Anodic Cyanation. Aromatic Nucleophilic Substitution of Monomethyl- and Dimethylnaphthalenes

Kunihisa Yoshida* and Shigeru Nagase

Contribution from the Department of Chemistry, Faculty of Engineering Science, Osaka University, Toyonaka, Osaka 560, Japan. *Received January 22, 1979*

Abstract: Monomethylnaphthalenes and a series of dimethylnaphthalenes were potentiostatically oxidized with a platinum sheet. The anolyte was methanol–sodium cyanide and the reference electrode SCE. Aromatic substitution with cyanide ion occurred preferentially at the free α position for all of the molecules investigated. 1-Methylnaphthalene gave all three possible α-cyanation products, together with a small amount of side-chain methoxylation product. The preferred point of attack was at the para position to the substituent methyl group. 2-Methylnaphthalene afforded mainly the 1 isomer, along with small amounts of three other α-naphthyl-type isomers. Dimethylnaphthalenes, which contain both methyl groups in the β position, all resemble the parent 2-methylnaphthalene in giving predominantly the 1-substituted compounds. Likewise, substrates with the methyl groups in the α position, such as 1,4-, 1,5-, and 1,8-dimethylnaphthalene, give mainly α-substituted products plus smaller amounts of products substituted at a β position vicinal to a methyl group. It is evident that activation of the nuclear positions depends on the substituent action of methyl groups. There appears to be no evidence of any steric interference. A scheme involving initial electron loss from the aromatic compounds, followed by a fast chemical reaction, can well elucidate voltammetric results, coulometric data, and products. Positional reactivities are rationalized in terms of the LUMO electron densities.

Anodic cyanation of organic compounds is expected to provide a promising method for synthesis of nitriles by reason of its positional reactivity, clean reaction products, and mild conditions.[1] As a part of our effort to define the scope and limitations of this electrode process in a polar nucleophilic solvent containing sodium cyanide as both electrolyte and reactant, our attention was directed toward naphthalene derivatives. They have relatively low ionization potentials[2-4] and so readily undergo oxidation by electron transfer,[5] the desired reactants are readily available, and the possible products are not only valuable in themselves but also are useful as general synthetic precursors.

Heretofore, the behavior of methylnaphthalenes in electrophilic substitution reactions has been discussed extensively.[11-21] However, surprisingly little work has been concerned with the aromatic nucleophilic substitution involving cation-radical intermediates, most likely because of the difficulty in finding a suitable reaction system. Application of the powerful one-electron oxidant such as cobalt(III), manganese(III), or lead(IV), causes an electron-transfer reaction involving cation-radical intermediates, which give preferentially side-chain substitution products.[22] The oxidation of methyl substituents in naphthalene to carboxyl by alkaline ferricyanide is a similar reaction which can be well rationalized in terms of electron transfer.[23-25] Another possible example is the oxidation of 1-methylnaphthalene to aldehyde or quinone by ceric ammonium sulfate.[26]

We have recently studied the factors affecting the competition between nuclear and side-chain substitution in cation radicals of alkylbenzenes.[27] The findings suggest that the use of cyanide anion as a strong nucleophile and of an electrochemical technique may overcome the previous inaccessibility of aromatic nucleophilic substitution of methylnaphthalene cation radicals. If this materializes, this reaction would have potential synthetic value since the products could well differ from those given by other types of oxidation. This paper describes the effect of methyl substituents on the substitution pattern of anodic cyanation for naphthalene derivatives from the viewpoint both of mechanism and potential use in synthesis. Prior to this work, the only report of this type of oxidative substitution of methylnaphthalenes is anodic acetoxylation, whose orientation was not determined.[28] The identified monoacetoxylation products are, respectively, 4-acetoxy-1-methylnaphthalene and 1-acetoxy-2-methylnaphthalene. No description of the existence of side-chain substitution products has been given.

Results

Oxidations were performed potentiostatically in a three-compartment cell with a platinum anode at room temperature. The reference electrode was an SCE. The anolyte and catholyte were methanol–0.4 M sodium cyanide. The desirable reaction requires a net two-electron process in agreement with the voltammetry and coulometry in cases with high yields of substitution products. After the theoretically calculated amount of charge had passed, the electrolyte was extracted with ether, evaporated, and analyzed by GLC. *Caution!* This operation should be conducted in a hood because some hydrogen cyanide may be evaporated with solvent methanol.

The products reported in Table I were isolated by preparative GLC. They were identified by standard spectroscopic and GLC techniques and by comparison with the authentic samples prepared by other routes.

Monomethyl- and dimethylnaphthalenes were all converted to nuclear cyanation products under these reaction conditions. It can see from Table I that exhaustive oxidation eventually converts any methylnaphthalenes to the corresponding methylnaphthonitriles, which are resistant to further oxidation. The yield maximally rose to 95%. The coulometry showed two electrons lost per organic molecule. GLC gave no evidence for side-chain cyanation. In some cases, small amounts of methoxylation products were produced as byproducts.

1-Methylnaphthalene afforded all possible α-cyanation products, 4-, 8-, and 5-cyano isomers in an approximate ratio of 7:5:1, together with a small amount of side-chain methoxylation product. 2-Methylnaphthalene resulted in the formation of all four possible α isomers with 2-methyl-1-naphthonitrile predominating.

For the above-mentioned monomethylnaphthalenes though, all seven α- and β-substituted products could be produced in principle. In order to diminish all possible isomeric products in this synthesis, the action of this electrode process on the dimethylnaphthalenes has been investigated since, for naphthalenes possessing a C_2 axis of symmetry, maximally three isomers can be formed.

Compounds which contain both methyl groups in α position produced α-substituted derivatives, together with smaller amounts of the products substituted at the β position vicinal to a methyl group. Some methoxylation products were also obtained. Substrates with the methyl groups in the β position all resemble the parent 2-methylnaphthalene in giving predominantly 1-substituted products.

Cyclic voltammograms were recorded for each compound.

0002-7863/79/1501-4268$01.00/0

Table I. Anodic Cyanation of Naphthalenes. Voltammetric Data and Products

naphthalene	E_p,[a] V	E,[b] V	$E_{1/2}$,[c] V	Ip,[h] eV	n,[l] faradays/mol	product	CE,[m] %
unsubstituted	1.68	1.7	1.34[d,f]	8.12[i]	2.4	naphthalene-1-carbonitrile	74
			1.54[e]	8.15[j]		naphthalene-2-carbonitrile	6
			1.72[g]				
1-methyl	1.54	1.5	1.24[d,f]	7.95[i,j]	2.3	4-methylnaphthalene-1-carbonitrile	34
			1.43[e]			5-methylnaphthalene-1-carbonitrile	5
			1.53[g]			8-methylnaphthalene-1-carbonitrile	23
						1-methoxymethylnaphthalene	0.5
2-methyl	1.58	1.4-1.5	1.22[d,f]	7.93[j]	2.4	2-methylnaphthalene-1-carbonitrile	60
			1.45[e]	7.96[i]		3-methylnaphthalene-1-carbonitrile	4
			1.55[g]			6-methylnaphthalene-1-carbonitrile	6
						7-methylnaphthalene-1-carbonitrile	7
1,4-dimethyl	1.44	1.8			2.0	1,4-dimethylnaphthalene-2-carbonitrile	14
	1.75					5,8-dimethylnaphthalene-2-carbonitrile	trace
						5,8-dimethylnaphthalene-1-carbonitrile	27
						1-methoxymethyl-4-methylnaphthalene	2
1,5-dimethyl	1.46	1.8			2.0	1,5-dimethylnaphthalene-2-carbonitrile	3
	1.81					4,8-dimethylnaphthalene-1-carbonitrile	73
1,8-dimethyl	1.41	1.7			1.8	1,8-dimethylnaphthalene-2-carbonitrile	14
	1.74					4,5-dimethylnaphthalene-1-carbonitrile	56
						1-methoxymethyl-8-methylnaphthalene	trace
acenaphthene	1.36	1.45-1.65	1.21[e]	7.66[k]	2.0	acenaphthene-3-carbonitrile	9
	1.49		1.36[g]			acenaphthene-5-carbonitrile	36
	1.67					5-methoxyacenaphthene	3
						1-methoxyacenaphthene	7
						acenaphthylene	small amount
2,3-dimethyl	1.49	1.7	1.08[d,f]		1.9	2,3-dimethylnaphthalene-1-carbonitrile	60
	1.98		1.35[e]			6,7-dimethylnaphthalene-1-carbonitrile	16
2,6-dimethyl	1.47	1.6	1.08[f]		2.1	2,6-dimethylnaphthalene-1-carbonitrile	76
	1.91		1.36[e]			3,7-dimethylnaphthalene-1-carbonitrile	16
2,7-dimethyl	1.52	1.8	1.12[f]		2.1	2,7-dimethylnaphthalene-1-carbonitrile	69
	1.99					3,6-dimethylnaphthalene-1-carbonitrile	20
						3,6-dimethylnaphthalene-2-carbonitrile	6

[a] Peak potential from cyclic voltammetry; Pt anode, CH_3OH, 0.4 M NaCN, SCE reference. Scan rate is 0.1 V/s. Substrate concentration is 2×10^{-2} M. [b] Potential for preparative electrolysis. [c] Half-wave potential; $Ag|Ag^+$ vs. SCE = +0.302 V. [d] Vs. $Ag|Ag^+$.[7] [e] Vs. SCE.[8] [f] Vs. $Ag|Ag^+$.[9] [g] Vs. $Ag|Ag^+$.[10] [h] Ionization potential. [i] Reference 8. [j] Reference 2. [k] Reference 3. [l] Preparative-scale coulometry. [m] Current efficiency.

The E_P values are in Table I. The current is proportional to naphthalene concentration. E_P and $i_P/V^{1/2}$ change with scan rate, and cathodic waves on reversal are absent in all cases. The second oxidation peaks were due to the oxidation of the products.

Discussion

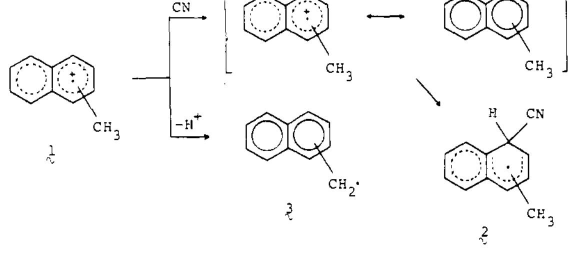
As expected, most of the methylnaphthalenes do not give side-chain substitution products but form naphthonitriles by aromatic substitution. The resultant carbonitriles are not only meaningful substrates in themselves like the photosensitizer but also are synthetic intermediates for the preparation of, e.g., naphthoic acids.[29-33] Naphthonitriles are, by way of several stages, usually obtained from aryl halides and cuprous cyanide in aprotic solvents under rather severe reaction conditions[11,12,14,34-36] (see also the preparation of reference compounds in the Experimental Section). The isolation of nitriles from such reaction mixtures is usually laborious and lengthy.

Mechanism. The nuclear cyanation is formally a 2-equiv change. Controlled potential coulometric data support this experimentally. The voltammetric characteristics indicate that oxidation is initiated by electron transfer from the substrate molecule, followed by a fast chemical reaction. A mechanism involving a cation-radical intermediate would be reasonable.

The ionization potential of the methyl-substituted naphthalenes is relatively low,[2-4] and the existence of their cation radicals has clearly been recognized in mass spectrometry[37-40] and studied in solution by ESR[41,42] and optical spectroscopy.[43] The theoretical procedures to analyze data are now well developed. Intervention of the cation radicals has also been invoked to account for the products obtained from the reaction by means of metal oxidants.[22]

Earlier electrochemical studies of the methyl-substituted naphthalenes have been concerned with the effects of structure on $E_{1/2}$, i.e., the ease of oxidation.[7-9] Table I shows cyclic voltammetry peaks in this work. A major problem with the reaction medium is the inability to obtain thermodynamically significant oxidation potentials because the electron-transfer process is not reversible. The peak potential was a function of sweep rate; accordingly, all of the peak potentials were measured using a fixed sweep rate in order to obtain comparable correlations.

Scheme I



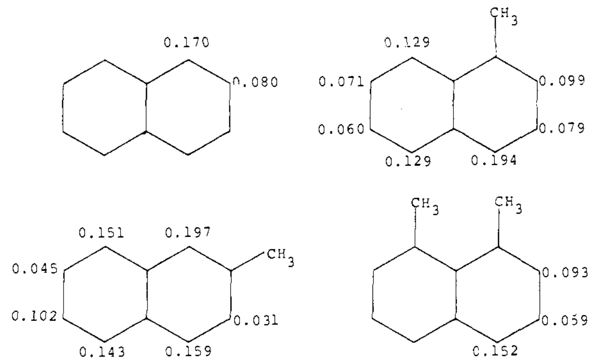


Figure 1. LUMO electron densities of the naphthalene cation radicals calculated by the INDO-UHF method.

A mechanism presented in Scheme I would therefore be reasonable to account for the anodic substitution of methylnaphthalenes. This mechanism involves two competitive pathways. The relevant cation radical **1** is highly nucleophile selective and preferentially combines with a powerful nucleophile, CN^-, to produce the radical **2**. This bond-forming step will be discussed later in more detail using MO calculations. The radical **2** undergoes further anodic oxidation and successive proton release, leading to the aromatic cyanation products. The cation radical **1** can also lose a proton to afford the usual benzylic intermediate **3**, which should eventually give rise to side-chain oxidation products.

The above parallel mechanism is what we previously proposed for the anodic oxidation of alkylbenzenes and is closely related to those proposed for the oxidation of toluene by oxidizing agents such as ceric ammonium nitrite,[44] cobaltic acetate,[22] iron perchlorate,[45] manganic acetate,[46] or peroxydisulfate.[47-49] We demonstrated that the factors governing the competition between nuclear and side-chain substitution in alkyl aromatic compounds were ascribable to reactivities of the cation radicals themselves (viz., both the degree of positive charge on the aromatic carbon atoms in the cation radicals[27c] and the relative stability of initially formed cation radical and benzylic radical produced by deprotonation[27a]) as well as the nucleophilicity of attacking agents. Almost simultaneously with our previous publication, Ledwith and Russell arrived at an analogous conclusion concerning the nuclear chlorination of aromatics using peroxydisulfate as initiator.[47b] The interpretation in the latter case has, however, been challenged mechanistically.[50]

Orientation. Positional reactivities in these nucleophilic substitution reactions agree fairly well with those in conventional electrophilic substitutions. The order of reactivity of 1-methylnaphthalene follows the sequence $C_4 > C_8 > C_5$, while that in the 2-methyl derivative has been found to be $C_1 \gg C_8 \simeq C_5 > C_4$. In nitration of 1-methylnaphthalene, a reactivity sequence of nuclear positions is $C_4 > C_8 \simeq C_5$.[19] Likewise, a reactivity order in electrophilic substitution of 2-methylnaphthalene generally follows the sequence $C_1 \gg C_8 > C_4 > C_5$.[15]

1,4-, 1,5-, and 1,8-dimethylnaphthalene give mainly α-substituted products as well as small amounts of 2-substituted products. The appearance of 2-cyano derivatives has shown that the β position adjacent to the α-methyl group is also activated, though less so than the α positions.

For 1,4-dimethylnaphthalene the 5-substituted derivative was the most abundant product. This appears to be the first instance of nuclear substitution at the 5 (peri) position of this hydrocarbon.[51] This compound is usually subject to massive steric hindrance at the peri position with respect to electrophilic substitutions.[53,54]

It is of interest to compare the isomer distribution of 1,8-dimethylnaphthalene with that of the related acenaphthene, since these two hydrocarbons form a pair in which the steric and electronic effects of the alkyl substituents are expected to fall into different sequences. Electronic considerations suggest nucleophilic attack would lead to a mixture of 2- and 4-substituted 1,8-dimethylnaphthalenes or the corresponding 3- and 5-substituted acenaphthene. Molecular dimensions[55,56] suggest that substitution ortho to the ethylene bridge in acenaphthene might not be so sterically hindered as 2 substitution in 1,8-dimethylnaphthalene. The fact of the matter is that the percentage of isomeric products for 1,8-dimethylnaphthelene is similar to that for acenaphthene. Some increase in strain in the transition state for para substitution would be expected in the former hydrocarbon compared with the latter because of interaction with the peri hydrogen and this may partly offset the steric hindrance at the ortho position.

The 1 position of 2,3-, 2,6-, and 2,7-dimethylnaphthalenes is substituted to the greatest extent. This is a naphthalene α position, which is flanked by a methyl group, and which appears to offer considerable steric hindrance to attack by the bulky electrophilic reagents, such as acetylating reagents.[11,12,14] This observation, which is in line with the high reactivity of the peri position in 1,4-dimethylnaphthalene, indicates that the orientation in the present system is governed in terms of electronic activation. There appears to be no evidence of any steric retarding influence.

MO Approach to Nucleophilic Attack of Cyanide Ion on the Cation Radical. The cation radical–cyanide anion combination reaction shown in Scheme I can be conveyed by means of two diabatic wave functions $\Phi_1(Ar^{+}\cdot CN^-)$ and $\Phi_2(Ar^0CN\cdot)$.[57] Before we discuss the positional reactivities, it seems important to mention a characteristic of Φ_1 and Φ_2 states. In all systems of our interest, the Φ_1 state lies only by ~4 eV above Φ_2, as is readily estimated from the ionization potentials of naphthalenes given in Table I and the electron affinity (3.8 eV)[58] of CN^-. How the relative energy levels of Φ_1 and Φ_2 are changed owing to intermolecular interactions was determined by the INDO-UHF method.[59] We observed that, as two molecules approach each other, the Φ_1 state is strongly stabilized, while Φ_2 undergoes a destabilization. For instance, the stabilization of Φ_1 is as large as ~3 eV for all the systems even at an intermolecular distance of 4.0 Å. Furthermore, the Φ_1 state should be more significantly stabilized in polar solvents. Consequently, Φ_1 comes closer to Φ_2 and tends to fall below Φ_2 at a very early stage of molecular approach.

As the energy gap between Φ_1 and Φ_2 decreases, the coupling between the two states, which leads to electron transfer, plays an important role in the shapes of adiabatic potential energy surfaces. Attacking reagents should choose a pathway along which the coupling is large. The coupling arises from an interaction matrix, $\langle \Phi_1 | H | \Phi_2 \rangle$. Under the usual assumption, the interaction matrix is written simply as

$$\langle \psi_1 | F | \psi_2 \rangle \propto C_r{}^1 C_s{}^2 S_{rs}$$

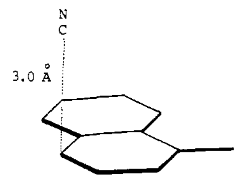
where F is the Fock operator, $C_r{}^1$ is the rth LCAO coefficient of the LUMO, ψ_1, of the isolated aromatic cation radical, $C_s{}^2$ is the sth coefficient of the HOMO, ψ_2, of the isolated CN^-, and S_{rs} is the overlap integral between the rth and sth atomic orbitals. Accordingly, it is expected that nucleophilic attack takes place preferably at the high LUMO electron density $(C_r{}^1)^2$ of the relevant cation radicals. This expectation is clearly shown in Figure 1.

It may be instructive to comment briefly on the utility of LUMO electron densities. The LUMO of 1-methylnaphthalene gives rise to the same electron densities at positions C_8 and C_5, indicating a reactivity order of $C_4 > C_5 = C_8$. However, the absolute values (kilocalories/mole) of $\langle \psi_1 | F | \psi_2 \rangle$ obtained, for instance at an intermolecular distance, 3.0 Å, give a reactivity order of C_4 (12.5) > C_8 (10.1) > C_5 (9.7), which

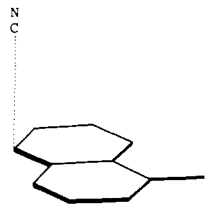
Table II. Melting Points and ^{1}H NMR Data of Cyanation Products

nitrile	mp,[a] °C	^{1}H NMR,[i] δ, ppm (methyl proton)
2-methylnaphthalene-1-carbonitrile	86-86.5 (85-87[b])	2.73
3-methylnaphthalene-1-carbonitrile	52.5-53.5	2.49
4-methylnaphthalene-1-carbonitrile	52-53 (53-54[c])	2.73
5-methylnaphthalene-1-carbonitrile	89.5-91.5	2.72
6-methylnaphthalene-1-carbonitrile	63-64	2.54
7-methylnaphthalene-1-carbonitrile	oil	2.58
8-methylnaphthalene-1-carbonitrile	93.5-94.5	3.08
2,3-dimethylnaphthalene-1-carbonitrile	84.5-85.5 (79.5-80[d])	2.44, 2.64
2,6-dimethylnaphthalene-1-carbonitrile	87-88 (88-89[e])	2.53, 2.73
2,7-dimethylnaphthalene-1-carbonitrile	93-94 (93.5-94[f])	2.53, 2.68
3,6-dimethylnaphthalene-1-carbonitrile	106-107	2.50
3,7-dimethylnaphthalene-1-carbonitrile	64.5-66	2.47, 2.52
4,5-dimethylnaphthalene-1-carbonitrile	111.5-112.5	2.93, 2.96
4,8-dimethylnaphthalene-1-carbonitrile	93.5-95	2.72, 3.07
5,8-dimethylnaphthalene-1-carbonitrile	68-71	2.65, 3.03
6,7-dimethylnaphthalene-1-carbonitrile	75-77 (77-78[d])	2.44, 2.47
1,4-dimethylnaphthalene-2-carbonitrile	107.5-108.5	2.64, 2.85
1,5-dimethylnaphthalene-2-carbonitrile	100.5-101.5	2.68, 2.91
1,8-dimethylnaphthalene-2-carbonitrile	104.5-105.5	2.95, 3.17
3,6-dimethylnaphthalene-2-carbonitrile	150-151.5 (157-158[f])	2.51, 2.63
5,8-dimethylnaphthalene-2-carbonitrile	98-100.5	2.64
acenaphthene-3-carbonitrile	152.5-153.5 (ligroin, 150[g])	3.52, 3.55[j]
acenaphthene-5-carbonitrile	111-112 (ligroin, 111-112[h])	3.45[j]

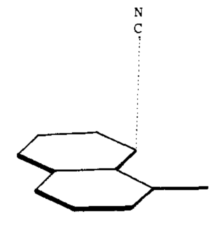
[a] Ethanol solvent except where noted. [b] Reference 62. [c] Reference 34. [d] Reference 11. [e] Reference 12. [f] Reference 14. [g] Reference 81. [h] Reference 35. [i] 60 MHz, $CDCl_3$ solution. [j] Methylene proton.



attack on C_4



attack on C_5



attack on C_8

is in reasonable agreement with the order of experimental reactivities. Thus, care may have to be taken in the simple application of LUMO electron densities to positional reactivity, especially when almost equal electron densities are observed at different positions.

One may argue that the site of attack is also predictable from net charge distributions. However, the highest charge density is found at C_4 (+0.134) in the case of 2-methylnaphthalene. The experimentally most reactive position C_1 possesses rather a lower charge density (+0.111). This may suggest that a net charge density (electrostatic interaction) plays a less important role in the order of orientational preference observed in the present naphthalene derivatives, compared with charge-transfer interaction.

Experimental Section

General. Spectrometers and electrochemical equipment have been described previously.[60]

Materials. Methanol and sodium cyanide were used without purification. 1- and 2-methylnaphthalene, 1,4-, 1,5-, 1,8-, 2,3-, and 2,6-dimethylnaphthalene, and acenaphthene were commercial samples and were purified by either distillation or recrystallization. 2,7-Dimethylnaphthalene was prepared by the method of Wolinska-Mocydlarz, Canonne, and Leitch.[61]

The following reference materials were prepared according to the literature procedure: 2-methylnaphthalene-1-carbonitrile,[62] 4-methylnaphthalene-1-carbonitrile,[34] 7-methylnaphthalene-1-carbonitrile,[15] 1-methylnaphthalene-2-carbonitrile,[63] 1-naphthalenecarboxaldehyde,[64] 1-naphthaleneacetonitrile,[65] 2-naphthaleneacetonitrile,[66] 1-methoxymethylnaphthalene,[67] 2,3-dimethylnaphthalene-1-carbonitrile,[11] 2,6-dimethylnaphthalene-1-carbonitrile,[12] 2,7-dimethylnaphthalene-1-carbonitrile,[14] 6,7-dimethylnaphthalene-1-carbonitrile,[11] acenaphthene-5-carbonitrile,[35] and 1-methoxyacenaphthene.[68]

3-Methylnaphthalene-1-carbonitrile, 5-methylnaphthalene-1-carbonitrile, 4,5-dimethylnaphthalene-1-carbonitrile, 4,8-dimethylnaphthalene-1-carbonitrile, and 1,5-dimethylnaphthalene-2-carbonitrile were obtained by the reaction of the corresponding aryl bromides[17,69-72] and cuprous cyanide according to the method of Friedman and Shechter.[35]

6-Methylnaphthalene-1-carbonitrile, 3,7-dimethylnaphthalene-1-carbonitrile, and 5,8-dimethylnaphthalene-2-carbonitrile were prepared by the dehydration[73] of the amides, which were made from the corresponding acids.[12,54,74] 8-Methylnaphthalene-1-carbonitrile was synthesized by the dehydration of the oxime of 8-methylnaphthalene-1-carboxaldehyde.[75] Attempts to prepare this nitrile from 8-chloro-1-methylnaphthalene[76] employing the method of Friedman and Shechter[35] did not give satisfactory results. 1,4-Dimethylnaphthalene-2-carbonitrile was similarly made from the oxime of 1,4-dimethylnaphthalene-2-carboxyaldehyde.[77] Attempts to obtain this nitrile from 2-bromo-1,4-dimethylnaphthalene failed. The desired bromide[77] could not be prepared following the method of Campaigne and Ashby.

2-Methoxymethylnaphthalene was prepared by refluxing 2-chloromethylnaphthalene[78] in methanolic potassium hydroxide according to the procedure of Sharp and Patrick.[67] 1-Methoxymethyl-8-methylnaphthalene and 1,8-bismethoxymethylnaphthalene were made from the corresponding bromide[71,75] in methanolic solution of sodium methoxide. 5-Methoxyacenaphthene was prepared by the methylation[79] of 5-acenaphthenol.[80]

Controlled Potential Electrolysis. A three-compartment cell which has been previously described[60] was employed. The reference electrode was an SCE. The anolyte and catholyte were 0.4 M sodium cyanide in methanol. The amount of organic substrate was 5 mmol. A platinum

(2 × 2 cm) sheet anode was used, and the anolyte (50 mL) was stirred magnetically. The anode compartment was kept under an atmosphere of nitrogen.

A background current was recorded before addition of naphthalene (negligible up to 1.4 V). The potential was set in the region of the first voltammetric wave, and reaction was performed until either 2 faradays/mol of naphthelene added was passed or the current dropped to some low value near the original background level.

To the electrolyzed mixture were added internal standards for GLC analyses, the mixture was treated with water, and the organic material was extracted with ether. The ethereal solution was concentrated and analyzed. The columns employed for the analyses were Bentone 34 or PEG 6000.

Each product was separated in pure form by preparative GLC and the IR, MS, and NMR spectra of the products were compared with those of the corresponding authentic sample (Table II). The products isolated showed satisfactory elemental analyses.

Cyclic Voltammetry. Voltammograms were recorded for each naphthalene in distilled methanol. The SCE reference electrode was separated from the working electrode by a glass frit. The auxiliary electrode was a platinum sheet, and the working electrode a platinum wire sealed in glass.

All the voltammograms showed no cathodic peak corresponding to reduction of an initially formed cation radical. In several cases, a sweep rate of 100 V/s was employed to look for this peak.

References and Notes

(1) (a) K. Yoshida and T. Fueno, *Chem. Commun.*, 711 (1970); (b) K. Yoshida and T. Fueno, *J. Org. Chem.*, **37**, 4145 (1972); (c) K. Yoshida and T. Fuendo, *ibid.*, **38**, 1045 (1973); (d) K. Yoshida, *J. Am. Chem. Soc.*, **99**, 6111 (1977).
(2) E. Heilbronner, V. Hornung, F. H. Pinkerton, and S. F. Thames, *Helv. Chim. Acta*, **55**, 289 (1972).
(3) (a) J.-i. Aihara and H. Inokuchi, *Bull. Chem. Soc. Jpn.*, **43**, 1265 (1970); (b) J.-i. Aihara, M. Tsuda, and H. Inokuchi, *ibid.*, **43**, 3067 (1970).
(4) O. B. Nagy, S. Dupire, and J. B. Nagy, *Tetrahedron*, **31**, 2453 (1975).
(5) A platinum electrode in methanol–sodium cyanide can be polarized to +1.6 V vs. SCE without substantial oxidation of the electrolyte mixture.[6] Within this potential range, naphthalenes can be oxidized.[7-10]
(6) K. Yoshida and T. Fueno, *J. Org. Chem.*, **36**, 1523 (1971).
(7) J. W. Loveland and G. R. Dimeler, *Anal. Chem.*, **33**, 1196 (1961).
(8) E. S. Pysh and N. C. Yang, *J. Am. Chem. Soc.*, **85**, 2124 (1963).
(9) W. C. Neikam and M. M. Desmond, *J. Am. Chem. Soc.*, **86**, 4811 (1964).
(10) L. Eberson and K. Nyberg, *J. Am. Chem. Soc.*, **88**, 1686 (1966).
(11) P. H. Gore, C. K. Thadani, and S. Thorburn, *J. Chem. Soc. C*, 2502 (1968).
(12) P. H. Gore and M. Yusuf, *J. Chem. Soc. C*, 2586 (1971).
(13) F. M. Aslam, P. H. Gore, and M. Jehangir, *J. Chem. Soc., Perkin Trans. 1*, 892 (1972).
(14) P. H. Gore and A. S. Siddiquei, *J. Chem. Soc., Perkin Trans. 1*, 1442 (1972).
(15) P. H. Gore, A. S. Siddiquei, and S. Thorburn, *J. Chem. Soc., Perkin Trans. 1*, 1781 (1972).
(16) L. W. Deady, P. M. Gray, and R. D. Topsom, *J. Org. Chem.*, **37**, 3335 (1972).
(17) E. Berliner, J. B. Kim, and M. Link, *J. Org. Chem.*, **33**, 1160 (1968).
(18) I. K. Lewis, R. D. Topsom, J. Vaughan, and G. J. Wright, *J. Org. Chem.*, **33**, 1497 (1968).
(19) P. G. E. Alcorn and P. R. Wells, *Aust. J. Chem.*, **18**, 1377 (1965).
(20) S. R. Hartshorn, R. B. Moodie, K. Schofield, and M. J. Thompson, *J. Chem. Soc. B*, 2447 (1971).
(21) P. H. Gore and A. S. Siddiquei, *J. Chem. Soc., Perkin Trans. 1*, 2344 (1972).
(22) E. I. Heiba, R. M. Dessau, and W. J. Koehl, Jr., *J. Am. Chem. Soc.*, **91**, 6830 (1969).
(23) R. Weissgerber and O. Kruber, *Ber.*, **52**, 346 (1919).
(24) O. Kruber and W. Schade, *Ber.*, **68**, 11 (1935).
(25) L. Ruzicka and E. A. Rudolph, *Helv. Chim. Acta*, **10**, 915 (1927).
(26) M. Periasamy and M. V. Bhatt, *Synthesis*, 330 (1977).
(27) (a) K. Yoshida, T. Saeki, and T. Fueno, *J. Org. Chem.*, **36**, 3673 (1971); (b) K. Yoshida and T. Fueno, *ibid.*, **37**, 4145 (1972); (c) K. Yoshida, M. Shigi, and T. Fueno, *ibid.*, **40**, 63 (1975).
(28) W. J. Koehl, Jr., U.S. Patent 3 252 876 (1966).
(29) E. Brandbrook and R. P. Linstead, *J. Chem. Soc.*, 1739 (1936).
(30) M. J. S. Dewar and P. J. Grisdale, *J. Am. Chem. Soc.*, **84**, 3541 (1962).
(31) Y. Dozen, *Bull. Chem. Soc. Jpn.*, **41**, 668 (1968).
(32) Y. Dozen, *Bull. Chem. Soc. Jpn.*, **45**, 519 (1972).
(33) Y. Dozen and S. Fujishima, *Yuki Gosei Kagaku Kyokai Shi*, **30**, 150 (1972).
(34) H. G. Rule, N. Campbell, A. G. McGregor, and A. A. Woodham, *J. Chem. Soc.*, 1816 (1950).
(35) L. Friedman and H. Shechter, *J. Org. Chem.*, **26**, 2522 (1961).
(36) M. S. Newman and H. Boden, *J. Org. Chem.*, **26**, 2525 (1961).
(37) P. Nounou, *J. Chim. Phys.*, **63**, 994 (1966).
(38) R. V. Poponova, I. M. Lukashenko, A. A. Polyakova, S. Rang, and E. O. Silvia, *Zh. Org. Khim.*, 7, 2032 (1971).
(39) V. M. Topmyshev, M. I. Gorfinkel, V. K. Manzhos, and V. A. Koptyrig, *Zh. Org. Khim.*, **12**, 736 (1976).
(40) A. G. Loudon and R. Z. Mazengo, *Org. Mass Spectrom.*, **8**, 179 (1974).
(41) H. Yoshimi, *J. Chem. Phys.*, **57**, 1361 (1972).
(42) H. Yoshimi and K. Kuwata, *Mol. Phys.*, **23**, 297 (1972).
(43) T. Shida and S. Iwata, *J. Am. Chem. Soc.*, **95**, 3473 (1973).
(44) E. Baciocchi and C. Rol, *J. Org. Chem.*, **42**, 3682 (1977).
(45) S. Uemura, S. Tanaka, and M. Okano, *J. Chem. Soc., Perkin Trans. 1*, 1966 (1976).
(46) P. J. Andrulis, Jr., M. J. S. Dewar, R. Dietz, and R. L. Hunt, *J. Am. Chem. Soc.*, **88**, 5473 (1966).
(47) (a) A. Ledwith and P. J. Russell, *J. Chem. Soc., Chem. Commun.*, 292 (1974); (b) *ibid.*, 959 (1974); (c) *J. Chem. Soc., Perkin Trans. 2*, 1503 (1975).
(48) (a) C. Walling and D. M. Camaioni, *J. Am. Chem. Soc.*, **97**, 1603 (1975); (b) C. Walling, D. M. Camaioni, and S. S. Kim, *ibid.*, **100**, 4814 (1978).
(49) M. K. Eberhardt, *J. Org. Chem.*, **42**, 832 (1977).
(50) R. Filler and R. C. Rickert, *J. Chem. Soc., Chem. Commun.* 133 (1976).
(51) It has been reported that 1,4-dimethylnaphthalene yields the 5-nitro product,[52] but it was argued later that this assignment was erroneous.[53]
(52) A. Davies and K. D. Warren, *J. Chem. Soc. B*, 873 (1969).
(53) A. Fischer and A. L. Wilkinson, *Can. J. Chem.*, **50**, 3988 (1972).
(54) H. Gore and J. A. Hoskins, *J. Chem. Soc. C*, 3347 (1971).
(55) In the peri-substituted dimethyl derivative it was found that interaction between the methyl groups spread the $C_1C_9C_8$ bond angle to 125.2° and reduced the $C_4C_{10}C_5$ angle to 119.5°: D. Bright, I. E. Maxwell, and J. de Boer, *J. Chem. Soc., Perkin Trans. 2*, 2101 (1973).
(56) The crystallographic result indicates that the CH_2-CH_2 bridge pulls together the 1- and 8-carbon atoms of the naphthalene skeleton, reducing the angle to 112.4° and correspondingly spreading the bottom angle to 128.4°: H. W. W. Ehrlich, *Acta Crystallogr.*, **10**, 699 (1957).
(57) Φ_1 and Φ_2 are represented in terms of Slater determinants built up of orthonomal spin orbitals of each isolated system. An adiabatic wave function of the entire interaction system will be expressed by use of the diabatic basis sets. A characteristic of diabatic and adiabatic representations for molecular collision processes is reviewed by T. F. O'Malley, *Adv. At. Mol. Phys.*, **7**, 223 (1971). For the contributions to various interaction energies with the progress of reaction, for instance, see S. Nagase and T. Fueno, *Theor. Chim. Acta*, **35**, 217 (1974); **41**, 572 (1976); S. Nagase and K. Morokuma, *J. Am. Chem. Soc.*, **100**, 1660 (1978).
(58) J. Berkowitz, W. A. Chupka, and T. A. Walter, *J. Chem. Phys.*, **50**, 1497 (1969).
(59) (a) J. A. Pople and D. L. Beveridge, "Approximate Molecular Orbital Theory", McGraw-Hill, New York, 1970. (b) The molecular geometries of naphthalene and CN are taken from D. W. J. Cruickshank and R. A. Sparks, *Proc. R. Soc. London, Ser. A*, **258**, 270 (1960), and R. Bonaccorsi, C. Petrongolo, E. Scrocco, and J. Tomasi, *J. Chem. Phys.*, **48**, 1500 (1968). As for the CH_3 parts of naphthalene, standard geometries (J. A. Pople and M. Gordon, *J. Am. Chem. Soc.*, **89**, 4253 (1967)) were employed to examine the substituent effects systematically.
(60) K. Yoshida, *J. Am. Chem. Soc.*, **101**, 2116 (1979).
(61) J. Wolinska-Mocydlarz, P. Canonne, and L. C. Leitch, *Synthesis*, 566 (1974).
(62) J. F. Eastham and D. Y. Cannon, *J. Org. Chem.*, **25**, 1504 (1960).
(63) V. F. Raaen and J. F. Eastham, *J. Am. Chem. Soc.*, **82**, 1349 (1960).
(64) S. J. Angyal, J. R. Tetaz, and J. G. Wilson, *Org. Synth.*, **30**, 67 (1950).
(65) N. G. Gaylord and E. I. Becker, *J. Org. Chem.*, **15**, 305 (1950).
(66) M. Lamant and M. L. Moine, *Bull. Soc. Chim. Fr.*, 1144 (1961).
(67) D. B. Sharp and T. M. Patrick, Jr., *J. Org. Chem.*, **26**, 1389 (1961).
(68) H. Gault and G. Kalopissis, *C. R. Acad. Sci.*, **229**, 624 (1949); *Chem. Abstr.*, **44**, 2965e (1950).
(69) A. Fischer, W. J. Mitchell, G. S. Ogilvie, J. Packer, J. E. Packer, and J. Vaughan, *J. Chem. Soc.*, 1426 (1958).
(70) W. Davies and J. R. Wilmshurst, *J. Chem. Soc.*, 4079 (1961).
(71) W. J. Mitchell, R. D. Topsom, and J. Vaughan, *J. Chem. Soc.*, 2526 (1962).
(72) N. N. Vorozhtsov and A. I. Tochilkin, *NDVS Khim. Khim. Tekhnol.*, 325 (1959); *Chem. Abstr.*, **54**, 445a (1960).
(73) S. M. McElvain and C. L. Stevens, *J. Am. Chem. Soc.*, **69**, 2663 (1947).
(74) C. C. Price, E. C. Chapin, A. Goldman, E. Krebs, and H. M. Shafer, *J. Am. Chem. Soc.*, **63**, 1857 (1941).
(75) L. P. Zalukaev and V. V. Moiseev, *J. Org. Chem. USSR (Engl. Transl.)*, **2**, 272 (1966).
(76) L. F. Fieser and A. M. Seligman, *J. Am. Chem. Soc.*, **61**, 136 (1939).
(77) E. Campaigne and I. Ashby, *J. Heterocycl. Chem.*, **8**, 487 (1971).
(78) D. S. Tarbell, D. K. Fukushima, and H. Dam, *J. Am. Chem. Soc.*, **67**, 197 (1945).
(79) Modification of G. S. Hiers and F. D. Hager, "Organic Syntheses", Collect. Vol. I, Wiley, New York, 1932, p 58.
(80) H. Rapoport, T. P. King, and J. B. Lavigne, *J. Am. Chem. Soc.*, **73**, 2718 (1951).
(81) M. Janczewski and W. Rodkoscielny, *Roczniki Chem.*, **39**, 201 (1965); *Chem. Abstr.*, **62**, 16158e (1965).