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FRIEDEL-CRAFTS CYANATION OF SOME REACTIVE AROMATIC HYDROCARBONS

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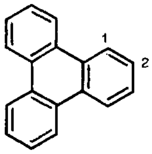
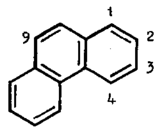
Abstract—Direct cyanation, using the heterogeneous Friedel-Crafts system cyanogen bromide/aluminium chloride, has given good yields of the following carbonitriles: anthracene-9-, chrysene-6-, 2-methyl-1-naphtho-, 4-methyl-1-naphtho-, 1-naphtho-, phenanthrene-9-, 2,4,6-trimethylbenzo-, triphenylene-1- and triphenylene-2-carbonitriles.

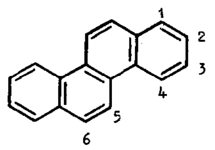
The direct cyanation of reactive aromatic compounds, with cyanogen halide [CNX, (I)] and aluminium chloride (Friedel-Crafts-Karrer reaction),[1,2] has proved successful for phenolic ethers.[2,3] Both cyanogen chloride[4] (I, X = Cl) and bromide[1,2] (I, X = Br) have been used, but at best only moderate yields have been achieved.



II



III



IV

We report here the formation in good yield of monocyano-derivatives of reactive aromatic hydrocarbons, by the use of a modified procedure (Table), employing cyanogen bromide with aluminium chloride as catalyst. No substitution resulted on using aluminium bromide as the catalyst; presumably homogeneous catalysis by this halide, which readily dissolves in the solvent used, carbon bisulphide, is not as effective as the heterogeneous catalysis provided at the surface of solid aluminium chloride. It has been postulated that the actual electrophilic reagent in cyanation is either the free cyano cation (CN^+),[5] of the addition complex ($X—\overset{+}{C}{=}N—\overset{-}{Al}X_3$).[4] The involvement of a kinetically free CN^+ species must be considered unlikely. On the other hand an addition complex of the above type would not possess the low steric requirements[6] for the substitution process that is consequent on the regioselectivity of the cyanations here reported. For the present system we prefer an ion-pair of the type $[CN^+]$ $[AlX_4^-]$ as the actual electrophilic species.

In all these cyanations, except for triphenylene (II), high positional selectivity was achieved. No evidence of disubstitution, e.g. in the favourable case of anthracene-9,10-dicarbonitrile, could be obtained. This high regioselectivity contrasts sharply with results from Friedel-Crafts acetylations, i.e. of 2-methylnaphthalene,[7] anthracene,[8]

Cyanation of aromatic hydrocarbons by cyanogen bromide and aluminium chloride in carbon disulphide for 18 hours at 48°C.

Hydrocarbon	Product	
	Carbonitrile	Yield (%)
1,3,5-trimethylbenzene	2,4,6-trimethylbenzo-	92
naphthalene	1-naphtho-	42
	2-naphtho-	1.0
1-methylnaphthalene	4-methyl-1-naphtho-	72
2-methylnaphthalene	2-methyl-1-naphtho-	85
anthracene	anthracene-9-	92
phenanthrene	phenanthrene-9-	83
chrysene	chrysene-5-	2.1
	chrysene-6-*	66
triphenylene	triphenylene-1-	32
	triphenylene-2-	48

*There is also evidence (g.l.c.) of two other isomers (<1%)

and phenanthrene,[9] where anomalous product distribution is observed as the result of steric hindrance and reversibility. The cyanation reaction permits predominant attack at the electronically most activated aromatic position, even if this is sterically the least accessible, *viz* for the 9-anthryl or 2-methyl-1-naphthyl positions. The method therefore provides synthetic routes to a range of carbon-derivatives (e.g. COOH, COR), which are not accessible *via* direct Friedel–Crafts acetylation. Triphenylene(II) affords a mixture of isomers. Formation of triphenylene-1-carbonitrile, though favoured electronically (Dewar's reactivity numbers,[10] $\Delta E_\pi = 2.000$ for 1-triphenylyl and $= 2.121$ for 2-triphenylyl) is sterically severely hindered, in this respect analogous to the 4-position of phenanthrene(III). In electrophilic substitutions of triphenylene the 1-/2- isomer ratios (R) are critically dependent on the size of the attacking reagent. In the sequence of increasing spatial demand we have $R = 2.8/1$ for chlorinations,[11] 1.2/1 for nitrations,[12] 0.67/1 for Friedel–Crafts–Karrer cyanation, and (0.001–0.17)/1 for Friedel–Crafts acetylations.[13]

With chrysene(IV) at least 4 isomeric chrysene-carbonitriles are formed, with the expected[10] 6-isomer predominating. In this reaction the next most abundant product is the 5-isomer (ratio 5-/6- = 1/31); the 5-position of chrysene, like the 4-position, is sterically analogous to the hindered 4-phenanthryl and 1-triphenylyl positions.

EXPERIMENTAL

General. Temps are in °C. All mps are uncorrected. PMR spectra were obtained, unless otherwise stated, for solns in $CDCl_3$. IR spectra were recorded, unless otherwise stated, for discs in KBr.

Cyanation procedure. The hydrocarbon (5 mmol) and resublimed anhyd $AlCl_3$ (10 mmol) in anhyd CS_2 (15 ml) were stirred for 10 min at 20°. Cyanogen bromide (10 mmol) in more CS_2 (15 ml) was then added over 15 min with stirring. The mixture was then stirred and boiled under reflux for 18 hr, then cooled, and added to crushed ice/conc HCl. The combined $CHCl_3$ extracts were washed with water, dried (Na_2SO_4), and the solvent evaporated. The residue was dissolved in benzene (30 ml) and the soln passed through a short column of Al_2O_3 (Spence, type H), and the product eluted with benzene. Evaporation then gave the product, which was then recrystallised. A portion of the product was examined by glc.; the columns were filled with 5% OV 17 (100–120 mesh) on washed celite, with N_2 as carrier gas, and were used at 120° for the reaction with mesitylene, at 160° for naphthalene and the methylnaphthalenes, at 200° for anthracene and phenanthrene, and at 250° for chrysene and triphenylene.

Yields obtained in these reactions (Table) are near-optimal, since amounts of recovered hydrocarbons were small. The products isolated were:

2,4,6-*Trimethylbenzonitrile*, crystals, m.p. 53° (EtOH) (lit.[14] m.p. 55°); IR 2220 cm.$^{-1}$ (C≡N); PMR δ 2.38 (s, 4-$C\underline{H}_3$), 2.53 (s, 2- and 6-$C\underline{H}_3$), 7.09 (s, 3$\underline{H}$ and 5-$\underline{H}$.

1-*Naphthonitrile*, oil, b.p. 112°/0.5 mm Hg; IR (as film) 2228 cm^{-1} (C≡N); PMR δ 7.45 (d, 3-$\underline{H}$), 7.6–8.2 (c, arom.-$\underline{H}$), 8.32 (m,8-$\underline{H}$), $J_{3,4}$ 8.5 Hz.

2-*Naphthonitrile*, crystals, m.p. 65° (EtOH) (lit.[15] m.p. 66°).

1-*Methyl*-4-*naphthonitrile*, crystals, m.p. 51–52° (EtOH) (lit.[16] m.p. 53–54°); IR 2212 cm.$^{-1}$ (C≡N); PMR δ 2.80 (s, $C\underline{H}_3$), 7.4–7.8 (c, 6- and 7-$\underline{H}$), 7.85–8.7 (c, arom.-$\underline{H}$).

From 1-methylnaphthalene an unidentified by-product was obtained [yield 18% (w/w), isolated by tlc on silica-gel, with 1:1 (v/v) benzene/light petroleum], forming crystals, m.p. 199–200° (EtOH) (Found: C, 84.74; H, 6.27; N, 9.52%); IR 1513 (s) cm.$^{-1}$; PMR δ 2.88 (c, $C\underline{H}_3$), 7.4–8.0 (c, 3 protons), 8.2–8.5 (c, 1 proton), 8.6–9.0 (c, 1 proton), 9.3–9.8 (c, 1 proton).

2-*Methyl*-1-*naphthonitrile*, crystals, m.p. 86° (EtOH) (lit.[17] m.p. 87–88°); IR 2220 cm.$^{-1}$ (C≡N); PMR δ 2.80 (s, $C\underline{H}_3$), 7.5–8.0 (c, arom.-$\underline{H}$), 8.10 (d, 4-$\underline{H}$), 8.37 (m, 8-$\underline{H}$), $J_{3,4}$ 8.6 Hz.

Anthracene-9-*carbonitrile*, crystals, m.p. 173–174° (EtOH) (lit.[18] m.p. 174–175°); IR 2217 cm.$^{-1}$ (C≡N); PMR δ 7.5–8.0 (c, arom.-$\underline{H}$), 8.11–8.28 (m, 4- and 5-$\underline{H}$), 8.46–8.63 (m, 1- and 8-$\underline{H}$), 8.78 (s, 10-$\underline{H}$).

Phenanthrene-9-*carbonitrile*, crystals, m.p. 105–106° (EtOH) (lit.[19] m.p. 103–104°); IR 2220 cm.$^{-1}$ (C≡N); PMR δ 7.7–8.2 (c, arom.-$\underline{H}$), 8.32 (s, 10-$\underline{H}$), 8.43 (m, 8-$\underline{H}$), 8.72–8.83 (c, 4- and 5-$\underline{H}$).

Chrysene-5-*carbonitrile*, crystals, m.p. and mixed m.p. 165° (lit.[20] m.p. 165.5°); IR was identical with that of an authentic specimen.[20]

Chrysene-6-*carbonitrile*, crystals, m.p. and mixed m.p. 196° (lit.[20] m.p. 196–197°); IR was identical with that of an authentic specimen.[20]

Triphenylene-1-*carbonitrile.* (i) By cyanation, crystals, m.p. and mixed m.p. 128–129°; IR was identical with that of a specimen synthesised independently, under (ii) below. (ii) 1-*Bromotriphenylene.* Prepared (yield 63%) in the usual way from 1-aminotriphenylene[12] by the Sandmeyer reaction, 1-*bromotriphenylene* formed crystals, m.p. 54–55° (benzene/light petroleum) (Found: C, 70.3; H, 3.9; Br, 26.0. $C_{18}H_{11}Br$ requires C, 70.37; H, 3.61; Br, 26.02%).

Triphenylene-1-*carbonitrile.* A mixture of 1-bromotriphenylene (0.19 g) and copper(I) cyanide (0.10 g) in dry pyridine (5 ml) was heated (bath 200°) for 8 h. After cooling, the mixture was extracted with benzene, the extract washed with NH_4OH, dil HCl, and water, dried, and the solvent evaporated, to give pale-yellow *triphenylene*-1-*carbonitrile* (0.10 g, 62%), m.p. 128–129° (benzene/light petroleum) (Found: C, 89.7; H, 4.6; N, 5.4. $C_{19}H_{11}N$ requires C, 90.09; H, 4.38; N, 5.53%); IR 2245 cm.$^{-1}$ (C≡N); PMR δ 7.32–7.72 (c, β-arom.-$\underline{H}$), 7.86 (dd, 2-$\underline{H}$), 8.22–8.52 (c, α-arom.-$\underline{H}$), 8.62 (dd, 4-$\underline{H}$), 9.28–9.55 (m, 12-$\underline{H}$), $J_{2,3}$ 7.6 Hz, $J_{2,4}$ 1.4 Hz, $J_{3,4}$ 8.4 Hz.

Triphenylene-2-*carbonitrile.* (i) By cyanation, crystals, m.p. and mixed m.p. 215–216°; IR was identical with that of a specimen prepared under (ii) below. (ii) Prepared from 2-bromotriphenylene,[12] as for the 1-isomer, *Triphenylene*-2-*carbonitrile* (yield 26%) had m.p. 215–216° (benzene) (Found: C, 90.3; H, 4.4; N, 5.2. $C_{19}H_{11}N$ requires C, 90.09; H, 4.38; N, 5.53%); IR 2248 cm.$^{-1}$ (C≡N); PMR (D_6-DMSO) δ 7.57–7.87 (c, β-arom.-$\underline{H}$), 7.98 (dd, 3-$\underline{H}$), 8.63–9.03 (c, α-arom.-$\underline{H}$), 9.28 (d, 1-$\underline{H}$), $J_{1,3}$ 1.7 Hz, $J_{3,4}$ 8.0 Hz.

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