Tetrahedron Letters No.29, pp. 3341-3344, 1968. Pergamon Press. Printed in Great Britain.

ELECTROCHEMICAL SUBSTITUTION BY CYANATE ION

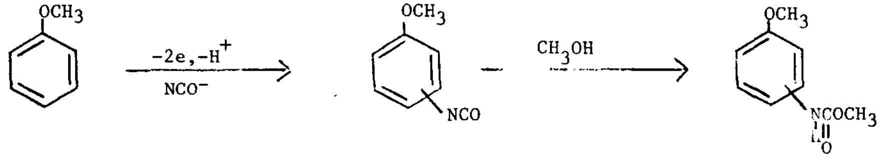
V. D. PARKER AND B. E. BURGERT

Physical Research Laboratory
The Dow Chemical Company
Midland, Michigan

(Received in USA 11 March 1968; received in UK for publication 25 April 1968)

Both nuclear and side chain anodic aromatic substitution reactions involving substitution by acetoxy (1,2), cyano (3,4,5,6), and methoxy (7) groups have been reported recently. That anodic aromatic substitution reactions involve oxidation of the aromatic substrate at the anode was first proposed by Eberson (8). That discharge of the aromatic substrate takes place in nuclear acetoxylation has now been well established (1). Anodic substitution by cyanide ion was believed to involve discharge of cyanide ion to a reactive radical which attacked the aromatic species (5). It was later shown that substitution by cyanide only occurs at anode potentials great enough to discharge the aromatic compound although cyanide is discharged at much lower anode potentials (3). While the mechanism of nuclear anodic substitution proposed by Eberson (1) is generally accepted, there remains conflicting views on anodic side chain substitution. We prefer a mechanism in which the predominant mode of side chain acetamidation (9), methoxylation (4,10), and acetoxylation (11) involves an initial oxidation of solvent or electrolyte which then abstracts hydrogen from the side chain of the alkylaromatic compound. The resulting radical may then undergo anodic substitution. Eberson advocates a mechanism similar to that observed in nuclear substitution for side chain acetoxylation (1) and side chain acetamidation (12). Ross and coworkers (13) support Eberson's view of side chain acetoxylation, however, propose that side chain anodic substitutions occurring in the presence of easily oxidized nitrate ion involve the hydrogen abstraction mechanism.

We now wish to report anodic aromatic substitution by cyanate. Electrolysis of methanolic solutions of anisole containing potassium cyanate at an anode potential of +1.8V (vs SCE) results in substituion of hydrogen by a methylcarbamyl group along with formation of methyl carbamate.



(1)

$$NCO^{\ominus} + H^{+} \longrightarrow HNCO \xrightarrow{CH_3OH} CH_3O\overset{O}{\overset{\|}{C}}NH_2 \qquad (2)$$

When the electrolysis was conducted at an anode potential of +1.0V (vs SCE) the only product detected was methyl carbamate (eqn. 2). Since the anode potential necessary to discharge anisole in this system would be expected to be about +1.6V (vs SCE)*, the formation of carbamates derived from anisole apparently results from the reaction of cyanate ion with a species formed by oxidation of anisole at the anode (eqn. 1). That the substitution reaction indeed does involve cyanate ion rather than methyl carbamate as the substituting species was shown by the failure to isolate aromatic carbamates when the aromatic species was electrolyzed in methanol containing methylcarbamate and sodium perchlorate (as supporting electrolyte). Thus the mechanism of anodic nuclear substitution by cyanate ion has the same general characteristics as acetoxylation (1) and cyanation (3).

We have applied this reaction to anisole, anthracene, benzene, napthalene, and toluene. In general the reaction is not of much preparative value since the yield is low ($<$ 20%). However, it may find application in the preparation of carbamates that cannot be synthesized by more common techniques.

We have also observed anodic side chain substitution by cyanate. Triphenylmethylisocyanate was obtained when triphenylmethane was electrolyzed in the presence of mercuric cyanate in acetone. This reaction required the presence of a supporting electrolyte (sodium perchlorate). The solution did not conduct current in the absence of the electrolyte indicating the covalent character of mercuric cyanate. Eberson has shown that nuclear acetoxylation of alkylaromatics can be completely suppressed by employing a non-nucleophilic anion (sodium perchlorate) rather than acetate ion (1). Exclusive side chain acetoxylation is observed and is attributed to the action of acetic acid as the nucleophile. Other examples of substitution by neutral species can be found in acetamidation (9,12) and methoxylation (4,5,10). There has been no indication that neutral species can participate in nuclear substitutions. Therefore, it is not surprising that only side chain substitution by mercuric cyanate is observed in view of its covalent character. We were unable to detect isocyanates when anisole, napthalene, or anthracene were electrolyzed in acetone containing mercuric cyanate and sodium perchlorate.

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*The oxidative polarographic halfwave potential of anisole in acetic acid (14) is +1.67 V (vs SCE) and +1.65V(vs SCE) in acetonitrile (15).

We propose that substitution by mercuric cyanate on the side chain of triphenylmethane takes place by the same mechanism that has been proposed for acetamidation (9), acetoxylation (11), methoxylation (10), and for the formation of benzyl nitrate from electrolysis of toluene containing solutions (13). That is, some species other than the aromatic substrate is discharged at the anode to form a free radical. The free radical then abstracts side chain hydrogen to form the substituted benzyl radical which undergoes anodic oxidation and reaction with a nucleophile (eqn. 3). In the present case mercuric cyanate may be capable of oxidizing the triphenylmethylradical to the carbonium ion. However, triphenylmethane does not react with mercuric cyanate under the conditions of the electrolysis until current is passed.

$$\begin{aligned} &X \xrightarrow{-e} X\bullet \\ &(Ph)_3C\text{-}H + X\cdot \longrightarrow (Ph)_3C\bullet + HX \\ &(Ph)_3C\bullet \xrightarrow{-e} (Ph)_3C+ \xrightarrow{Hg(NCO)_2} (Ph)_3C\text{-}NCO \end{aligned} \tag{3}$$

This work has shown that the cyanate group may participate in both nuclear and side chain **anodic** substitutions. Nuclear subsitituion by cyanate fulfills the accepted criteria for a mechanism involving discharge of the aromatic substrate as the primary anode reaction.

Our present state of knowledge does not allow us to propose that the hydrogen abstraction mechanism accounts for all anodic side chain substitution products. Evidence that this mechanism occurs is compelling (9,10,11,13). On the other hand, there is no concrete evidence that side chain anodic substitution ever involves direct anodic oxidation of the alkylaromatic compound.

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