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TRANSFORMATIONS OF DODECYL PYRIDINIUM BROMIDE

I. REACTION WITH CYANIDE ION

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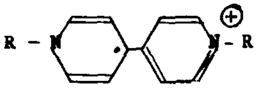
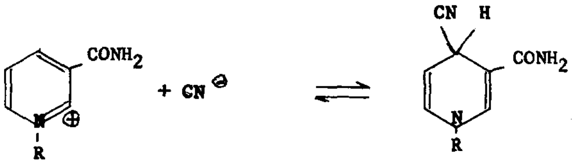
We are reporting a novel reaction of dodecyl pyridinium bromide with aqueous sodium cyanide at room temperature to form dodecyl viologen cation radical (I). This represents



I

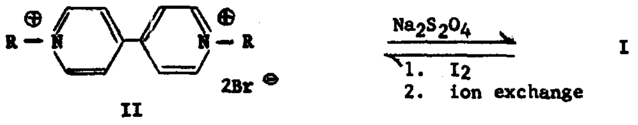
R = n - $C_{12}H_{25}$

the first example of a reaction between a simple unsubstituted pyridinium compound and cyanide ion. The addition of cyanide ion to appropriately substituted pyridinium compounds has been extensively investigated[1] and appears to require electron withdrawing substituents. The example cited below is typical and is in striking contrast to our results:



Under conditions used to generate the cation radical (I), ethyl pyridinium bromide is inert. Under more forcing conditions (prolonged heating at 100°C), the characteristic spectrum of a viologen cation radical becomes evident. The striking difference between ethyl and dodecyl pyridinium bromide in this reaction may be due to micelle formation; dodecyl pyridinium bromide undergoes micelle formation in aqueous solution at the concentrations used in our experiments.

In a typical experiment, 10 ml of degassed aqueous 0.2M NaCN solution was mixed with 10 ml of degassed aqueous .052M dodecyl pyridinium bromide solution. An aliquot was extracted from the solution and transferred to an ultraviolet-visible absorption cell which was sealed to exclude oxygen. A complex visible absorption spectrum and blue color were noted almost immediately. The intensity of the absorption spectrum increased with time. Concurrently, turbidity developed and a precipitate formed. The precipitate could be collected under nitrogen, dissolved in degassed acetonitrile to give an absorption spectrum virtually identical to that observed in the original solution. The product of the reaction was clearly demonstrated to be the dodecyl viologen cation radical (I) by independently generating I through the reduction of dodecyl viologen bromide (II) with sodium hydrosulfite. The visible spectrum of this product proved to be identical in all respects to that described above.



Furthermore, the spectrum was almost identical with the spectrum of the methyl viologen cation radical[2].

Additionally, the reaction product can be oxidized by alcoholic iodine followed by ion exchange with an Amberlite IRA-400 column to give II as demonstrated by comparison of infrared spectra. Using this procedure, we can establish a minimum yield of 25% for the conversion of dodecyl pyridinium bromide to the dodecyl viologen cation radical (I).

In following the formation of dodecyl viologen cation radical by monitoring the visible spectrum, we find no evidence for any side products or long-lived intermediates. The sensitivity of I to oxygen renders a complete product analysis by conventional separation techniques difficult.

Currently, we are investigating the detailed mechanism of the reaction, specifically with respect to the nature of the one-electron transfer involved in the sequence of steps leading from reactants to product and the importance of micelle formation. The possibility of other novel reactions of long-chain alkyl pyridinium compounds with nucleophilic reagents also is being explored.

Acknowledgement

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2. E. M. Kosower and J. L. Cotter, J. Am. Chem. Soc., 86, 5524 (1964).