Nuclear Cyanation of Diphenylacetylene

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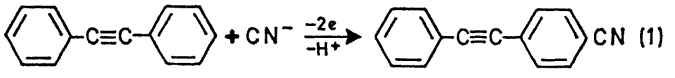
Summary Electrochemical oxidation of diphenylacetylene in methanol in the presence of sodium cyanide yields *p*-cyanodiphenylacetylene.

CONSIDERABLE interest has been focused recently on the anodic cyanation of aromatic compounds.[1–4] We report the nuclear substitution of diphenylacetylene by cyanide to give *p*-cyanodiphenylacetylene (Equation 1).[5] This reaction provides a new method for preparing cyanotolanes and demonstrates a new mode by which nucleophiles may attack the ring positions in arylacetylenes.



The electrolyses were performed using the electrolysis cell described previously.[4] In a typical case a methanolic solution (50 ml) of diphenylacetylene (1·78 g, 0·01 mol) and sodium cyanide (1·96 g, 0·04 mol) was electrolysed at 25° for 24 h, using an anode potential of +2·0 v (*vs.* SCE). The electrical charge was 3·9 Faradays per mol of reactant. Conventional isolation procedures afforded 0·74 g of unreacted diphenylacetylene and 0·71 g of a compound melting at 108·5—109·5°. The elemental analysis and spectral data indicated that this material was *p*-cyanodiphenylacetylene (60% yield based on diphenylacetylene consumed); i.r. spectrum 2240, 2230 (CN and C≡C), 845, 760, 690 cm^{-1} mono-*p*-substituted); M^+ 203; n.m.r. (100 MHz, 10% in CCl_4) τ 2·40 (4H, s), 2·4—2·7 (5H, m).† Hydrolysis of the product yielded *p*-carboxydiphenylacetylene.[6]

By analogy with other anodic substitution reactions,[7] the primary electrode process is considered to be the oxidation of diphenylacetylene to a cationic species (most likely a cation radical) which subsequently reacts with cyanide ion. A mechanism involving the concerted nucleophile-assisted one-(or two-) electron transfer may be reasonable in view of the great nucleophilicity of cyanide ion.[3]

One major advantage of the present reaction lies in its high selectivity with regard to the position of attack. The reaction product was *p*-cyanodiphenylacetylene exclusively.

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† The proton chemical shift τ of diphenylacetylene was 2·4—2·7 (m).

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