The Bidentate Nature of Cyanide Ion in Anodic Addition Reactions

By VERNON D. PARKER*

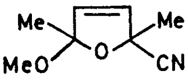
(*Department of General and Organic Chemistry, The H. C. Ørsted Institute, University of Copenhagen, Universitetsparken* 5, DK-2100 *Copenhagen, Denmark*)

and LENNART EBERSON

(*Division of Organic Chemistry, Chemical Center, University of Lund, Lund* 7, *Sweden*)

Summary Anodic addition of the cyanide ion to 9,10-dialkylanthracenes gives products containing both nitrile and isonitrile groups.

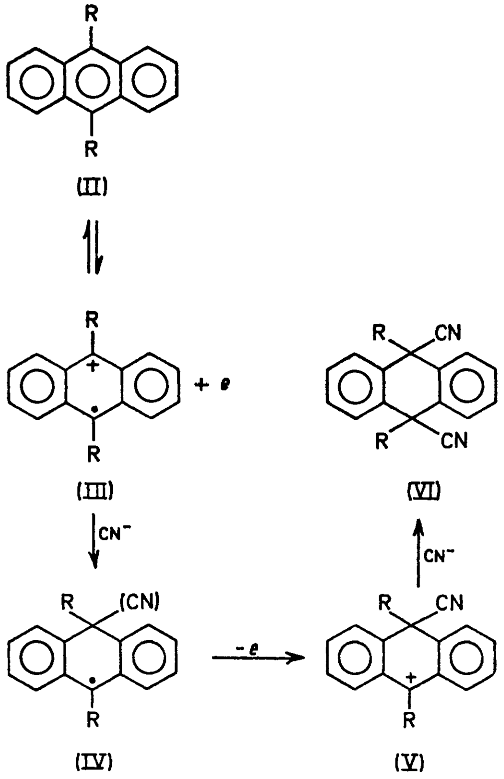
THE anodic addition of cyanide ion to aromatic compounds or olefins has not previously been achieved.[1] When cyanation is attempted in methanol, cyanomethoxylation has been observed, for example 2,5-dimethylfuran forms the adduct, (I).[2] In all previous reports of anodic substitution or addition involving cyanide ion, the carbon atom of cyanide ion acts as the nucleophilic centre.



(I)

We report the first case of anodic addition of cyanide ion to an aromatic compound as well as the first case of the generation of an isonitrile by anodic substitution.

The cyclic voltammogram of 9,10-di-n-propylanthracene (10 mM) in acetonitrile containing tetraethylammonium perchlorate (0·1 M) showed a nearly reversible oxidation at +1·08 V *vs.* SCE. Addition of a slight excess of tetraethylammonium cyanide (22 mM) brought about an increase in the oxidation current to almost double the original value and no reduction peak for the cation radical was observed. Exhaustive coulometric oxidation showed that 2·0 F per mol of substrate were consumed.



The i.r. spectrum of the crystalline product showed a nitrile band at 2230 cm^{-1} and an isonitrile band at greater intensity at 2125 cm^{-1}. The mass spectrum showed a strong parent ion at *m/e* of 314. The ^{1}H n.m.r. spectrum in $CDCl_3$ was consistent with structure (VI). The aliphatic region of the spectrum was complicated due to the coupling between the isonitrile and propyl groups.[3] Similar products were observed for both 9,10-diethyl- and 9,10-dimethylanthracene.

A possible mechanism for the formation of products containing nitrile and isonitrile groups is shown in the Scheme.

Two different electrophilic species are involved in going from the substrate to the product. The cation radical (III) might be expected to give a product containing the nitrile grouping in analogy with other known addition and substitution reactions. The isonitrile grouping would then have to be formed by reaction of the cation (V) with the cyanide ion in agreement with the known behaviour of ambient nucleophiles in S_N1 reactions.[4]

(*Received*, 17*th February* 1972; *Com.* 249.)

---

[1] For a review see: N. L. Weinberg and H. R. Weinberg, *Chem. Rev.*, 1968, **68**, 449.

[2] K. Yoshida and T. Fueno, *Bull. Chem. Soc. Japan*, 1969, **42**, 2411.

[3] P. Von R. Schleyer, *J. Chem. Phys.*, 1961, **35**, 1533.

[4] E. S. Gould, 'Mechanism and Structure in Organic Chemistry', Holt, Rinehart and Winston, New York, 1959, p. 297