

## Studies on the Addition of Nitrile Oxides to 1-Phenylthiobuta-1,3-diene, a New Directed Aldol Condensation

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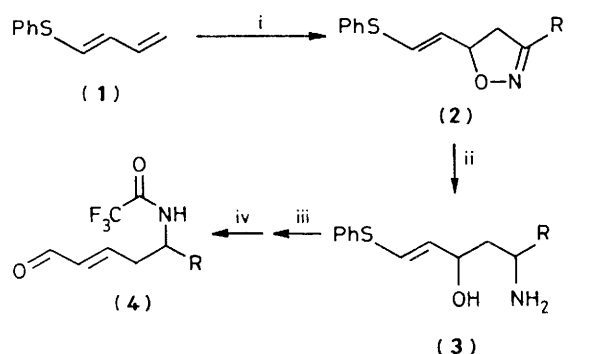
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Addition of nitrile oxides to 1-phenylthiobuta-1,3-diene is regiospecific, allowing preparation of the hitherto unknown amino phenylthioallylic alcohols (**3**) and hence the unsaturated aldehydes (**4**).

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Although the addition of nitrile oxides to alkenes has been extensively studied,<sup>1</sup> their reactions with dienes have received little attention.<sup>2</sup> We find that the reaction of 1-phenylthio-

buta-1,3-diene (**1**) with nitrile oxides is regiospecific, thus permitting the preparation of the amino alcohols (**3**), a class of compounds possessing latent enone functionality.<sup>3</sup> We



R	(a)	(b)	(c)	(d)	(e)	(2f) and (3f)
	Me	Et	Ph	CH <sub>2</sub> Ph	CH <sub>2</sub> CH=CH <sub>2</sub>	CO <sub>2</sub> Et
Yield (2)/%	65	56	61	58	44	82
Yield (4) <sup>a</sup> /%	31	33	26	25	26	— <sup>b</sup>

<sup>a</sup> Overall yield from (1). <sup>b</sup> Compound too unstable to permit isolation.

*Reagents:* i, R-C=N<sup>+</sup>-O<sup>-</sup>; ii, LiAlH<sub>4</sub>; iii, (CF<sub>3</sub>CO)<sub>2</sub>O-Na<sub>2</sub>CO<sub>3</sub>; iv, HgCl<sub>2</sub>-MeCN.

further show that the alcohols (3) are easily converted into the unsaturated aldehydes (4), a new class of compound with great synthetic potential.

The adducts (2a–f) were prepared by procedure A or B:

*Procedure A:* A solution of triethylamine (2 mmol) and nitroalkane (10 mmol) in benzene (10 ml) was added as drops to a well stirred solution of (1) (10 mmol) and phenyl isocyanate (20 mmol) in dry benzene (50 ml). The reaction mixture was stirred for 24 h, filtered, and concentrated. Chromatography of the residue on silica gave the adducts (2a–e).

*Procedure B:* Triethylamine (20 mmol) in ether (5 ml) was added as drops over 1 h to a stirred solution of (1) (10 mmol) and the hydroxamic acid chloride<sup>4</sup> (10 mmol) at –20 °C under nitrogen. The reaction mixture was stirred at room temperature for a further 1 h, filtered, and concentrated. Chromatography of the residue on silica gave the adducts (2d) and (2f).

Reduction of the adducts (2a–f) with LiAlH<sub>4</sub> in boiling ether<sup>5</sup> followed by trifluoroacetylation<sup>6</sup> and hydrolysis with mercuric chloride in wet acetonitrile<sup>3</sup> gave the aldehydes (4a–f).†

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† All compounds were fully characterised.