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ELECTOPHILIC CYANATION OF AROMATIC COMPOUNDS BY ANODIC OXIDATION OF CYANIDE ION

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In the course of our studies (1 — 6) on the free-radical reactions in organic electrode processes, it appeared of interest to investigate the behavior of an active species, which might be generated by anodic oxidation of inorganic salts, towards organic compounds in non-aqueous media.

The present communication deals with the direct introduction of cyano groups into organic compounds by the electrolytic oxidation of inorganic cyanide.

Anodic oxidation of cyanide ion was carried out in a mixture of hydrogen cyanide (20 ml.), tetralin (80 ml.) and methanol (150 ml.) containing sodium cyanide (5 g.), at 0.5 amp. with an applied potential of 4 v. at 5 — 10 °C under a nitrogen atmosphere. Two platinum foil electrodes having an area of 60 X 25 mm^2. for the anode and 80 X 50 mm^2. for the cathode, and spaced about 10 mm. apart, were used.

After 0.5 faraday had been passed through the cell, the electrolyzed mixture was worked up in the usual manner, distilled under reduced pressure and chromatographed on alumina. Elution with benzene gave 10 g. of 1-methoxytetralin (I), b.p. 126 — 129 °C/23 mmHg, $n_D^{15} = 1.5371$, (Found: C, 81.27; H, 8.81. Calcd. for $C_{11}H_{14}O$: C, 81.44; H, 8.70), and 1.3 g. of 6-cyanotetralin (II) which was, after hydrolysis, identified as 1,2,3,4-tetrahydro-6-naphthoic acid (III), m.p. and mixed m.p. 152 — 153 °C, (Found: C, 74.80; H, 6.70. Calcd. for $C_{11}H_{12}O_2$: C, 74.97; H, 6.86).

When a solution of sodium cyanide (8.6 g.) and anisole (36 g.) in methanol (160 g.) was electrolyzed under similar conditions, except that a mercury cathode was employed in place of platinum, a mixture (3 g.) of 38% o-cyanoanisole (IV) and 62% p-cyanoanisole (V) was obtained. Acid-hydrolysis of IV gave o-anisic acid (VI), m.p. 95 — 96 °C, mixed m.p. with authentic o-anisic acid, 99 — 100 °C, (Found: C, 63.84; H, 5.82. Calcd. for $C_8H_8O_3$: C, 63.15; H, 5.30). Recrystallization of V, which was isolated by filtration, from aqueous alcohol afforded white needles, m.p. 59 — 60 °C, undepressed by admixture with an authentic sample (Found: C, 72.00; H, 5.48. Calcd. for C_8H_7ON: C, 72.16; H, 5.30).

The infrared spectra of these compounds (I, III, V and VI) were identical with those of authentic samples.

Furthermore, toluene gave a mixture (0.78 g.) of o-, m- and p-cyanotoluene as a ring-substituted product when subjected to electrolysis in a sodium cyanide — methanol medium under similar conditions to that described in the case of anisole.

Takig together with the results (4) described previously, both methanol and cyanide might be oxidized anodically during these electrolyses. 1-Methoxytetralin would be formed by attack of methoxy radical on tetralin in anodic oxidation of methanol.

On the other hand, the experiment with tetralin indicates that the cyano radical, which might be generated at the anode, attacks only the aromatic nucleus to give 6-cyanotetralin as a homolytic cyanated product. The similar result was obtained with toluene, and benzylcyanide could not be detected.

Moreover, the observed orientation in this aromatic substitution has much analogy with that in electrophilic one. The electrolysis of the cyanide in anisole, as indicated above, afforded the <u>ortho</u>- and <u>para</u>-isomers without any <u>meta</u>-cyanoanisole. Although toluene gave all of three ring-substituted isomers, the ratio of the isomers was 1 (<u>ortho</u>) : 0.2 (<u>meta</u>) : 2.5 (<u>para</u>).

On the basis of the observations presented above, it seems most reasonable to conclude that the electrochemically generated cyano radical is a strong electron acceptor, and, thus, preferentially attacks the points of high electron density in the aromatic compounds.

Further experiments concerning this subject are in progress, and the detailed description will be published elsewhere.

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