

## Synthesis of (*E*)- and (*Z*)-1-Thiocyanatobuta-1,3-dienes and their Diels–Alder Reaction

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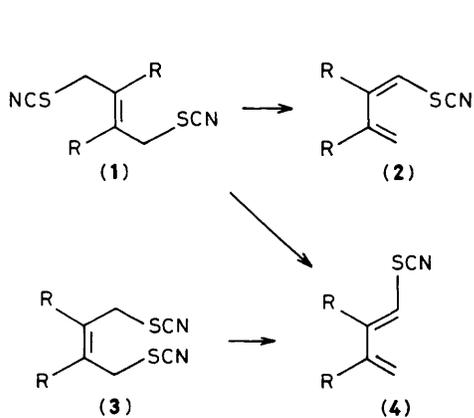
1-Thiocyanatobuta-1,3-dienes react with strong dienophiles to produce directly the rearranged products of type (6) via a combination of a Diels–Alder reaction with a [3,3] sigmatropic shift.

Functionalized 1,3-dienes are of great importance in Diels–Alder reactions, especially if the substituent can easily be transformed after the cycloaddition reaction.<sup>1</sup> Of particular synthetic interest are those 1,3-dienes which can undergo a [4 + 2] cycloaddition followed by a rearrangement reaction, e.g. a [2,3] sigmatropic reaction or the reaction of an allyl silane with electrophiles.<sup>2</sup> The combination of a cycloaddition reaction and a rearrangement reaction yields substituted cyclohexene derivatives which may be otherwise inaccessible via the direct Diels–Alder reaction.

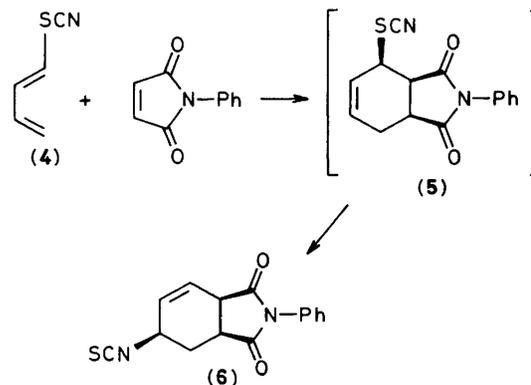
We report the synthesis of (*E*)- and (*Z*)-1-thiocyanatobuta-1,3-dienes in two steps from readily available starting

materials (Scheme 1).† The (*E*)-1-thiocyanatobuta-1,3-dienes (4) react with reactive dienophiles like *N*-phenylmaleimide. The product isolated from this reaction is not the Diels–Alder adduct (5) but the allylically rearranged isomeric isothiocyanate (6) (Scheme 2). These isothiocyanates are attractive intermediates for further transformations.

The dithiocyanates (1) and (3) can be synthesized either by addition of thiocyanogen to the corresponding dienes<sup>4</sup> or by the substitution of the appropriate 1,4-dihalogenobut-2-enes with potassium thiocyanate.<sup>5</sup> The dithiocyanates (1) and (3) could be smoothly transformed into the substituted dienes



a; R = H  
 b; R = Me  
 Scheme 1



Scheme 2

† In the literature only the synthesis of 2-thiocyanatobuta-1,3-diene has been described.<sup>3</sup>

**Table 1.** Formation of dienes (**2a**), (**4a**), and (**4b**).<sup>a</sup>

Starting material	Product	Yield/%	Characterisation
( <b>1a</b> )	( <b>2a</b> )	60	Isolated as the mixture of isomers
	( <b>4a</b> )	15	
( <b>3a</b> )	( <b>4a</b> )	85	Isolated product ( <i>E</i> ) > 95%
( <b>1b</b> )	( <b>4b</b> )	85	Isolated product ( <i>E</i> ) > 95%

<sup>a</sup> All new compounds were fully characterized by i.r. and n.m.r. spectroscopy and where appropriate also by elemental analysis and mass spectra.

**Table 2.** Diels–Alder reaction of the dienes (**2**) and (**4**).

Starting material	Dienophile	Conditions	Yield/%
( <b>4a</b> )	<i>N</i> -phenyl-4 <i>H</i> - <i>s</i> -triazolodione	CDCl <sub>3</sub> , 1 h, 20 °C	<sup>a</sup>
	TCNE <sup>b</sup>	EtOAc, 6 h, 60 °C	70 <sup>c</sup>
	<i>N</i> -phenylmaleimide	toluene, 12 h, reflux	70
( <b>2a</b> ) + ( <b>4a</b> ) <sup>d</sup>	<i>N</i> -phenylmaleimide	toluene, 42 h, reflux	45
( <b>4b</b> )	<i>N</i> -phenyl-4 <i>H</i> - <i>s</i> -triazolodione	CH <sub>2</sub> Cl <sub>2</sub> /1 h/0 °C	42

<sup>a</sup> The n.m.r. spectrum of the reaction mixture showed complete transformation of the diene. <sup>b</sup> TCNE = tetracyanoethylene. <sup>c</sup> The product of the reaction with TCNE is the non-rearranged thiocyanate. <sup>d</sup> The mixture (**2a**):(**4a**) = 60:15 was used for this reaction.

(**2**) and (**4**) by treatment with base. The use of 1,8-diazabicyclo[5.4.0]undec-7-ene for this elimination proved to be advantageous because it reduced considerably the amount of side products. Starting with the (*E*)-butene (**1a**) the (*Z*)-butadiene (**2a**) was preferentially formed (**2a**:**4a** = 80:20) while the elimination reaction of the (*E*)-butene (**1b**) produced the (*E*)-butadiene (**4b**) in 85% isolated yield (Table 1). The (*E*)-substituted butadiene (**4a**) could be synthesized in 85% yield starting with the (*Z*)-substituted butene (**3a**). The stereochemistry of these transformations corresponds to a transition state for the elimination reaction where the thiocyanato group is preferentially synclinal to the double bond for the reaction starting from (**1a**), whereas the thiocyanato group is in an anticlinal orientation for the reaction starting from (**3a**).

The dienes (**2a**), (**4a**), and (**4b**) reacted in a [4 + 2] cycloaddition followed by the [3,3] sigmatropic rearrangement in moderate to good yields only with very reactive dienophiles like *N*-phenyl-4*H*-*s*-triazolodione and *N*-phenylmaleimide (Table 2). The relative configuration of (**6**) was determined from the n.m.r. spectrum of the aniline adduct of (**6**). The configuration corresponds to a Diels–Alder reaction passing through an *endo* transition state.

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## References

- M. Petrzilka and J. I. Grayson, *Synthesis*, 1981, 753.
- D. A. Evans, C. A. Bryan, and C. L. Sims, *J. Am. Chem. Soc.*, 1972, **94**, 2891; M. J. Carter and I. Fleming, *J. Chem. Soc., Chem. Commun.*, 1976, 679; T. H. Chan and I. Fleming, *Synthesis*, 1979, 761.
- M. Kotake, J. Mitu, and Y. Mikami, *Nippon Kagaku Kaishi*, 1941, **62**, 88; *Chem. Abstr.*, 1943, **37**, 4055.
- E. G. Kataev and M. F. Obukhova, *Uch. Zap. Kazan. Gos. Univ.*, 1953, **113**, 125; *Chem. Abstr.*, 1958, **52**, 3691c; E. Müller and A. Freytag, *J. Prakt. Chem.*, 1936, **146**, 58; H. A. Brusen and W. A. Calvert, *J. Am. Chem. Soc.*, 1928, **50**, 1735.
- J. v. Braun and G. Lemke, *Ber. Dtsch. Chem. Ges. B*, 1922, **55**, 3536; L. H. Amundsen, R. H. Mayers, L. S. Pitts, and L. A. Malentacchi, *J. Am. Chem. Soc.*, 1951, **73**, 2118.