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THE STEREOSPECIFIC NATURE OF THE CYCLOADDITION REACTION OF VINYL ETHERS WITH 2, 3-DIMETHYLISOQUINOLINIUM SALTS

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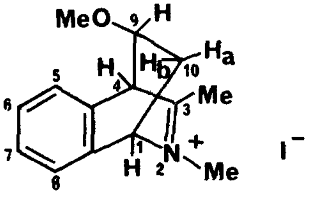
It was shown recently[1] that the addition of ethyl or n-butyl vinyl ether to 2, 3-dimethylisoquinolinium iodide occurs regiospecifically affording a good yield of the 1, 4-cycloaddition product. We now report that single crystal X-ray analysis of the methyl vinyl ether adduct (I), dec. >155°, reveals that the only stereoisomer obtained (97% yield) is the one with the methoxyl group directed over the phenylene ring. This structure would be predicted from the assumption that in the transition state the preferred orientation is that affording maximum separation of like charges. Moreover, comparison of the nmr spectrum of (I) with those for the higher homologues described earlier indicates that the reaction occurs stereospecifically and that these other compounds possess the same stereochemistry as (I).



I

Crystals of (I) are orthorhombic, space group P b c a, with $\underline{a} = 12.43$, $\underline{b} = 11.30$, $\underline{c} = 20.20$ Å, $Z = 8$. Three dimensional X-ray data were recorded by equi-inclination Weissenberg photography and visually estimated. The structure was solved by the heavy-atom method, and atomic position and anisotropic thermal parameters of the non-hydrogen atoms were refined by full-matrix least-squares calculations to the present R of 0.097 over 1659 independent reflections.

Spectral assignments of (I) are given in the Table; these were confirmed by spin-decoupling experiments operating in the frequency sweep mode. Vicinal coupling (9Hz) between the resonances at δ4.57 (H-9) and δ3.00 (H-10a) is indicative of a dihedral angle close to 0°. Geminal coupling (14 Hz) between H-10a and H-10b (δ1.78) was also observed.

Table 1

Observed Chemical Shifts of (I) in $CF_3 \cdot CO_2H$ Relative to Tetramethylsilane

Protons	δ	Multiplicity	Coupling Constants
5-8	7.78-7.38	multiplet	
1	5.75	quartet	$J_{1,10a} \sim 3Hz$
4	5.38	doublet	$J_{4,9} \sim 3Hz$
9	4.57	multiplet	$J_{9,10b} \sim 2Hz$
2(Me)	3.87	broad singlet	
9(MeO)	3.60	singlet	
10a	3.00	octet	$J_{9,10a} \sim 9Hz$
3(Me)	2.88	broad singlet	
10b	1.78	multiplet	$J_{10a,10b} \sim 14Hz$

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1. C. K. Bradsher and F. H. Day, Tetrahedron Letters, 409 (1971).