Anodic Nucleophilic Displacement on Bromine

By VERNON D. PARKER and LENNART EBERSON*

(*Division of Organic Chemistry, University of Lund, Chemical Center, P.O.B. 740, S-22007, Lund, Sweden*)

Summary Nucleophilic displacement on bromine of the monolutidinium salt of the dication from 9,10-dibromoanthracene is observed during anodic lutidination.

WHILE nucleophilic displacement on carbon, hydrogen, silicon, phosphorus, and sulphur are common, displacements on halogen are rare.[1] We report the first case of anodic nucleophilic displacement on halogen. The EC_NE mechanism has been demonstrated for anodic substitution by nucleophiles[2,3] and is illustrated for 9,10-dibromoanthracene (9,10-DBA) in the Scheme. The intermediate (IV) contains two possible sites for nucleophilic attack to occur, either on bromine to give the monolutidinium ion (V) or on carbon to give the dilutidinium ion (VI).†

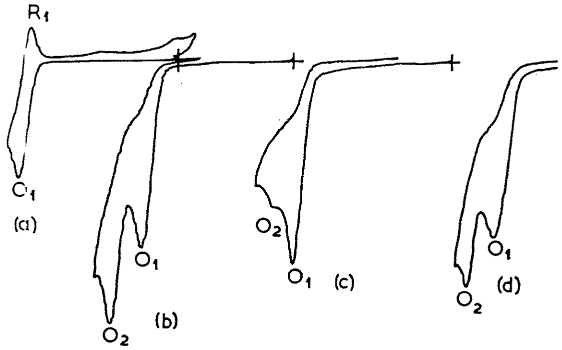
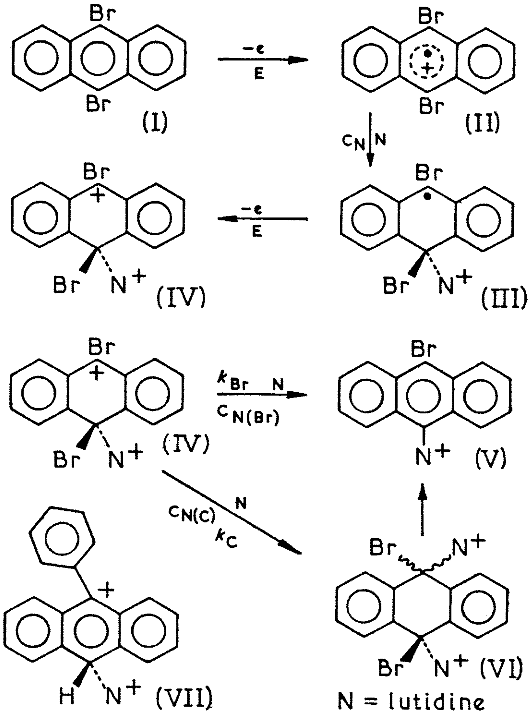


FIGURE. *Cyclic voltammograms of* 9,10-*dibromoanthracene in acetonitrile containing lithium perchlorate. Sweep rate* = 10 v/*min.* (a) *No added nucleophile,* (b) 10 mM *in* 3,5-*lutidine,* (c) 10 mM *in 2,5-lutidine,* (d) 10 mM *in 2,6-lutidine.*

The Figure (a) is the cyclic voltammogram of 9,10-DBA in acetonitrile containing lithium perchlorate as supporting electrolyte. An oxidation peak, O_1, is observed at +1·42 v (*vs.* SCE) and on reversing the direction of the scan a cathodic peak is observed at +1·34 v which is due to reduction of the cation-radical formed at the first oxidation peak. The Figure (b), (c), and (d) is for the same solution made 10 mM in 3,5-lutidine, 2,5-lutidine, and 2,6-lutidine, respectively. The first oxidation peak in the latter three cases now corresponds to the transfer of 2e and no reduction current is observed on the reverse scan. A second oxidation peak, O_2, is observed in all three cases. The height of this peak, however, is dependent on the nucleophile.‡ The solution containing 3,5-lutidine produces a second oxidation peak of nearly the same height as O_1 while the solution containing 2,5-lutidine gives a voltammetric peak, O_2, which is barely visible and 2,6-lutidine gives a voltammogram with O_2 intermediate in height between the other two cases.

Controlled potential coulometry of 9,10-DBA in the presence of 3,5-lutidine at the voltage of the first peak verifies the transfer of two electrons. The voltammogram of the resulting solution shows the presence of a single oxidation peak identical in position to O_2. The height of the oxidation peak is very nearly the same as O_1 of the solution before coulometry, showing that the substrate is quantitatively converted into an oxidation product, which undergoes voltammetric oxidation at the potential of O_2.

Coulometry in the presence of 2,5-lutidine or 2,6-lutidine was accompanied by the consumption of two Faradays per mole of substrate. Voltammetry of the resulting solutions showed single oxidation peaks, O_2, in either case considerably smaller than O_1 of the solution before coulometry. However, upon heating the solutions at the boiling point for 1 hr., the oxidation peaks increased in height to about the same height as O_1 of the original solutions. This shows that the oxidizable product can be formed by a homogeneous chemical reaction, but at a rate much too low to account for the observation of O_2 during the time-scale of cyclic voltammetry.



Controlled potential electrolysis was conducted on a solution of 9,10-DBA in acetonitrile containing 3,5-lutidine (10 mM). The product was isolated and the structure shown to be (V), in which N represents 3,5-lutidine. Voltammetry showed that (V) is oxidized at the potential of O_2. Similarly, Lund isolated and identified the monopyridinium

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† The terms nucleophile and lutidine are used interchangeably in this communication.

‡ The position of both O_1 and O_2 are dependent on the nucleophile. The voltammetry in the presence of the lutidines is summarized in the Table.

salt from electrolysis of 9,10-DBA in acetonitrile containing pyridine.[4] However, he assumed that the initial product was the unstable dipyridinium salt which decomposed to the monopyridinium salt during work-up. Our results show that this reaction indeed does occur but is slow during the time-scale of both voltammetry and coulometry and thus cannot account for the direct observation of (V) during voltammetric oxidation of 9,10-DBA.

TABLE

Voltammetry of 9,10-dibromoanthracene in the presence of lutidines

Nucleophile	O_1 (v)	O_2 (v)
3,5-Lutidine	1·24	1·48
2,5-Lutidine	1·34	1·50
2,6-Lutidine	1·36	1·56

Substrate concentration = 1·0 mM.
Nucleophile concentration = 10 mM.
Voltage scan rate = 10 v/min.

The reactions that occur are summarized in the Scheme. For the unhindered nucleophile, 3,5-lutidine, $k_{Br} \gg k_C$ (Scheme) since voltammetry shows that (V) is the only product. In the case of the more hindered nucleophile, 2,5-lutidine, $k_C \gg k_{Br}$ as shown by voltammetry, with only a small degree of attack occuring on bromine. Voltammetry indicates that k_{Br} = *ca.* k_C for the severely hindered nucleophile, 2,6-lutidine. In an analogous case, lutidination of 9-phenylanthracene takes place with the intermediate formation of (VII) which affords the nucleophile the choice of reacting at carbon or as a base at hydrogen.[5] The unhindered nucleophile, 3,5-lutidine, reacts predominantly at carbon while hydrogen is the point of attack for the two more hindered nucleophiles. The fact that the severely hindered nucleophile, 2,6-lutidine, partitions itself almost equally between bromine and carbon during reaction with (IV) indicates that the two sites are almost equally hindered. Factors other than steric hindrance must be responsible for the reverse order observed for the other two nucleophiles.

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[1] J. F. Bunnett, *Ann. Rev. Phys. Chem.*, 1963, **14**, 271.
[2] G. Manning, V. D. Parker, and R. N. Adams, *J. Amer. Chem. Soc.*, in the press.
[3] V. D. Parker and L. Eberson, *Tetrahedron Letters*, in the press.
[4] H. Lund, *Acta Chem. Scand.*, 1957, **11**, 1323.
[5] V. D. Parker and L. Eberson, *Tetrahedron Letters*, in the press.