

New Route to 1*H*-Aziridines: *O*-Mesitylenesulphonylhydroxylamine Addition to Electrophilic Alkenes

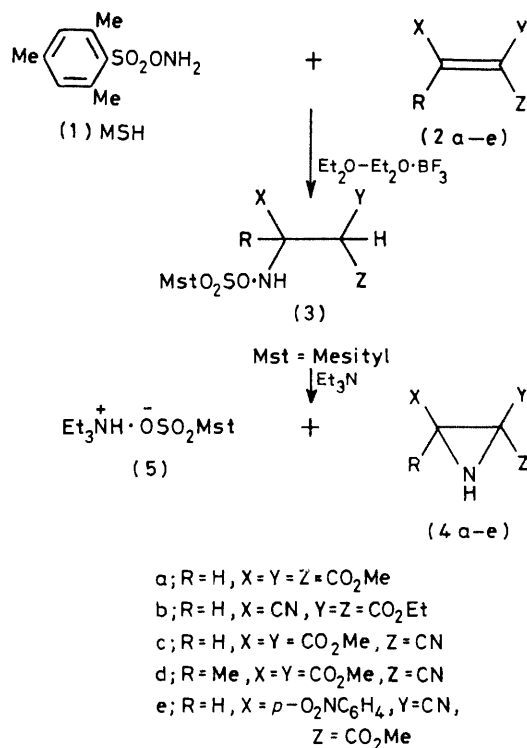
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Summary *O*-Mesitylenesulphonylhydroxylamine (MSH) reacts with electrophilic alkenes and, after treatment with triethylamine, 1*H*-aziridines are formed.

purification for analytical and spectroscopic purposes was achieved by distillation in a Kugelrohr apparatus at 3×10^{-2} mm Hg.†

IN the review of nucleophilic and electrophilic properties of MSH by Tamura,¹ the reactivity towards alkenes is not discussed, and Marmer and Maerker² have reported the failure of *O*-acylhydroxylamine addition to inactivated olefins. We now describe our preliminary results related to the successful addition of MSH(1) to electrophilic alkenes (2) with formation of 1*H*-aziridines (Scheme 1).



SCHEME 1

In a typical experiment, MSH was added under nitrogen in ether at room temperature to equimolecular amounts of (2) and Et₂O·BF₃ in ether solution. After 48 h, addition of an equivalent amount of triethylamine gave rise to the formation of a crystalline compound (5) which was filtered off; the filtrate was washed with 10% aqueous ammonium chloride, then with water, and finally dried (MgSO₄). Evaporation of ether afforded the aziridines (4) in moderate-to-good yields (Table) depending on the alkene substituents. Further

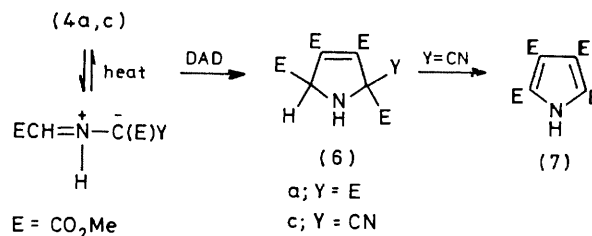
TABLE

(4)	X	Y	Z	R	% Yield†
a	CO ₂ Me	CO ₂ Me	CO ₂ Me	H	50
b	CN	CO ₂ Et	CO ₂ Et	H	90
c	CO ₂ Me	CO ₂ Me	CN	H	80
d	CO ₂ Me	CO ₂ Me	CN	Me	76
e	<i>p</i> -NO ₂ C ₆ H ₄	CN	CO ₂ Me	H	32

In the particular case of (2a) we observed after 48 h the formation of a crystalline compound (3a), the structure of which was assigned on the basis of ¹H n.m.r. and mass spectrometric analysis. Dissolution of (3a) in CH₂Cl₂ and treatment with Et₃N gave (4a) quantitatively. This result suggests primary nucleophilic attack of MSH on the alkene with formation of (3), and then removal of the most acidic hydrogen with Et₃N, followed by intramolecular substitution at the nitrogen atom. In the absence of Et₂O·BF₃ the reaction proceeds more slowly and the yields are lower, the Lewis acid probably enhancing the electrophilic character of the alkene;³ furthermore, the higher the alkene electrophilicity, the higher the yields (Table).

For all the other cases, precipitation of (3) was not observed, and triethylamine was directly added to the reaction mixture after 48 h.

In the case of (4a) and (4c) we also obtained chemical evidence of the aziridine structure by trapping the azomethine ylides, which are in thermal equilibrium with the aziridines, in the presence of dimethyl acetylenedicarboxylate (DAD) in refluxing toluene under nitrogen according to Scheme 2.



SCHEME 2.

Compound (4a) leads to the pyrrole (6a), and (4c) affords the pyrrole (7)⁴ by loss of HCN and a 1,5 hydrogen shift.

† Satisfactory spectroscopic and analytical or accurate mass data have been obtained for all new compounds. Yields were not optimized.

Finally, addition of MSH to the alkene (**2**, X = CO₂Me, Y = Z = CN, R = Me), does not lead to the desired aziridine, but results in the formation of the oxime MeO₂C(Me)C = NOSO₂Mst, presumably *via* an intermediate of type (**3**) with elimination of CH₂(CN)₂. Various attempts to

add MSH to DAD or dimethyl fumarate led only to low yields of reduction products, *i.e.* dimethyl maleate and dimethyl succinate.

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³ G. Muller and R. Merten, *Chem. Ber.*, 1965, **98**, 1097

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