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SIDE CHAIN ANODIC SUBSTITUTION: METHOXYLATION OF TETRALIN

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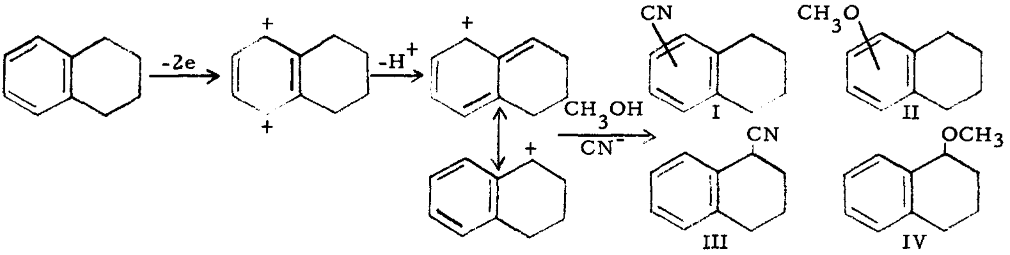
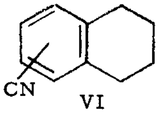
In a previous communication we presented evidence that the anodic acetamidation of toluene does not involve a direct anodic oxidation of toluene (1). A mechanism was proposed in which an electroactive species, other than toluene, was oxidized to a radical which reacted with toluene to form the benzyl radical. The benzyl radical could then undergo anodic acetamidation.

When tetralin is subjected to electrolysis in the presence of sodium cyanide in methanol, side chain methoxylation is observed as the major reaction whereas, cyanation occurs only on the aromatic nucleus (2). We have verified that the mechanism of the cyanation reaction involves anodic oxidation of the aromatic species followed by reaction with cyanide ion (3) as shown for anodic acetoxylation by Eberson and Nyberg (4). Tsutsumi and coworkers (5) still favor a mechanism involving attack by cyano radical on the aromatic species. It should be pointed out that these workers do not use controlled potential techniques and therefore have no means for distinguishing between mechanisms.

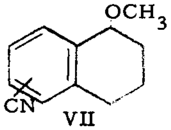
It would appear likely that nuclear substitution and side chain substitution involve different mechanisms. Tsutsumi and coworkers have postulated that side chain methoxylation results from reaction of methoxyl radical with the hydrocarbon (6). We are inclined to support this mechanism since Eberson and Nyberg's mechanism would predict that substitution by methanol and cyanide would take place on both nucleus and side chain.



We have observed that 1-methoxytetralin is formed when a methanol solution of tetralin is electrolyzed in the presence of sodium cyanide at potentials as low as +0.5V (vs. S.C.E.). At this potential no other products volatile by gas chromatography are observed in significant amounts. However, at higher potentials (+2.5V vs. S.C.E.) several products are observed including the cyano substituted compounds, VI and VII.

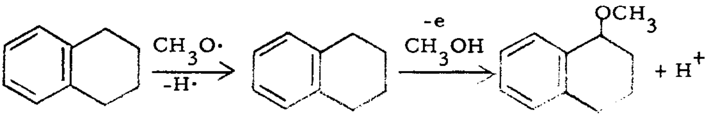


VI



VII

Tetralin has an oxidative halfwave potential of +1.87V (vs. S.C.E.) (7). We conclude that 1-methoxytetralin arises via hydrogen abstraction on tetralin since an anode potential of



+0.5V (vs. S.C.E.) is far below the potential at which tetralin would be oxidized. The observation that cyano compounds are formed at the higher potentials indicates that electrolytic oxidation of the organic substrate is involved in their formation.

The anodic oxidation of methanol is believed to occur via discharge of methoxide ion (6).

$$CH_3O^{\ominus} \longrightarrow CH_3O\cdot + e$$

Although the observation that side chain substitution occurs at anode potentials considerably lower than $E_{1/2(ox)}$ of the hydrocarbon may not be conclusive evidence that direct anodic oxidation of the hydrocarbon is not taking place, we feel that caution must be taken in accepting mechanisms for electrode reactions on the basis of the very limited available data.

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