CHEMISTRY LETTERS, pp. 643-644, 1976. Published by the Chemical Society of Japan

FORMATION OF DIPHENYL(9-PHENYL-10-ANTHRYL)METHYL, A POSTULATED INTERMEDIATE OF THE SIDE-CHAIN OXIDATION OF 9-BENZHYDRYL-10-PHENYLANTHRACENE, FROM 9,10-BENZHYDRYL-10-PHENYL-9,10-EPIDIOXYANTHRACENE IN LIQUID SULFUR DIOXIDE

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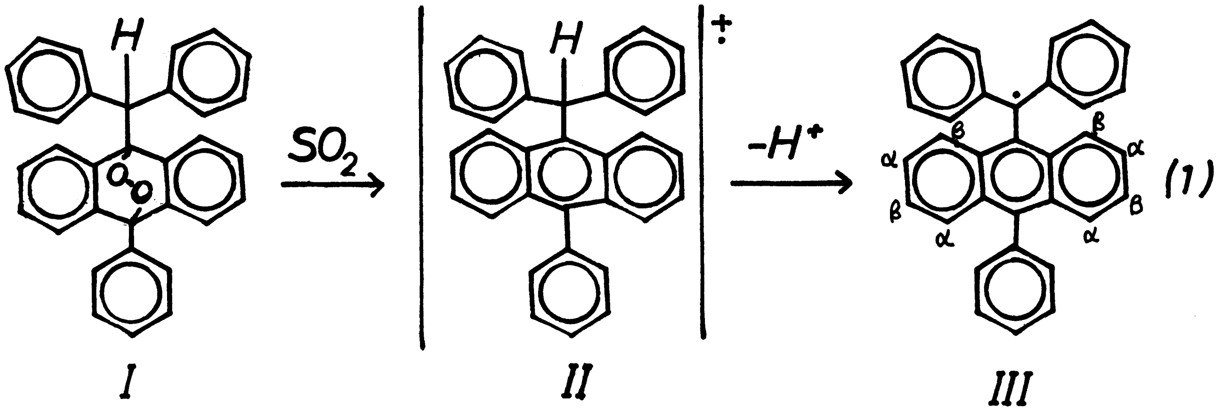
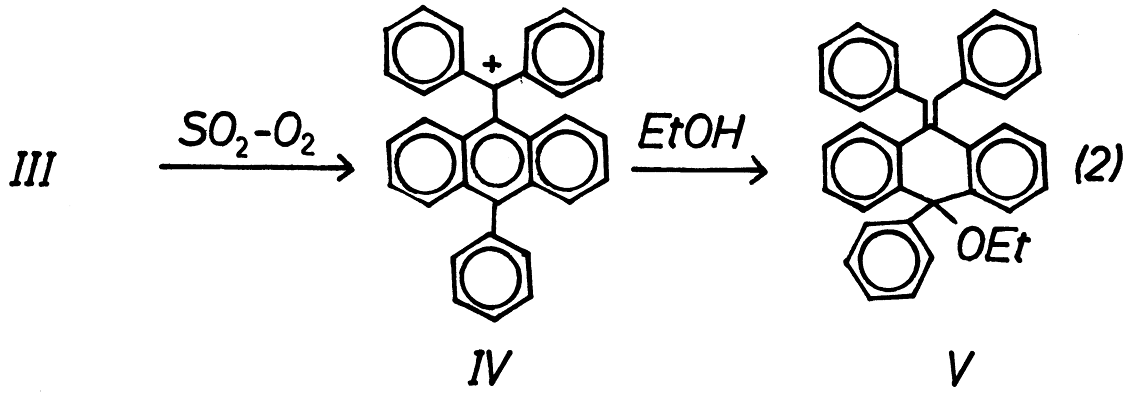
By dissolving 9,10-dihydro-9-benzhydryl-10-phenyl-9,10-epidioxyanthracene in liquid sulfur dioxide, diphenyl(9-phenyl-10-anthryl)methyl was obtained, which was conveniently oxidized to diphenyl(9-phenyl-10-anthryl)methyl cation by introducing oxygen into this solution , and after treatment with ethanol 9-ethoxy-9-phenyl-10-diphenylmethylene-9,10-dihydroanthracene was isolated.

The side-chain oxidation of alkylbenzene has been effected either electrochemically1) or by metal oxidations,2) and the proposed mechanism for this reaction was an initial one-electron transfer to give the corresponding cation radical followed by an irreversible proton loss to give a benzyl radical, which is oxidized at slightly more negative potentials. In these reactions cation radicals of polyalkylbenzenes have been observed by esr spectroscopy,3) but the detection of benzyl radicals, which may support strongly the operation of the proposed processes, has not been accomplished.4) Recently we found the novel preparation of the cation radicals of anthracene derivatives from the corresponding peroxides in sulfur dioxide.5)

To know whether the proton loss from 9-benzhydryl-10-phenylanthracene cation radical (II) in liquid sulfur dioxide occurs, we investigated the reaction of 9,10-dihydro-9-benzhydryl-10-phenyl-9,10-epidioxyanthracene (I) in this medium. When I was treated with degassed sulfur dioxide in the dark, only the formation of diphenyl-(9-phenyl-10-anthryl)methyl (III) ($a_H(\alpha)=3.7$ G, $a_H(\beta)=0.80$ G) was observed even in the first stage of the reaction,6) and the intensity of the esr signal increased during





24 hr, which did not change for a week. This result suggests the slow formation of the cation radical (II) with the rapid loss of proton to afford the neutral radical (III) (scheme 1). By introducing oxygen into this solution, III was slowly oxidized to diphenyl(9-phenyl-10-anthryl)methyl cation (IV) (λ_{max} 810 nm, ε 4600), which afforded 9-ethoxy-9-phenyl-10-diphenylmethylene-9,10-dihydroanthracene (V) (λ_{max} 290 nm, ε 8000) in a yield of 34% by the reaction with ethanol (scheme 2).

References

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6) The cation radical (II) was obtained by oxidation of 9-benzhydryl-10-phenylanthracene with conc. sulfuric acid (a_H=6.4 G, λ_{max} 716, 639, and 582 nm).

(Received April 15, 1976)