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

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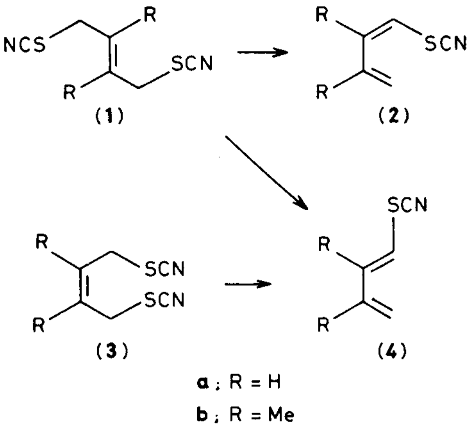
1-Thiocyanatobuta-1,3-dienes react with strong dienophiles to produce directly the rearranged products of type (**6**) *via* a combination of a Diels–Alder reaction with a [3,3] sigmatropic shift.

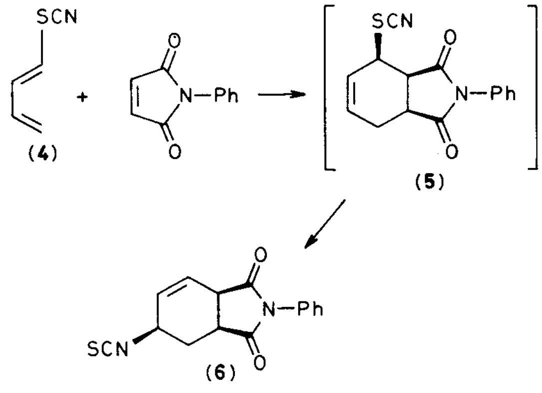
Functionalized 1,3-dienes are of great importance in Diels–Alder reactions, especially if the substituent can easily be transformed after the cycloaddition reaction.[1] Of particular synthetic interest are those 1,3-dienes which can undergo a [4 + 2] cycloaddition followed by a rearrangement reaction, *e.g.* a [2,3] sigmatropic reaction or the reaction of an allyl silane with electrophiles.[2] 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[4] or by the substitution of the appropriate 1,4-dihalogenobut-2-enes with potassium thiocyanate.[5] The dithiocyanates (**1**) and (**3**) could be smoothly transformed into the substituted dienes



Scheme 1



Scheme 2

Table 1. Formation of dienes (**2a**), (**4a**), and (**4b**).[a]

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

[a] 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/%
(**4a**)	*N*-phenyl-4*H*-*s*-triazoledione	$CDCl_3$, 1 h, 20 °C	[a]
	TCNE[b]	EtOAc, 6 h, 60 °C	70[c]
	N-phenylmaleimide	toluene, 12 h, reflux	70
(**2a**) + (**4a**)[d]	*N*-phenylmaleimide	toluene, 42 h, reflux	45
(**4b**)	*N*-phenyl-4*H*-*s*-triazoledione	CH_2Cl_2/1 h/0 °C	42

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

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† In the literature only the synthesis of 2-thiocyanatobuta-1,3-diene has been described.[3]

(**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*-triazoledione 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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