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ANODIC OXIDATION OF ANTHRACENES AND RELATED COMPOUNDS. PART VIII (1).

OXIDATION OF A QUINONE-METHIDE.

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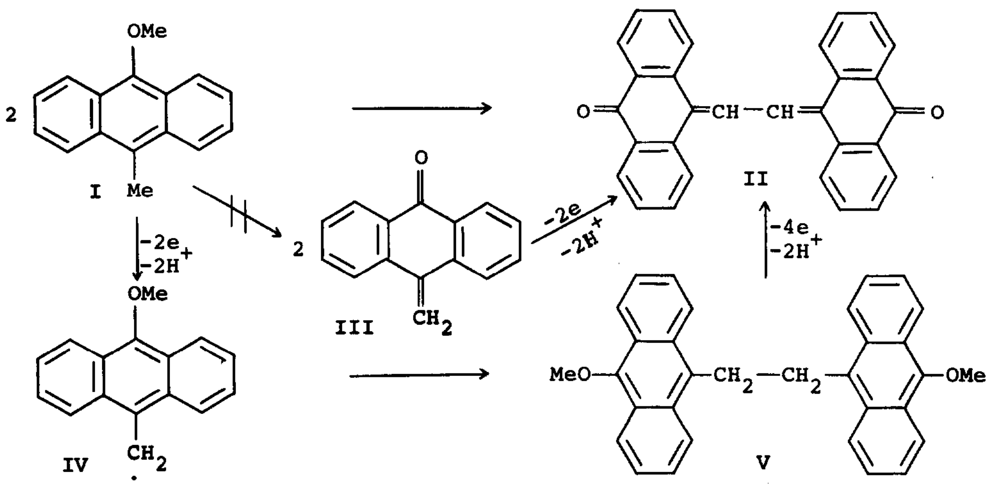
Quinone-methides are frequently suspected to be intermediates formed during the oxidation of phenols and related compounds (2). During a study of the anodic oxidation of I we observed the quantitative formation of II which could conceivably form via the quinone methide, III (Scheme). Since the quinone-methide is a stable compound, this system offered a unique case in which the oxidative behavior of the suspected intermediate could be examined.

Anodic oxidation of 10-methylene-9-anthrone in acetonitrile containing lithium perchlorate was accompanied by the precipitation of slightly soluble dimer, II, in about 50% yield. Voltammatric analysis revealed that the quinone-methide exhibited an oxidation peak at +1.9 V. (3) and that the dimeric product, II, gave an oxidation peak at +1.6 V. Thus, it is remarkable that II can be isolated in reasonable yields from oxidation of III even though it is oxidized 0.3 V. more readily than it's precursor. Cyclic voltammetry of a solution of I in the same medium showed an oxidation peak at +0.9 V. and no reduction peak was observed corresponding to the cation radical of I. This is indeed surprising since the related compounds, 9,10-dimethoxyanthracene and 9,10-dimethylanthracene both form relatively stable cation radicals in acetonitrile.

Consideration of the fact that I is oxidized about 1 volt more easily than III eliminates III as an intermediate in the formation of II even though anodic oxidation of III does produce II. The most likely mechanism for the formation of II from I is deprotonation of the initially formed cation radical to (IV)



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followed by dimerization to V. The dimer (V) could than undergo oxidative demethylation (4) yielding the dehydro dimer (II).

This is, to our knowledge, the first reported case of the anodic oxidation of a stable quinone methide. The fact that the quinone methide is oxidized so much more difficultly than the possible precursor and phenols in general makes previously proposed mechanisms in which intermediate quinone methides are oxidized appear very unlikely.

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2. For a general review of phenol oxidation see W. J. Taylor and A. R. Battersby, "Oxidative Coupling of Phenols", Marcel Dekker, New York, 1967.
3. All voltages refer to oxidation at a platinum electrode versus the aqueous saturated calomel electrode.
4. Both anodic demethylation (5) and dehydrogenation (6) of related compounds have been reported.
5. V. D. Parker, *Chem. Comm.*, 610 (1969).
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