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

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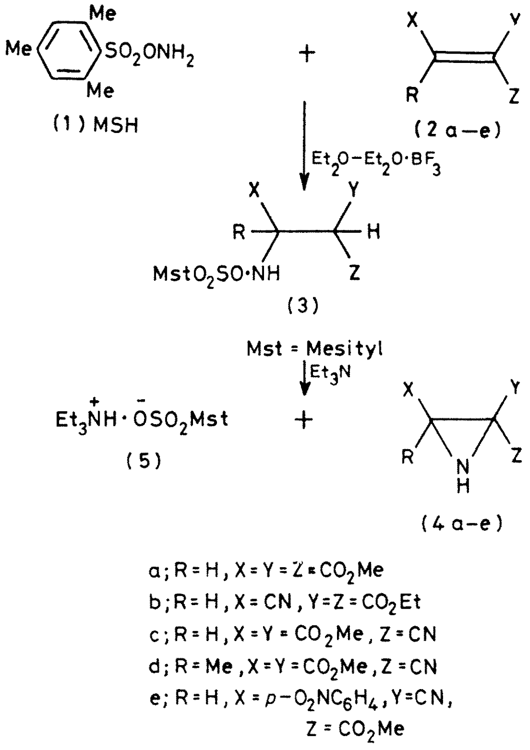
Summary *O*-Mesitylenesulphonylhydroxylamine (MSH) reacts with electrophilic alkenes and, after treatment with triethylamine, 1*H*-aziridines are formed.

In the review of nucleophilic and electrophilic properties of MSH by Tamura,[1] the reactivity towards alkenes is not discussed, and Marmer and Maerker[2] 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 $Et_2O{\cdot}BF_3$ 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 ($MgSO_4$). Evaporation of ether afforded the aziridines (**4**) in moderate-to-good yields (Table) depending on the alkene substituents. Further purification for analytical and spectroscopic purposes was achieved by distillation in a Kugelrohr apparatus at 3×10^{-2} mm Hg.†

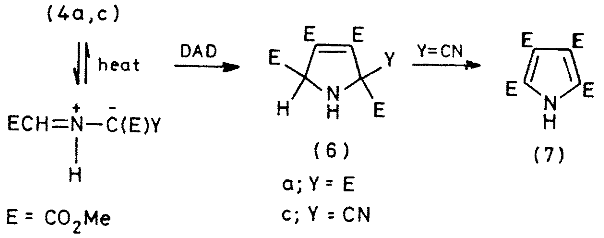
Table

(4)	X	Y	Z	R	% Yield†
a	CO_2Me	CO_2Me	CO_2Me	H	50
b	CN	CO_2Et	CO_2Et	H	90
c	CO_2Me	CO_2Me	CN	H	80
d	CO_2Me	CO_2Me	CN	Me	76
e	p-$NO_2C_6H_4$	CN	CO_2Me	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 CH_2Cl_2 and treatment with Et_3N 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 Et_3N, followed by intramolecular substitution at the nitrogen atom. In the absence of $Et_2O{\cdot}BF_3$ 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 pyrroline (**6a**), and (**4c**) affords the pyrrole (**7**)[4] by loss of HCN and a 1,5 hydrogen shift.

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† 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 = CO_2Me, Y = Z = CN, R = Me), does not lead to the desired aziridine, but results in the formation of the oxime $MeO_2C(Me)C=NOSO_2Mst$, presumably *via* an intermediate of type (**3**) with elimination of $CH_2(CN)_2$ 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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[1] Y Tamura, J Minamikawa, and M Ikeda, *Synthesis*, 1977, 1
[2] W N Marmer and G Maerker, *J Org Chem* , 1972, **37**, 3520
[3] G Muller and R Merten, *Chem Ber* , 1965, **98**, 1097
[4] R Nicolaus and G Oriente, *Gazz Chim Ital* , 1954, **84**, 230