2

[a] Mass spectrum of **2h**: *m/e* 156 (7.5), 157 (15.7), 158 (100), 159 (12.2).

The scan speed was 0.2 V s^{-1}, and temperature was kept at 23 ± 0.1 °C. Details were described separately.[17]

Spectral grade acetonitrile was used without further purification. All the arenes, *p*- and *m*-dicyanobenzenes, $NaBH_4$, $NaBD_4$, and $NaBH_3CN$ were used as received (Tokyo Kasei and Nakarai Chemicals). $NaBH(OCH_3)_3$ was prepared according to the known method.[18]

Photoreduction of Arenes. General Procedure. To 10 mL of an aqueous solution of $NaBH_4$ (100 mmol) in a Pyrex vessel was added 90 mL of an acetonitrile solution containing an arene (10 mmol) and *m*- or *p*-DCNB (2.5 mmol). The solution which was not homogeneous was bubbled with N_2 for 20 min and then irradiated with an Eikosha PIH-300 high-pressure mercury lamp under cooling with water. The progress of the reaction was followed by GLC. After the arenes had been completely consumed, 50 mL of brine and then 500 mL of diethyl ether were added to the irradiated solution. After vigorous shaking, the ether layer was separated, washed three times with water, dried ($MgSO_4$), and then evaporated. The residue was distilled under reduced pressure or chromatographed on silica gel (Merk, Art 7734, 70–230 mesh) by using hexane or 10–30% benzene in hexane as the eluents; the products were thus isolated. Irradiation time, yields, and product ratios are listed in Table I, and ^1H NMR spectra are summarized in Table V.

2-Methoxy-4-(4-cyanophenyl)-1,4-dihydronaphthalene (3k): mp 76–77 °C; IR (CCl_4) 2220 cm^{-1} (C≡N); mass spectrum, *m/e* 261 (M^+); NMR (CCl_4) δ 3.45–3.53 (br s, 2 H), 3.50 (s, 3 H), 3.66 (br s, 1 H), 6.76 (br s, 1 H), 6.7–7.0 (m, 4 H), 7.0–7.4 (AB q, 4 H).

Anal. Calcd for $C_{18}H_{15}NO$: C, 82.73; H, 5.79; N, 5.36. Found: C, 82.81; H, 5.56; N, 5.48.

Isomerization of 3k to 2-Methoxy-4-(4-cyanophenyl)-3,4-dihydronaphthalene (3k′). To a carbon tetrachloride solution of **3k** (20 mg/0.3 mL) in a NMR tube was added 1 drop of a carbon tetrachloride solution saturated with dry hydrogen chloride. After a while, the NMR spectrum was completely changed to that of **3k′**: NMR (CCl_4) 2.64 (m, 2 H), 3.66 (s, 3 H), 4.16 (t, 1 H), 5.52 (s, 1 H), 6.6–7.15 (m, 4 H), 7.16–7.6 (AB q, 4 H).

Deuteration Experiments with $NaBH_4$–D_2O, $NaBD_4$–H_2O, and $NaBD_4$–D_2O. A 9:1 acetonitrile–water or deuterium oxide solution (6 mL) containing 0.4 mmol of **1h**, 0.1 mmol of *m*-DCNB, and 2 mmol of $NaBH_4$ or $NaBD_4$ was irradiated for 5 h. After the complete disappearance of **1h**, the product was isolated by vacuum distillation and purified by recrystalization from methanol. Each pure product was subjected to mass spectral analyses; relative intensities at *m/e* 158, 159, 160, and 161 are listed in Table VI.

Acknowledgment. This work was supported by a Scientific Research Grant-in-Aid (No. 447067) from the Ministry of Education of Japan.

Registry No. **1a**, 85-01-8; **1b**, 120-12-7; **1c**, 91-20-3; **1d**, 90-12-0; **1e**, 91-57-6; **1f**, 69470-12-8; **1g**, 581-40-8; **1h**, 581-42-0; **1i**, 83-32-9; **1j**, 2216-69-5; **1k**, 93-04-9; **2a**, 776-35-2; **2b**, 613-31-0; **2c**, 612-17-9; **2d**, 21564-70-5; **2d′**, 4373-24-4; **2e**, 2717-43-3; **2e′**, 2717-46-6; **2f**, 75896-19-4; **2f′**, 75896-20-7; **2g**, 21564-72-7; **2g′**, 21564-73-8; **2h**, 21564-74-9; **2h**-d_1, 75908-20-2; **2h**-d_2, 75908-21-3; **2h**-d_3, 75908-22-4; **2i**, 75896-21-8; **2j**, 75896-22-9; **2j′**, 75896-23-0; **2k**, 40815-22-3; **3k**, 74232-83-0; **3k′**, 74232-84-1; $NaBH_4$, 16940-66-2; *m*-DCNB, 626-17-5; *p*-DCNB, 623-26-7.

(17) Majima, T.; Pac, C.; Sakurai, H. *J. Am. Chem. Soc.* **1980**, *102*, 5265.
(18) Brown, H. C.; Schlesinger, H. I.; Sheft, I.; Ritter, D. M. *J. Am. Chem. Soc.* **1953**, *75*, 192.

(β-Lysyloxy)myoinositol Guanidino Glycoside Antibiotics

William J. McGahren,* Bruce A. Hardy, George O. Morton, F. Maurice Lovell, Nancy A. Perkinson, Ronald T. Hargreaves, Donald B. Borders, and George A. Ellestad*

Medical Research Division of American Cyanamid Co., Lederle Laboratories, Pearl River, New York 10965

Received May 22, 1980

A *Nocardia* sp. was found to produce three broad-spectrum antibiotics, two of which exhibit potent antitubercular activity. They are related to the known antibiotic myomycin. The culture also produces the individual β-lysyl oligopeptide side chains as well as the pseudodisaccharide common to all three antibiotics. As a result of the characterization work done, mostly by using ^{13}C NMR spectral data on degradation fragments, a modification of the published structure of myomycin is presented. An unusual sulfated sugar methanolysis fragment is identified by X-ray crystallography.

A *Nocardia* sp. (Lederle culture BM782) yielded crude fermentation extracts which showed broad-spectrum activity against Gram-negative infections in mice. Initial characterization work indicated that the antimicrobial material present was similar to the known antibiotic myomycin.[1] The wild strain of BM782 first selected produced antibiotic material at very low levels in the fermentation broth. Later a mutant[2] was obtained which elaborated three antibiotics, LL-BM782α_{1a}, -α_1, and -α_2, and four related metabolites, LL-BM782β, -γ, -δ, and -ε, in isolable quantities.[3] Compounds LL-BM782α_1 and -α_2 were shown to be very effective in protecting mice infected with *Mycobacterium tuberculosis*.[4]

In common with most basic, water-soluble antibiotics, the LL-BM782 complex can be recovered from fermentation filtrates by extraction on a weak carboxylic acid cation exchanger in the basic cycle. Considerable purification was

(1) (a) U.S. Patent 3 795 688, 1974. (b) French, J. C.; Bartz, Q. R.; Dion, H. W. *J. Antibiot.* **1973**, *26*, 272.
(2) The mutant labeled BM782Ce82 was prepared by Dr. A. Fantini of the Medical Research Division at Pearl River, NY.
(3) The natural products are named in order of their polarity with respect to elution off a weak dextran cation exchanger. LL-BM782ε is the least polar compound.
(4) A detailed account of the biological activities of these materials will be published elsewhere.

0022-3263/81/1946-0792$01.00/0