Reactivity of 2,3-Dimethylthiiren 1,1-Dioxide as an Ambident Electrophile. Reaction with α-Metallated Nitriles

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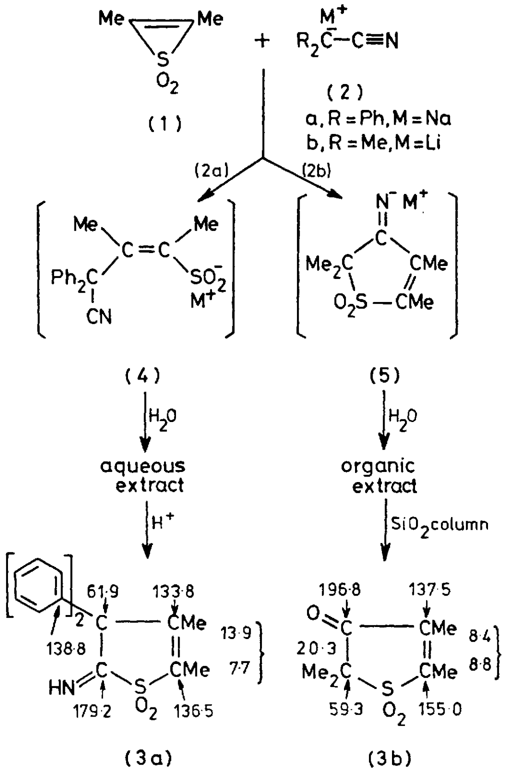
Summary 2,3-Dimethylthiiren 1,1-dioxide was found to behave as an ambident electrophile, and gave two kinds of dihydrothiophen derivatives in its reactions with α-metallated nitriles.

Recently interest has been shown from a theoretical and synthetic point of view in the reactivity of thiiren 1,1-dioxides.[1] We now report the reaction of 2,3-dimethylthiiren 1,1-dioxide (**1**)[2] with α-metallated nitriles (**2a**,**b**), as part of our studies on three-membered heterocycles as synthetic intermediates. The thiiren dioxide (**1**) was found to behave as an ambident electrophile and two kinds of dihydrothiophen derivatives (**3a**,**b**) were obtained depending on the substituents of the nitriles (**2a**,**b**).



Scheme. ^{13}C N.m.r. shifts, δ (p.p.m.; $CDCl_3$) are given for (**3a**) and (**3b**).

The thiiren (**1**) reacted readily with (**2a**) generated by treating diphenylacetonitrile with NaH in tetrahydrofuran (THF) at ambient temperature. After quenching with H_2O, no product was obtained from the organic extract except for a small amount of the starting nitrile. The aqueous layer was then made slightly acidic with dilute hydrochloric acid to afford the dihydrothiophen 1,1-dioxide (**3a**) in 84% yield.† It is interesting that (**3a**) separated out upon acidification in spite of the expected instability of such imines under acidic conditions. We assume that the precursor of (**3a**) in the aqueous extract is the sulphinate anion (**4**).

Another type of cycloadduct, the dihydrothiophen 1,1-dioxide (**3b**),‡ was obtained in 33% yield from the reaction of the thiiren (**1**) and α-lithioisobutyronitrile (**2b**). Isobutyronitrile was metallated with lithium di-isopropylamide in THF at −60 °C and the reaction with (**1**) was carried out at the same temperature for 2 h. The product (**3b**) was isolated by chromatography on silica gel (eluant: benzene–hexane) and was probably formed by hydrolysis of the 3-imino derivative during work-up.

The structural assignment of the products followed from their ^{13}C n.m.r. spectra. While the spectrum of (**3a**) seems to show normal chemical shifts for the vinyl carbons of αβ-unsaturated sulphones,[3] a large low-field shift for one of the vinyl carbons of (**3b**) is consistent with the presence of αβ-unsaturated carbonyl groups.[4] The presence of the conjugated carbonyl group was further supported by the u.v. spectrum: λ_{max} (MeOH) = 236·5 (ϵ 1·24 × 10^4) and 327·0 (ϵ 25) nm. I.r., ^{1}H n.m.r. and mass spectra and elemental analyses were also in good agreement with the assigned structures and several other possible structures were excluded by these data.

The above results suggest that the thiiren dioxide acts as an ambident electrophile: the vinyl carbons are the electrophilic sites in the reaction with (**2a**), but the sulphur atom is attacked by the anion from (**2b**) followed by ring opening and recyclisation to the intermediate (**5**). Thus the reaction is highly sensitive to the nucleophilicity of the anions.

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† M.p. 162·5—164 °C (decomp.); ν_{max} (Nujol) 1670 and 1640 cm^{-1}; *m/e* 311 (M^+).

‡ M.p. 84—85 °C; ν_{max} (Nujol) 1710 and 1640 cm^{-1}; *m/e* 188 (M^+).

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