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CYCLOADDITION OF ETHYLENE DERIVATIVES WITH ISOQUINOLINIUM SALTS

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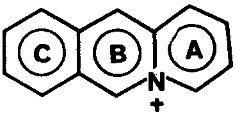
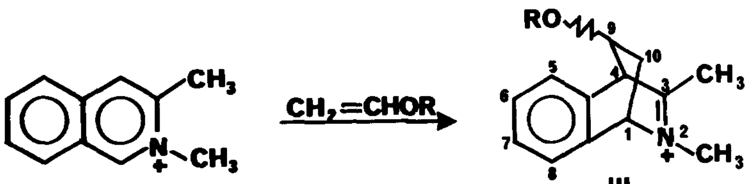
The acridizinium nucleus (I) was the first aromatic cation to undergo cycloaddition with an ethylene derivative[1]. It has been reported[2] that with suitable ethylenic derivatives cycloaddition is observed even if ring C of I is replaced by an anhydride ring, but not if replaced by a pair of methyl groups.



I

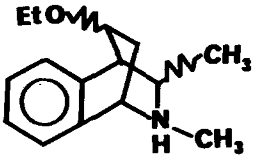
We wish to report a cycloaddition in which ring A of I is in effect replaced by a pair of alkyl groups. If 2,3-dimethylisoquinolinium iodide (II) is allowed to react for five days in acetonitrile solution with an excess of ethyl vinyl ether, in the presence of hydroquinone, an 83% yield of a colorless microcrystalline solid mp 212-215° with previous decomposition was afforded. The nmr spectrum showed a one proton quartet at 5.67 and a one proton doublet at 5.24. These chemical shifts and multiplicities for the bridgehead hydrogens suggest structure III (R=Et) as the only positional isomer. Catalytic reduction at atmospheric pressure using Adams' catalyst afforded a more stable salt (IV) as colorless prisms, mp 257-258°.

The free base from IV was a liquid which gave a mass spectrum characterized by strong peaks at m/e 231, 159, 158 and 144. These correspond to the parent ion, loss of ethyl vinyl ether, and subsequent loss of a hydrogen or methyl.

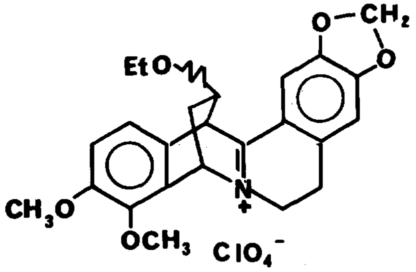


II

III



IV



V

The adduct (III, R=Et) was thermally unstable and refluxing it in acetonitrile for three hours led to recovery of 2,3-dimethylisoquinolinium iodide in quantitative yield.

The addition of butyl vinyl ether was found to afford the adduct III (R=Bu), mp 218-221° (dec.) in 60% yield.

As an illustration of the versatility of this reaction, ethyl vinyl ether was added to berberinium chloride affording V (isolated as the perchlorate) in 93% yield, mp ~300°.

Spectroscopic evidence indicates that simple isoquinolinium salts, without an alkyl group at position 3, likewise react with vinyl ethers, although no pure products have yet been obtained.

All salts described in this communication have the expected composition.

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1. C. K. Bradsher and T. W. G. Solomons, J. Amer. Chem. Soc., 80 933 (1958).
2. D. L. Fields, T. L. Regan, and Jean C. Dignan, J. Org. Chem., 33, 390 (1968).