

## Direct Conversion of Allylic Nitro Compounds into Allyl Sulphides and Allyl Sulphones

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Allylic nitro compounds are directly converted into allyl sulphides or allyl sulphones with high regioselectivity on treatment with sodium benzenethiolate alone or with sodium benzenesulphinat in the presence of a catalytic amount of Pd(PPh<sub>3</sub>)<sub>4</sub>.

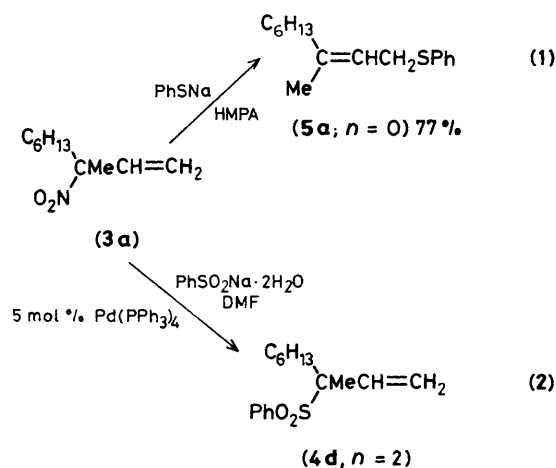
As aliphatic nitro compounds are available from various sources and undergo regio- and stereo-selective carbon-carbon bond forming reactions under mild conditions,<sup>1</sup> reactions which result in the replacement of a nitro group by another group are of considerable interest. Thus, direct replacement of a nitro group by hydrogen is a useful synthetic tool.<sup>2</sup> We now describe the replacement of the nitro group of allylic nitro compounds by organosulphur groups.

When the allylic nitro compound (**3a**) was treated with a solution of sodium benzenethiolate in hexamethylphosphoric triamide (HMPA) at 50 °C for 15 h, smooth conversion into the allyl sulphide (**5a**; *n* = 0) occurred, the nucleophile attacking the less hindered position regioselectively.

On the other hand, sodium benzenesulphinat did not react with (**3a**) at all even after prolonged periods in HMPA. However, on addition of a catalytic amount of Pd(PPh<sub>3</sub>)<sub>4</sub> a smooth reaction occurred in dimethylformamide (DMF) and the allyl sulphone (**4d**; *n* = 2) was obtained in good yield, the nucleophile attacking the more hindered position. Reaction (2) is catalysed by palladium, but reaction (1) is inhibited; in the presence of Pd(PPh<sub>3</sub>)<sub>4</sub> (5 mol %), reaction (1) gave only traces of (**5a**; *n* = 0), diphenyl disulphide being the main product. The results for various allylic nitro compounds are summarized in Table 1.

The cyclic allylnitro compounds (**1**) were readily prepared by the reaction of cyclic ketones with nitromethane,<sup>1</sup> followed

by reaction with electrophiles. The acyclic compounds (**3**) were also readily prepared either by introduction of a vinyl group into nitroalkanes<sup>3</sup> or isomerization of nitro-alkenes.<sup>4</sup> The regioselectivity of the present reaction is of special interest. The reactions of (**1**) gave (**2**) without allylic rearrangement. In acyclic systems, attack by PhS<sup>-</sup> occurred at the less hindered position while palladium-catalysed reactions with PhSO<sub>2</sub><sup>-</sup> led to substitution at the more hindered position to give (**4**) exclusively.† It is rather difficult to get compounds (**4**) selectively by other methods, for most allylic substitution



**Table 1.** Preparation of allyl sulphides and allyl sulphones.

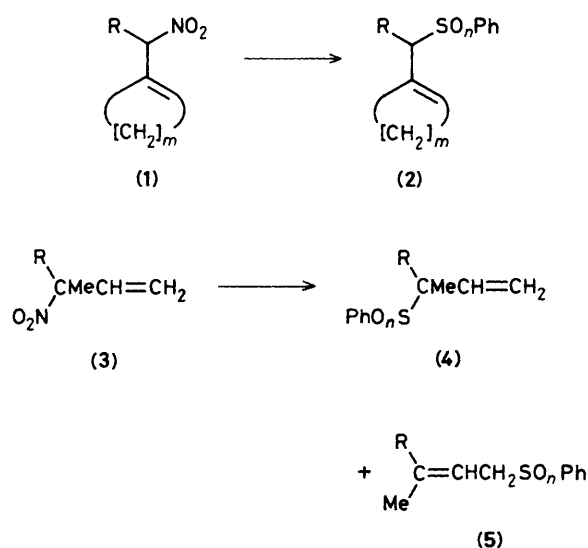
(a) From cyclic allylic nitro compounds (**1**)

Starting compound (1)					
R	<i>m</i>	<i>n</i>	Method <sup>a</sup>	% Yield of (2)	
a	H	3	0	A	62
b	[CH <sub>2</sub> ] <sub>2</sub> COMe	3	0	A	60
c	H	4	0	A	63
d	H	2	2	B	70
e	H	3	2	B	73
f	Me	3	2	B	75

(b) From acyclic allylic nitro compounds (**3**)

Starting compound (3)				% Yield	
R	<i>n</i>	Method <sup>a</sup>	(4)	(5) (E/Z)	
a	<i>n</i> -C <sub>6</sub> H <sub>13</sub>	0	C	0	77(77/23)
b	Ph	0	C	0	75(96/4)
c	[CH <sub>2</sub> ] <sub>2</sub> COMe	0	C	0	65(70/30)
d	<i>n</i> -C <sub>6</sub> H <sub>13</sub>	2	B	96	trace
e	[CH <sub>2</sub> ] <sub>2</sub> COMe	2	B	80	4
f	[CH <sub>2</sub> ] <sub>2</sub> CO <sub>2</sub> Me	2	B	76	trace

<sup>a</sup> Method A: PhSNa, HMPA, 50 °C, 2 h; B: PhSO<sub>2</sub>Na·2H<sub>2</sub>O, DMF, Pd(PPh<sub>3</sub>)<sub>4</sub> (5 mol %), room temp., 10 h; C: PhSNa, HMPA, 50 °C, 15 h.



† If excess of triphenylphosphine is present in the catalyst, (**4**) isomerizes to (**5**). The presence of sodium nitrite depresses this isomerization.

(by palladium-catalysed or non-catalysed reactions) takes place at the less hindered position.‡ Furthermore, allyl sulphones are readily isomerized to thermodynamically more stable isomers by various catalysts including palladium(0).<sup>5</sup>

The mechanism of the present reaction is also interesting, for there are few examples of the nitro group acting as a leaving group in nucleophilic substitution reactions,<sup>6</sup> and this and other synthetic applications are being studied.

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‡ Palladium-catalysed alkylation or amination of (3) takes place at the less hindered position selectively.<sup>3,4</sup>

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- 3 N. Ono, I. Hamamoto, and A. Kaji, *J. Chem. Soc., Chem. Commun.*, 1982, 821.
- 4 R. Tamura and L. S. Hegedus, *J. Am. Chem. Soc.*, 1982, **104**, 3727; R. Tamura, K. Hayashi, Y. Kai, and D. Oda, *Tetrahedron Lett.*, 1984, 4437;  $\alpha$ -nitro-alkenes were directly used as allylic nitro compounds, since they readily isomerize to the allylic forms under basic conditions. Similarly allyl sulphones were prepared by the reaction of  $\alpha$ -nitro-alkenes with sodium benzenesulphinate in the presence of triethylamine with Pd catalysis.
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