Synthesis of New Vinyl Thiocyanates by [3,3] Sigmatropic Rearrangement of Isothiocyanates[‡]

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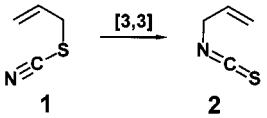
Dedicated to Professor Harald Günther on the occasion of his 65th birthday

Keywords: Alkynes / Allenes / Dienes / Isothiocyanates / Rearrangements / Thiocyanates

Propargyl isothiocyanates **3** and buta-2,3-dienyl isothiocyanates **20** were prepared conventionally from amines and thiophosgene, or by a new, one-pot procedure using nucleophilic substitution to generate azides, which in turn served as the starting materials for a Staudinger reaction, followed by treatment of the resulting iminophosphoranes or iminophosphates with CS_2. Equilibration, through a [3,3] sigmatropic rearrangement, of **3** and the allenyl thiocyanates **4** was established by flash vacuum pyrolysis or by thermolysis in solution. Even the reversible isomerization of the parent compounds **3f** and **4f** favors the allenyl thiocyanate. In the case of **20**, an irreversible rearrangement reaction gave high yields of 2-thiocyanatobuta-1,3-dienes **21**. A sequence of two [3,3] migration steps transformed 1,4-diisothiocyanatobut-2-ynes **3m** and **3n** into 2,3-dithiocyanatobuta-1,3-dienes **21m** and **22**, respectively. These reactions demonstrate that the [3,3] sigmatropic rearrangement of mustard oils, to afford high yields of thiocyanates bearing the thermodynamically less stable functional group, is possible if the conversion gives rise to a more stable carbon skeleton. The equilibration of 1-thiocyanatopent-2-en-4-ynes **12** and 1-thiocyanatopenta-1,2,4-trienes **14** could be explained by tandem [3,3]–[3,3] sigmatropic rearrangements through short lived 3-isothiocyanatopent-1-en-4-ynes **13**. Thiocyanato-substituted vinylallenes **4k** and **14** tended to electrocyclize to give cyclobutenes **7** and **15**, respectively. Thiocyanates **21a**, **21b**, **21m** and **14a**, which exhibit a buta-1,3-diene structure, could be used in Diels–Alder reactions to afford the cycloadducts **25a**, **25b**, **26a**, **26m**, **28m**, **29m**, and **30**.

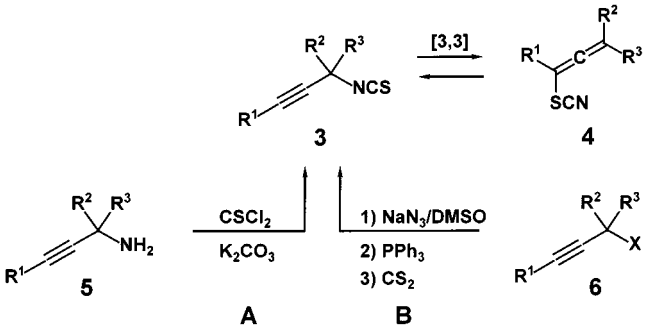
Introduction

As a rule, thiocyanates have not been prepared by isomerization of isothiocyanates, since the latter prove to be the thermodynamically more stable compounds.[1] Thus, rearrangements of thiocyanates to give mustard oils through ionization-recombination or [3,3] sigmatropic migration,[2] such as the transformation **1** → **2** (Scheme 1),[3] are irreversible processes in most cases. However, the difference in the thermodynamic stabilities of thiocyanates and isothiocyanates is not insurmountably high.[4,5] Therefore, we reasoned that the isomerization of mustard oils to afford high yields of thiocyanates by [3,3] sigmatropic rearrangement might be possible if the reaction gives rise to a more stable carbon skeleton. Here we report the synthesis of new types of vinyl thiocyanates from easily accessible isothiocyanates.



Scheme 1. Irreversible [3,3] sigmatropic rearrangement of allyl thiocyanate **1**

Several methods to prepare allenyl thiocyanates have been developed;[6,7] however, literature evidence of [3,3] sigmatropic rearrangements of propargyl isothiocyanates **3** to give **4** is rather rare (Scheme 2).[8] Moreover, early reports[6] on propargyl isothiocyanates **3a**–**e** and allenyl thiocyanates **4c** and **4d** arrived at the conclusion that the sigmatropic migration is always an irreversible process favoring **3** (Table 1).



Scheme 2. Synthesis of propargyl isothiocyanates **3** and equilibration of isothiocyanates **3** and allenyl thiocyanates **4** by [3,3] sigmatropic rearrangement; for the key see Table 1 and Table 2

Results and Discussion

Rearrangements of Propargyl Isothiocyanates

We have prepared isothiocyanates **3** by conventional[9] treatment of amines **5** with thiophosgene and potassium

[‡] Rearrangement Reactions, 9. – Part 8: K. Banert, W. Fendel, A. Müller, B. Müller, J. Schlott, *Phosphorus Sulfur Silicon Relat. Elem.* **1999**, 153–154, 325–326.

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Table 1. Equilibria of propargyl isothiocyanates **3** and allenyl thiocyanates **4**

3/4	R^1	R^2	R^3	Ratio **3/4** ref.[6]	Ratio **3/4** starting with **3** or **4**	Yield [%][a]
a	*n*-C_3H_7	CH_2CH_2Ph	H	100:0	90:10	ca. 100
b	*n*-C_3H_7	-$CH_2CH_2CH_2$-		100:0	99.5:0.5	94
c	*n*-C_3H_7	H	H	100:0	83:17	77
d	*n*-C_3H_7	Et	H	100:0	86:14	96
e	*n*-C_3H_7	Me	Me	100:0	65:35	89
f	H	H	H		33:67	97
g	H	Me	Me		15:85	ca. 100
h	Me	H	H		78:22	93
i	CH_2Cl	H	H		55:45	91
j	H	Ph	H		0:100	ca. 100

[a] The yields were based on the mixtures **3/4** recovered after flash vacuum pyrolysis of **3c** and **3f**−**i** at 400 °C, or of **3d** and **3e** at 300 °C. In the case of **4j**, the yield was relative to **3j** after keeping in CH_2Cl_2 for 24 h at 20 °C. The yields of the recovered equilibrium mixtures **3a/4a** and **3b/4b** were measured by ^1H NMR spectroscopy (standard) after thermolysis in $CDCl_3$ at 60 °C.

carbonate (Method A, Table 2). Alternatively, **3** may be synthesized by a novel, one-pot procedure starting with a compound **6** bearing a leaving group X, such as X = Br, OTs, OMs (Table 2). Nucleophilic substitution in the presence of sodium azide in dry DMSO, followed by a Staudinger reaction to transform the azide into an iminophosphorane, and final treatment with CS_2, resulted in the product **3** (Method B). Mixtures of **3a/4a**, **3b/4b**, or **3e/4e** were prepared by Zbiral′s method.[6] Thanks to the gentle workup, we have been able to characterize **4a**, **4b**, and **4e** for the first time.

Table 2. Synthesis of isothiocyanates **3** from **5** (Method A) or **6** (Method B), see also Scheme 2

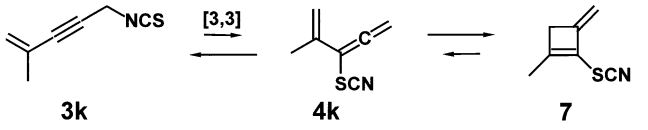
3	R^1	R^2	R^3	Method	Yield [%][a]
c	*n*-C_3H_7	H	H	B (X = Br)	36
d	*n*-C_3H_7	Et	H	B (X = OMs)	66
f	H	H	H	B (X = OTs)	52
g	H	Me	Me	A	92
h	Me	H	H	B (X = OTs)	61
i	CH_2Cl	H	H	A[b]	67
j	H	Ph	H	A	84
k	$CMe=CH_2$	H	H	B (X = Br)	28
l	H	$CH_2CH_2CH=CH_2$	H	B (X = OMs)	44

[a] Isolated yield of **3**. − [b] The hydrochloride of the amine **5i** was used.

We established the equilibration of **3** and **4** by flash vacuum pyrolysis of **3c**−**i** and by thermolysis of **3a**, **3b**, **3d**, **3e**, **3g**, and **3j** in solution (Table 1). The equilibria **3** ⇄ **4** were confirmed by renewed flash vacuum pyrolysis of **4c**−**i** and by heating of solutions of **4a**, **4b**, **4d**, **4e**, and **4g** − each compound isolated by liquid chromatography. On heating a solution of **3f**, the generation of **4f** was accompanied by several side reactions. However, the propargyl precursor **3j** underwent a clean, irreversible rearrangement to afford **4j** even in solution at room temperature, because a product with conjugated C=C bonds was formed. Furthermore, the equilibria **3b** ⇄ **4b** and **3g** ⇄ **4g** could also be observed in solution at room temperature. In general, equilibration of compounds **3**, which bear several alkyl groups, is already possible at lower temperatures. Some of these compounds, such as **3b**, **3d**, and **3e**, tended to eliminate thiocyanic acid during flash vacuum pyrolysis at higher temperatures to give hydrocarbon products. In the case of **4b**, the rearrangement to **3b** proceeded nearly irreversibly, since the bond angle strain of **4b** was increased by the sp^2 hybridized carbon atom in the four-membered ring. However, even the equilibration of the parent compounds **3f** and **4f** favored the allenyl thiocyanate, and the substituents R^1, R^2, and R^3 exercise a plausible influence on the position of the equilibria. For example, an alkyl substituent R^1 stabilizes the alkyne **3** more effectively than the allene **4**. On the other hand, alkyl substituents R^2 and R^3 favor the allenyl compound **4**. Thus, we have demonstrated that thiocyanates **4a**−**e** do not isomerize irreversibly to yield the mustard oils **3a**−**e**, respectively, as had previously been erroneously stated.[6b] In comparison with the analogous equilibrations of propargyl thiocyanates and allenyl isothiocyanates,[10,11] however, the positions of the equilibria **3f** ⇄ **4f**, **3h** ⇄ **4h**, and **3i** ⇄ **4i** are shifted significantly towards the propargyl compounds **3**.

In the case of **3k**, flash vacuum pyrolysis not only gave the rearrangement product **4k**, but also afforded cyclobutene **7**, which resulted from an electrocyclic ring-closure of **4k**. The data show that the isomerization of **3k** starts at temperatures as low as 300 °C (Table 3, entry 1). At higher temperatures, an equilibrium of **3k**, **4k**, and **7** is most probably established (Table 3, entries 2 and 3).

Table 3. Flash vacuum pyrolysis of **3k**



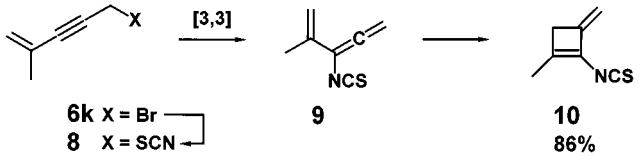
3k **4k** **7**

Entry	Temperature [°C]	Yields[a] of **3k** + **4k** + **7**	Ratio of products **3k**	**4k**	**7**
1	300	90	80	10	10
2	400	87	26	5	69
3	450	85	30	6	64

[a] Yields were based on weighed mixtures of **3k**, **4k**, and **7**.

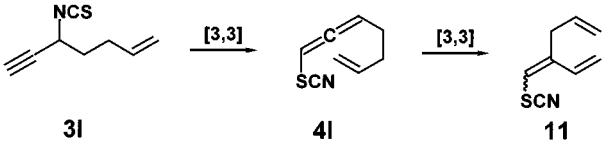
The thiocyanate **8** is easily accessible from bromide **6k**[12] (62% yield), and its flash vacuum pyrolysis at 400 °C, investigated for comparison, exclusively afforded isothiocyanate **10**, in a yield of 86% (Scheme 3). The intermediate **9** could be observed when the pyrolysis of **8** was performed at lower temperatures (270−320 °C). Whereas the isothiocyanatocyclobutene **10** was very unstable and could only be handled in solution, it was possible to isolate the analogous thiocyanate **7** by flash chromatography.

Flash vacuum pyrolysis of **3l** at 300 °C resulted in allene **4l** (47% yield) and buta-1,3-dienes **11** (16%, mixture of geometrical isomers 1:1.1), besides the starting material **3l** (8%). Clearly, **11** represents a product of a Cope rearrange-



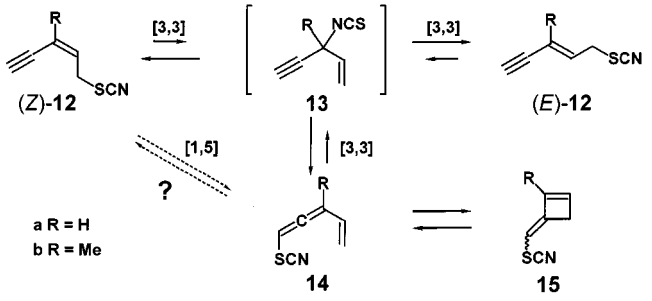
Scheme 3. Synthesis and rearrangement of thiocyanate **8**

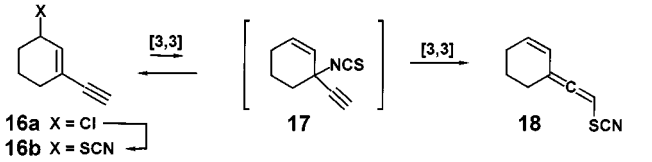
ment of **4l** (Scheme 4). Thus, on pyrolysis of **3l** at higher temperatures (400−500 °C) the amounts of recovered **3l** and allene **4l** were smaller, while **11** became the main product. In this case, however, the overall yield was reduced, due to several secondary reactions. Therefore the sequence of [3,3] sigmatropic rearrangements is not a straightforward method for the synthesis of **11**, whereas the analogous transformation of 1-ethynylpent-4-enyl thiocyanate gave the isomerization product (*E*)-3-isothiocyanatomethylene-hexa-1,5-diene in a smooth reaction in high yield.[13]



Scheme 4. Tandem rearrangement reaction of isothiocyanate **3l**

Propargyl isothiocyanates, necessary for synthesizing allenyl thiocyanates by [3,3] sigmatropic rearrangement, can be generated in situ from 1-thiocyanatopent-2-en-4-ynes **12**, easily accessible from the corresponding bromides[14,15] (Scheme 5). Thus, flash vacuum pyrolysis of (*Z*)-**12a** or (*E*)-**12a** resulted in mixtures of (*Z*)-**12a**, (*E*)-**12a**, and allene **14a** (Table 4). Separation of **14a** by chromatography and its subsequent equilibration by renewed pyrolysis confirmed the reversible nature of the processes. At higher temperatures, an equilibrium of (*Z*)-**12a**, (*E*)-**12a**, **14a**, and the additional product **15a** − formed from **14a** by electrocyclic ring-closure − was reached. The propargyl isothiocyanate **13** proved to be a plausible intermediate in the sequences of [3,3] sigmatropic rearrangement reactions. Nevertheless, the [1,5] sigmatropic migration of the thiocyanato group (*Z*)-**12** ⇄ **14** may be a competing reaction. However, flash vacuum pyrolysis of (*Z*)-**12a** and **14a** at 250 °C demonstrated that **14a** and (*Z*)-**12a** are not favored products in cases of low starting material conversion. Furthermore, flash vacuum pyrolysis (300 °C) of thiocyanate **16b**, which is easily accessible from chloride **16a**,[16] produced a mixture of **18** (34% yield) and recovered **16b** (8%). For geometrical reasons, **16b** cannot rearrange to afford **18** by a [1,5] sigmatropic migration of the thiocyanato group. Thus, **17** is a plausible intermediate in the isomerization of **16b** → **18**. The allene **18** can be isolated by chromatography, but it is very unstable. For this reason, and due to its low volatility, we have not been able to perform the flash vacuum pyrolysis of **18** to clarify whether an equilibrium **16b** ⇄ **18** is established.





Scheme 5. Sequential rearrangements of 1-thiocyanatopent-2-en-4-ynes

Table 4. Flash vacuum pyrolysis of (*Z*)-**12a**, (*E*)-**12a**, and **14a**

Starting material[a]	Temperature [°C]	Ratio of products (*Z*)-**12a**	(*E*)-**12a**	**14a**	**15a**[b]
(*Z*)-**12a**	250	72	13	15	−
(*Z*)-**12a**	400	43	21	36	trace
(*Z*)-**12a**	420	31	20	36	13
(*E*)-**12a**	250	16	64	20	−
(*E*)-**12a**	400	33	33	33	trace
(*E*)-**12a**	420	31	21	34	14
14a	250	8	7	85	trace
14a	400	30	18	34	18
14a	420	30	19	36	14

[a] Starting with (*Z*)-**12a** or (*E*)-**12a**, the yields, which were based on weighed mixtures of the isomeric products (*Z*)-**12a**, (*E*)-**12a**, **14a**, and **15a**, were in the range of 65−95%. These yields were lower (32−65%) when unstable **14a** was thermolyzed. − [b] Mixture of geometrical isomers with a ratio of ca. 1:1.2.

In the case of (*Z*)-**12b**, the thiocyanates (*E*)-**12b** and **14b** were formed by flash vacuum pyrolysis at 300 °C, while pyrolysis at higher temperatures resulted in the additional product **15b** as a result of electrocyclic ring-closure of **14b** (Table 5). An equilibrium of (*Z*)-**12b**, (*E*)-**12b**, **14b**, and **15b** is probably attained at higher temperatures, since the product distribution was nearly unchanged at 400 and 450 °C.

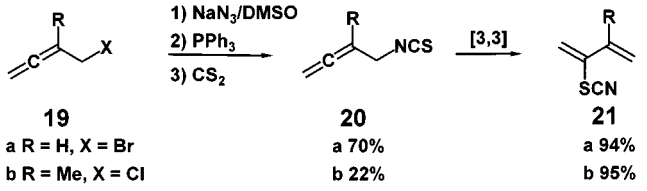
Table 5. Flash vacuum pyrolysis of (*Z*)-**12b**

Temperature [°C]	Ratio of products (*Z*)-**12b**	(*E*)-**12b**	**14b**	**15b**[a]	Yield [%][b]
300	58	9	33	0	75
400	23	7	23	47	64
450	21	6	26	47	31

[a] Mixture of geometrical isomers with a ratio of ca. 1.3:1 = (*E*)-**15b**:(*Z*)-**15b**. − [b] The yields were based on weighed mixtures of (*Z*)-**12b**, (*E*)-**12b**, **14b**, and **15b**.

Synthesis of Thiocyanate-Substituted Buta-1,3-dienes

Another route by which to transform isothiocyanates into vinyl thiocyanates by [3,3] sigmatropic rearrangement starts with buta-2,3-dienyl compounds **20** (Scheme 6), which are easily prepared by treatment of halides **19**[17,18] with sodium azide in dry DMSO, triphenylphosphane, and CS_2 in a one-pot procedure (compare Scheme 2 and Table 2, Method B). Flash vacuum pyrolysis of **20** at 400 °C afforded the isomerization products **21** in high yields. The irreversibility of the reactions demonstrates that the generation of the thermodynamically less stable functional group is overcompensated by the formation of a more stable carbon skeleton including a conjugated diene instead of a cumulene. In addition to this, the isothiocyanato group of **20** is isolated, whereas the lone electron pairs of the sulfur atom of **21** can interact with the adjacent C=C bond.

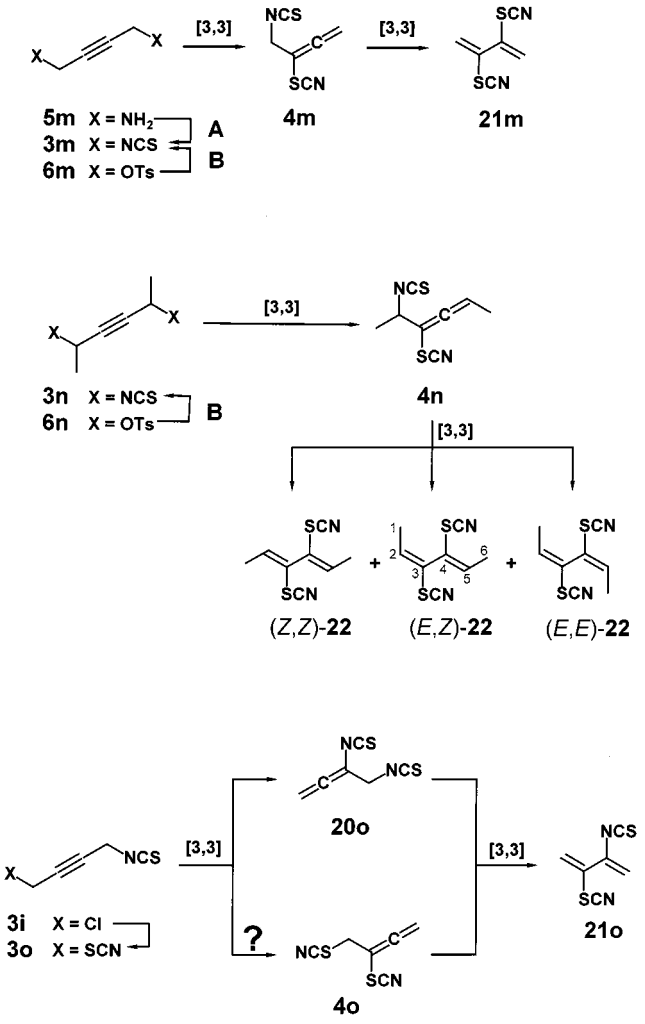


Scheme 6. Synthesis of 2-thiocyanatobuta-1,3-dienes

Some decades ago, the thiocyanate **21a** was prepared in 19.5% yield by addition of hydrogen thiocyanate[19] to but-1-en-3-yne[20] in the presence of mercury(II) oxide.[21] We have repeated this synthesis and have obtained **21a**, which proved to be identical to the thiocyanate prepared by rearrangement of **20a**, with a yield of 17%. However, we observed only traces of **21b** when 2-methylbut-1-en-3-yne was treated with hydrogen thiocyanate in an analogous way.

Allenyl thiocyanates produced by sigmatropic rearrangement can be short lived intermediates if another functional group in the molecule can initiate a rapid consecutive isomerization, affording thiocyanatobuta-1,3-dienes. Thus, diisothiocyanate **3m**, readily available from diamine **5m**[22] (Method A, 55% yield), was induced to rearrange by flash vacuum pyrolysis at 400−550 °C, to give dithiocyanate **21m** in a yield of 44−90% (Scheme 7). The starting material **3m** could also be prepared from ditosylate **6m**[23] (Method B, 22% yield, compare Scheme 2), but trimethyl phosphite was used instead of triphenylphosphane in order to facilitate the separation of slowly evaporating **3m** and the more volatile phosphorus compounds during workup. When the isomerization of **3m** was performed by flash vacuum pyrolysis at lower temperature (250 °C) or in solution (toluene, 70 °C), the intermediate **4m**, which combines the structures of allenyl thiocyanates with those of buta-2,3-dienyl isothiocyanates **20**, was observed (yield ≤ 24%). On the other hand, all attempts to confirm the intermediate allene involved in the conversion of 1,4-dithiocyanatobut-2-yne to 2,3-diisothiocyanatobuta-1,3-diene were without success.[10,11]

Another example of sequences of sigmatropic migrations producing thiocyanate-substituted 1,3-dienes starts with diisothiocyanate **3n**, prepared from ditosylate **6n**[24] (Method B). Thermolysis of **3n** in toluene at 90 °C can be conveniently monitored by ^{1}H NMR spectroscopy (Figure 1). After a few hours, the maximum concentration of the intermediate **4n** was reached, while prolonged heating (14−18 h) quantitatively afforded the isomerization products **22** [yields: 14.5% (*Z,Z*)-**22**, 71% (*E,Z*)-**22**, 14.5% (*E,E*)-**22**]. Flash vacuum pyrolysis of **3n** at 400−450 °C exclusively furnished (*Z,Z*)-**22** (18% yield), (*E,Z*)-**22** (43%), and (*E,E*)-**22** (18%); however, the allene **4n** was also detected when the pyrolysis was performed at lower temperature (300 °C). The assignments of the geometrical configurations of **22** are based on ^{13}C NMR spectroscopic data including γ effects.[25] Thus, the methyl groups in *E* positions induce γ effects, with Δδ = 5.15 ppm for the signal of C-3 and C-4 of (*E,E*)-**22**, relative to the corresponding value for (*Z,Z*)-**22**. A similar but smaller γ effect (Δδ = 2.70 ppm) was observed for the chemical shift of C-4 of (*E,Z*)-**22**, in comparison with that for C-3.



Scheme 7. Sequential [3,3] sigmatropic rearrangements of propargyl isothiocyanates

Flash vacuum pyrolysis of **3o**, which is easily accessible from **3i** and NH_4SCN (37% yield), afforded the very unstable product **21o** (53% yield). Most probably, this buta-1,3-diene is mainly formed via diisothiocyanate **20o**, since that intermediate was observed besides starting material **3o**

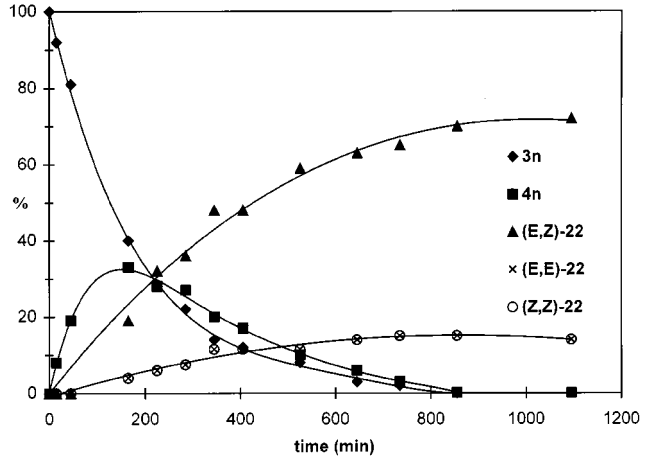
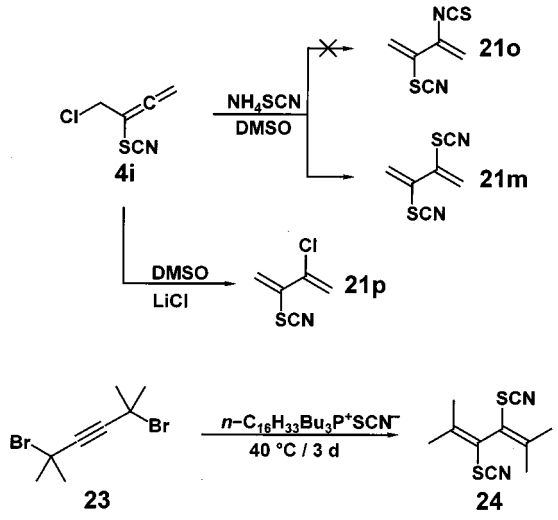


Figure 1. Thermolysis of **3n** in [D_8]toluene at 90 °C, monitored by ^{1}H NMR spectroscopy. After 1100 min, the yields of (*Z*,*Z*)-**22** (14.5%), (*E*,*Z*)-**22** (71%), and (*E*,*E*)-**22** (14.5%) indicated quantitative conversion of **3n**, via intermediate **4n**.

when the thermolysis of **3o** was carried out in solution. In that case, the dithiocyanate **4o** could not be detected, and the yield of **21o** was extremely low ($\leq$ 3.5%), due to extensive decomposition. This result demonstrates that the [3,3] sigmatropic migration of the thiocyanato group is more rapid than that of the isothiocyanato group.

On treatment with NH_4SCN/DMSO, the starting material **4i** did not produce **21o** as might have been expected if **4i** were able to react with thiocyanate ion by S_N2 displacement to give the intermediate **4o**, which should be able to afford **21o** through a [3,3] sigmatropic shift (Scheme 8). The dithiocyanate **21m** was formed instead, in 38% yield. Clearly, a dissociation to ionic intermediates is involved in this process, since stirring of **4i** in pure DMSO produced the buta-1,3-diene **21p** (35% yield), and the transformation **4i** → **21p** was accelerated by addition of lithium chloride. This reaction can be compared with the well-known[18] isomerization of **19b** (X = Cl) to yield 2-chloro-3-methylbuta-1,3-diene in the presence of concentrated hydrochloric acid, ammonium chloride, and cuprous chloride.



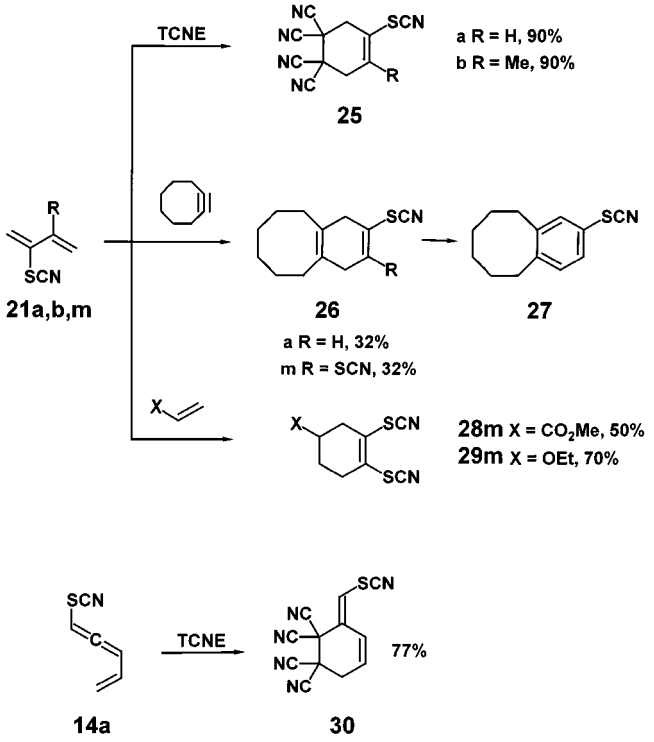
Scheme 8. Synthesis of 2,3-dithiocyanatobuta-1,3-dienes

Similarly, 4-chloro-3-isothiocyanatobuta-1,2-diene was converted into 2-chloro-3-isothiocyanatobuta-1,3-diene on treatment with LiCl/DMSO.[11] However, this starting material and NH_4SCN/DMSO furnished 2,3-diisothiocyanatobuta-1,3-diene, which can be explained by S_N2 displacement and subsequent [3,3] sigmatropic rearrangement.[11]

Another thiocyanate-substituted buta-1,3-diene was prepared by treatment of dibromide **23**[26] with a melt of hexadecyltributylphosphonium thiocyanate.[27,28] The product **24** was obtained with a yield of 55%.

Diels–Alder Reactions of Thiocyanate-Substituted Buta-1,3-dienes

Buta-1,3-dienes bearing one or two thiocyanato groups may find use as synthetic building blocks. Preliminary investigations indicated that [4 + 2] cycloadducts such as **25**, **26**, **28**, and **29** were formed from dienes **21a**, **21b**, and **21m** (Scheme 9). The Diels–Alder product **26a** was oxidized upon prolonged exposure to air, giving the aromatic compound **27**. The [4 + 2] cycloaddition of dithiocyanate **21m** to such very different dienophiles as strained cyclooctyne or electron-deficient acrylic ester, as well as to electron-rich ethyl vinyl ether, to yield **26m**, **28m**, and **29m**, respectively, is a noteworthy fact. These reactions might possibly be classified in the group of Diels–Alder reactions with neutral electron demand.[29]



Scheme 9. Diels–Alder reactions of thiocyanato-substituted buta-1,3-dienes

The Diels–Alder reaction between triene **14a** and tetracyanoethylene (TCNE) stereoselectively[30] produced the product **30**, exclusively in the *E* configuration. The equilibrium mixture of **12a** and **14a** could be used for performing

this [4 + 2] cycloaddition, as only **14a** reacted on treatment with the dienophile.

Conclusion

In summary, we have shown that the thiocyanato group can be very effectively directed into vinylic positions by [3,3] sigmatropic isomerization of isothiocyanates, if the rearrangement reaction gives rise to a more stable carbon skeleton. Thus, some of the allenyl thiocyanates, and especially the thiocyanato-substituted buta-1,3-dienes, were produced in high yields. The new compounds may find use as building blocks as, for example, starting materials for cycloaddition reactions.

Experimental Section

General Remarks: Melting points (uncorrected): Büchi SMP-20 apparatus and Boetius apparatus (Firma Pentakon, Dresden). − Elemental analyses: Firma Beller, Göttingen and Vario EL Elementar Analysensysteme GmbH (Hanau); elemental analyses of some thiocyanates and isothiocyanates could not be performed successfully due to their instability. − IR: Beckman Acculab 4 and Bruker IFS 28. − UV/Vis: Beckman Acta M VII. − ^{1}H NMR: Varian Gemini 300 (300 MHz), Bruker WP 80 (80 MHz); internal standard TMS (δ = 0) or solvent signals, recalculated relative to TMS. − ^{13}C NMR: Varian Gemini 300 (75 MHz) and Bruker WH 400 (100.6 MHz); internal standard TMS (δ = 0) or solvent signals, recalculated relative to TMS. The multiplicities were determined by the aid of *gated* spectra and/or DEPT 135 experiments. − MS (EI): Varian MAT 112. − GC MS (EI): Hewlett−Packard hp 5890 II, hp Engine 5989 A with helium as the carrier gas, the column used was an HP 5 capillary column (5% phenylmethylsilicone gum). − Preparative GC: Shimadzu GC-8A, helium was used as the carrier gas. − HPLC: Knauer HPLC Pump 64, Knauer UV detector (λ = 254 nm), column LiChrospher Si 60 (5 μm), 2 cm Ø × 20 cm. − Flash column chromatography was performed with 32−63 μm silica gel.

1-Isothiocyanatohex-2-yne (3c) by Method B: The known[31] bromide **6c** (X = Br) was prepared from hex-2-yn-1-ol (1.00 g, 10.2 mmol) and PBr_3 according to a general literature procedure,[32] in 75% yield (1.23 g).

Compound **6c** (X = Br, 0.97 g, 6.0 mmol) was added to a solution of NaN_3 (0.78 g, 12 mmol) in dry DMSO (30 mL). The resulting mixture was stirred for 1 h at room temperature. PPh_3 (3.16 g, 12.05 mmol) was then added, with cooling. After stirring for 4 h at room temperature, CS_2 (1.82 mL, 30.3 mmol) was added dropwise to the solution, which was cooled by ice/water. When the sometimes vigorous reaction had subsided, the mixture was stirred for an additional 30 min at room temperature, poured into water, and extracted repeatedly with diethyl ether. The combined organic layers were washed several times with water and dried with $MgSO_4$. After removal of the solvent in vacuo, the residue was recondensed by short-path distillation at 90 °C/0.001 Torr to give 0.30 g (36%) of **3c** as a colorless liquid. − IR ($CDCl_3$): $\tilde{\nu}$ = 2071 cm^{-1}, br. (NCS). − ^{1}H NMR ($CDCl_3$): δ = 0.99 (t, ^3J = 7.2 Hz, 3 H, 6-H), 1.54 (sext, ^3J = 7.2 Hz, 2 H, 5-H), 2.19 (tt, ^3J = 7.2 Hz, ^5J = 2.3 Hz, 2 H, 4-H), 4.25 (t, ^5J = 2.3 Hz, 2 H, 1-H). − ^{13}C NMR ($CDCl_3$): δ = 13.46 (q, C-5), 20.56 (t), 21.81 (t), 35.59 (t, C-1), 71.84 (s), 86.18 (s), 136.39 (s, NCS).

When the reactions were performed in [D$_6$]DMSO, the treatment of compounds **6** with NaN_3, the subsequent Staudinger reaction, and the final transformation to the product **3** could be monitored by ^{1}H NMR spectroscopy. This small-scale preliminary test was useful for optimization of the reaction times, since the intermediate propargyl azides tend to rearrange to give allenyl azides[11,33] which cyclize rapidly to generate highly reactive triazafulvenes. Thus, starting material **6**, transient azide, iminophosphorane, and the product **3** could be easily distinguished by their ^{1}H NMR spectroscopic data.

1-Azidohex-2-yne: ^{1}H NMR ([D$_6$]DMSO): δ = 0.91 (t, ^3J = 7.2 Hz, 3 H, 6-H), 1.44 (sext, ^3J = 7.2 Hz, 2 H, 5-H), 2.21 (br. t, ^3J = 7.2 Hz, 2 H, 4-H), 4.06 (br. s, 2 H, 1-H).

***N*-(Hex-2-ynyl)triphenyliminophosphorane:** ^{1}H NMR ([D$_6$]DMSO): δ = 0.74 (t, ^3J = 7.2 Hz, 3 H, 6-H), 1.19 (sext, ^3J = 7.2 Hz, 2 H, 5-H), 1.87 (br. t, ^3J = 7.2 Hz, 2 H, 4-H), 3.75 (d, $^3J(^{31}P,^1H)$ = 25.0 Hz, 2 H, 1-H). The signals due to the phenyl groups and those of the excess triphenylphosphane overlapped.

3-Isothiocyanatooct-4-yne (3d): Oct-4-yn-3-ol[34a] (7.00 g, 55.5 mmol), NEt_3 (11.2 g, 111 mmol), and CH_2Cl_2 (140 mL) were stirred at 0 °C. MsCl (9.45 g, 82.5 mmol) was added dropwise to this solution. The mixture was stirred at room temperature for 2 h, then diluted with water, and extracted three times with CH_2Cl_2. The combined organic layers were washed with dilute aqueous HCl and aqueous $NaHCO_3$, and dried with $MgSO_4$. Removal of the solvent in vacuo yielded 11.29 g (99.6%) of **6d** (X = OMs) as a reddish liquid. − ^{1}H NMR ($CDCl_3$): δ = 0.95 (t, ^3J = 7.4 Hz, 3 H, Me), 1.01 (t, ^3J = 7.4 Hz, 3 H, Me), 1.51 (sext, ^3J = 7.2 Hz, 2 H, 7-H), 1.85 (br. quint, ^3J = 7.4 Hz, 2 H, 2-H), 2.20 (td, ^3J = 7.1 Hz, ^5J = 2.0 Hz, 2 H, 6-H), 3.07 (s, 3 H, S−Me), 5.08 (tt, ^3J = 6.3 Hz, ^5J = 2.0 Hz, 1 H, 3-H). − ^{13}C NMR ($CDCl_3$): δ = 9.00 (q, Me), 13.23 (q, Me), 20.39 (t), 21.57 (t), 29.28 (t), 38.90 (q, S−Me), 73.75 (d, C-3), 75.73 (s), 89.77 (s).

The crude mesylate **6d** (X = OMs, 2.04 g, 9.99 mmol) was treated with NaN_3 in DMSO, PPh_3, and CS_2 according to the procedure described for the synthesis of **3c** (Method B). The product was recondensed by short-path distillation at 40 °C/0.001 Torr to give **3d** (1.10 g, 66%) as a light yellow liquid. − IR (CCl_4): $\tilde{\nu}$ = 2041 cm^{-1}, br. (NCS). − ^{1}H NMR ($CDCl_3$): δ = 0.96 (t, ^3J = 7.3 Hz, 3 H, Me), 1.04 (t, ^3J = 7.3 Hz, 3 H, Me), 1.52 (sext, ^3J = 7.2 Hz, 2 H, 7-H), 1.84 (qd, ^3J = 7.3 Hz, ^3J = 6.3 Hz, 2 H, 2-H), 2.17 (td, ^3J = 7.1 Hz, ^5J = 2.0 Hz, 2 H, 6-H), 4.35 (tt, ^3J = 6.3 Hz, ^5J = 2.1 Hz, 1 H, 3-H). − ^{13}C NMR ($CDCl_3$): δ = 9.96 (q, Me), 13.42 (q, Me), 20.50 (t), 21.89 (t), 30.76 (t), 50.75 (d, C-3), 75.60 (s), 85.54 (s), 135.22 (br. s, NCS).

The spectroscopic data of the product were compatible to those reported in ref.[6]

Monitoring of the reaction **6d** → **3d** by ^{1}H NMR spectroscopy furnished the data for the corresponding azide and the iminophosphorane.

3-Azidooct-4-yne: ^{1}H NMR ([D$_6$]DMSO): δ = 0.88−0.96 (m, 6 H, 1-H, 8-H), 1.45 (sext, ^3J = 7.1 Hz, 2 H, 7-H), 1.57 (quint, ^3J = 7.1 Hz, 2 H, 2-H), 2.23 (td, ^3J = 6.9 Hz, ^5J = 1.9 Hz, 2 H, 6-H), 4.30 (br. t, ^5J = 6.4 Hz, 1 H, 3-H).

***N*-(1-Ethylhex-2-ynyl)triphenyliminophosphorane:** ^{1}H NMR ([D$_6$]-DMSO): δ = 0.75 (t, ^3J = 7.3 Hz, 3 H), 0.84 (t, ^3J = 7.3 Hz, 3 H),

1.16 (sext, ^3J = 7.2 Hz, 2 H, 5-H), 1.52 (br. quint, ^3J = 6.8 Hz, 2 H, 1′-H), 1.84 (td, ^3J = 7.0 Hz, ^5J = 2.0 Hz, 2 H, 4-H), 3.59 (dtt, $^3J(^{31}P,^1H)$ = 17.3 Hz, ^3J = 6.5 Hz, ^5J = 2.0 Hz, 1 H, 1-H). The signals due to the phenyl groups overlapped with those of the excess triphenylphosphane.

3-Isothiocyanatoprop-1-yne (3f): The tosylate **6f** (X = OTs, 8.71 g, 41.4 mmol)[34b] was treated with NaN_3 in DMSO, PPh_3, and CS_2 according to the procedure described for the synthesis of **3c** (Method B). When the reaction with CS_2 had subsided, the mixture was stirred for a further 30 min. The CS_2 was then distilled off, and the residue was recondensed by short-path distillation at 70 °C/13 Torr. The resulting solution of **3f** in DMSO was poured into water. After workup as described for **3c**, the product was recondensed by short-path distillation again at 70 °C/13 Torr to give 2.11 g (52%) of **3f** as a yellowish liquid. − IR (Et_2O): $\tilde{\nu}$ = 2069 cm^{-1}, br. (NCS). − ^1H NMR ($CDCl_3$): δ = 2.48 (t, ^4J = 2.5 Hz, 1 H, 1-H), 4.28 (q, ^4J = 2.5 Hz, 2 H, 3-H). − ^{13}C NMR ($CDCl_3$): δ = 34.95 (t, C-3), 73.74 (d, C-1), 77.23 (s, C-2), 137.80 (s, NCS). − GC MS (70 eV); *m*/*z* (%): 97 (54) [M^+], 70 (36), 58 (11), 39 (100), 38 (31).

The product proved to be identical to **3f** synthesized by literature methods.[9] Monitoring of the transformation **6f** → **3f** by ^1H NMR spectroscopy afforded the corresponding data for the involved azide and iminophosphorane.

3-Azidoprop-1-yne: ^1H NMR ([D_6]DMSO): δ = 3.63 (t, ^4J = 2.5 Hz, 1 H, 1-H), 4.10 (br. d, ^4J = 2.5 Hz, 2 H, 3-H).

***N*-(Prop-2-ynyl)triphenyliminophosphorane:** ^1H NMR ([D_6]DMSO): δ = 2.80 (t, ^4J = 2.5 Hz, 1 H, 3-H), 3.75 (dd, $^3J(^{31}P,^1H)$ = 23.7 Hz, ^4J = 2.5 Hz, 2 H, 1-H). The signals due to the phenyl groups overlapped with those of the excess triphenylphosphane.

3-Isothiocyanato-3-methylbut-1-yne (3g): Starting with thiophosgene in CH_2Cl_2, K_2CO_3 in water, and **5g**[35] (5.00 g, 60.1 mmol), the product **3g** (6.86 g, 91%) was prepared, in analogy to a known[9] procedure (Method A), as a colorless liquid. − IR ($CDCl_3$): $\tilde{\nu}$ = 3306 cm^{-1} (HC≡C), 2058, br. (NCS). − ^1H NMR ($CDCl_3$): δ = 1.67 (s, 6 H, Me), 2.50 (s, 1 H, 1-H). − ^{13}C NMR ($CDCl_3$): δ = 31.52 (Me), 53.72 (C-3), 70.82 (C-1), 84.00 (C-2), 137.32 (NCS). − GC MS (70 eV); *m*/*z* (%): 125 (13) [M^+], 110 (11), 67 (55), 41 (100). − C_6H_7NS (125.2): calcd. C 57.57, H 5.64, N 11.19, S 25.61; found C 57.25, H 5.61, N 11.09, S 25.67.

The equilibration **3g** ⇄ **4g** can be observed even in solution at room temperature.

1-Isothiocyanatobut-2-yne (3h): The tosylate **6h** (X = OTs, Lancaster, 600 mg, 2.7 mmol) was treated with NaN_3 in DMSO, PPh_3, and CS_2 according to the procedure described for the synthesis of **3c** (Method B). The product was recondensed by short-path distillation at 40 °C/0.001 Torr to yield **3h** (180 mg, 61%) as a colorless liquid. − IR ($CDCl_3$): $\tilde{\nu}$ = 2072 cm^{-1}, br. (NCS). − ^1H NMR ($CDCl_3$): δ = 1.86 (t, ^5J = 2.4 Hz, 3 H, 4-H), 4.21 (q, ^5J = 2.4 Hz, 2 H, 1-H). − ^{13}C NMR ($CDCl_3$): δ = 3.66 (C-4), 35.69 (C-1), 71.04, 82.03, 136.32 (NCS). − C_5H_5NS (111.2): calcd. C 54.02, H 4.53, N 12.60, S 28.84; found C 54.23, H 4.63, N 12.56, S 28.88.

Monitoring of the reaction **6h** → **3h** by ^1H NMR spectroscopy furnished the data for the corresponding azide and the iminophosphorane.

1-Azidobut-2-yne: ^1H NMR ([D_6]DMSO): δ = 1.88 (t, ^5J = 2.4 Hz, 3 H, 4-H), 4.06 (q, ^5J = 2.4 Hz, 2 H, 1-H).

***N*-But-2-ynyl-triphenyliminophosphorane:** ^1H NMR ([D_6]DMSO): δ = 1.56 (br. s, 3 H, 4-H), 3.73 (d, $^3J(^{31}P,^1H)$ = 24.3 Hz, 2 H, 1-H). The signals due to the phenyl groups overlapped with those of the excess PPh_3.

1-Chloro-4-isothiocyanatobut-2-yne (3i): This product was synthesized, starting from the hydrochloride of amine **5i**[36] (5.00 g, 35.7 mmol), in analogy to a known[9] procedure (Method A), as a colorless liquid (3.50 g, 67% yield). − IR ($CDCl_3$): $\tilde{\nu}$ = 2091 cm^{-1} (NCS). − ^1H NMR ($CDCl_3$): δ = 4.17 (t, ^5J = 2.0 Hz, 2 H), 4.33 (t, ^5J = 2.0 Hz, 2 H). − ^{13}C NMR ($CDCl_3$): δ = 29.74 (C-1), 35.17 (C-4), 78.08, 80.20, 137.73 (NCS). − C_5H_4ClNS (145.6): calcd. C 41.24, H 2.77, N 9.62, S 22.02; found C 41.05, H 2.63, N 9.81, S. 21.70.

(1-Isothiocyanatoprop-2-ynyl)benzene (3j): The product **3j** (780 mg, 84%) was prepared as a yellowish liquid, starting from the amine **5j**[37] (700 mg, 5.34 mmol), in analogy to a known[9] procedure (Method A). − IR ($CDCl_3$): $\tilde{\nu}$ = 3306 cm^{-1} (HC≡C), 2025 (NCS). − ^1H NMR ($CDCl_3$): δ = 2.71 (d, ^4J = 2.5 Hz, 1 H, 3′-H), 5.59 (d, ^4J = 2.5 Hz, 1 H, 1′-H), 7.27−7.54 (m, 5 H, Ph). − ^{13}C NMR ($CDCl_3$): δ = 52.00 (C-1′), 74.90 (C-3′), 78.63 (C-2′), 126.33, 128.91, 128.96, (Ph, *para*), 135.72 (Ph, *ipso*), 140.20 (NCS).

The irreversible reaction **3j** → **4j** was already taking place in solution at room temperature. Thus, small signals due to **4j** could be observed when NMR spectra of **3j** were measured at this temperature.

5-Isothiocyanato-2-methylpent-1-en-3-yne (3k): The bromide **6k** (X = Br, 2.00 g, 12.6 mmol)[12] was treated with NaN_3 in DMSO, PPh_3, and CS_2 according to the procedure described for the synthesis of **3c** (Method B). The product was recondensed by short-path distillation at 90 °C/0.001 Torr to yield **3k** (490 mg, 28%) as a colorless liquid. − IR ($CDCl_3$): $\tilde{\nu}$ = 2067 cm^{-1}, br. (NCS). − ^1H NMR ($CDCl_3$): δ = 1.89 (s, 3 H, Me), 4.38 (s, 2 H, 5-H), 5.30 (s, 1 H, 1-H), 5.36 (s, 1 H, 1-H). − ^{13}C NMR ($CDCl_3$): δ = 23.10 (Me), 37.75 (C-5), 79.55, 86.45, 123.46 (C-1), 125.50 (C-2), 137.32 (br., NCS). − GC MS (70 eV); *m*/*z* (%): 137 (69) [M^+], 79 (100), 77 (94), 53 (25). − C_7H_7NS (137.2): calcd. C 61.28, H 5.14, N 10.21, S 23.37; found C 60.68, H 5.25, N 9.99, S 23.54.

Monitoring of the reaction **6k** → **3k** by ^1H NMR spectroscopy afforded data for the corresponding azide and the iminophosphorane.

5-Azido-2-methylpent-1-en-3-yne: ^1H NMR ([D_6]DMSO): δ = 1.85 (s, 3 H, Me), 4.26 (s, 2 H, 5-H), 5.31 (s, 1 H, 1-H), 5.37 (s, 1 H, 1-H).

***N*-(4-Methylpent-4-en-2-ynyl)triphenyliminophosphorane:** ^1H NMR ([D_6]DMSO): δ = 1.61 (s, 3 H, Me), 3.91 (d, $^3J(^{31}P,^1H)$ = 25.6 Hz, 2 H, 1-H), 4.92 (s, 1 H, 5-H), 5.06 (s, 1 H, 5-H). The signals due to the phenyl groups overlapped with those of the excess PPh_3.

5-Isothiocyanatohept-1-en-6-yne (3l): Hept-6-en-1-yn-3-ol[38] was prepared in 59% yield from pent-4-enal[39] and ethynylmagnesium bromide.[13] This alcohol (1.00 g, 9.08 mmol), NEt_3 (1.84 g, 18.2 mmol), and CH_2Cl_2 (5 mL) were stirred at 0 °C. MsCl (1.56 g, 13.6 mmol) was added dropwise to this solution. The mixture was stirred at room temperature for 24 h, then diluted with CH_2Cl_2, and washed with aqueous HCl. The organic layer was washed with water and dried with $MgSO_4$. Removal of the solvent in vacuo gave 1.62 g (95%) of **6l** (X = OMs) as a yellowish liquid. − IR ($CDCl_3$): $\tilde{\nu}$ = 3305 cm^{-1} (HC≡C). − ^1H NMR ($CDCl_3$): δ = 2.01 (m, 2 H, 4-H), 2.25 (m, 2 H, 5-H), 2.75 (d, ^4J = 2.1 Hz, 1 H, 1-H), 3.10 (s, 3 H, Me), 5.02 (dq, $^3J_{cis}$ = 10.1 Hz, $^2J \approx {}^4J \approx$ 1.6 Hz, 1 H, 7-H),

5.08 (dq, $^3J_{trans}$ = 17.0 Hz, $^2J \approx {}^4J \approx$ 1.6 Hz, 1 H, 7-H), 5.14 (td, ^3J = 6.5 Hz, ^4J = 2.1 Hz, 1 H, 3-H), 5.77 (ddt, $^3J_{trans}$ = 17.0 Hz, $^3J_{cis}$ = 10.1 Hz, ^3J = 6.5 Hz, 1 H, 6-H). − ^{13}C NMR ($CDCl_3$): δ = 27.75 (t), 33.71 (t), 38.23 (q), 69.68 (d), 78.20 (d), 83.32 (d, C-2), 115.45 (t, C-7), 135.08 (d, C-6).

The mesylate **6l** (X = OMs, 600 mg, 3.19 mmol) was treated with NaN_3 in DMSO, PPh_3, and CS_2 according to the procedure described for the synthesis of **3c** (Method B). The product was recondensed by short-path distillation at 0.001 Torr to yield **3l** (210 mg, 44%) as a colorless liquid. − IR ($CDCl_3$): $\tilde{\nu}$ = 2045 cm^{-1} (NCS). − ^{1}H NMR ($CDCl_3$): δ = 1.95 (m, 2 H, 4-H), 2.28 (m, 2 H, 3-H), 2.52 (d, ^4J = 2.1 Hz, 1 H, 7-H), 4.45 (td, ^3J = 6.8 Hz, ^4J = 2.1 Hz, 1 H, 5-H), 5.06 (dq, $^3J_{cis}$ = 10.0 Hz, $^2J \approx {}^4J \approx$ 1.3 Hz, 1 H, 1-H), 5.11 (dq, $^3J_{trans}$ = 17.0 Hz, $^2J \approx {}^4J \approx$ 1.6 Hz, 1 H, 1-H), 5.77 (ddt, $^3J_{trans}$ = 17.0 Hz, $^3J_{cis}$ = 10.0 Hz, ^3J = 6.7 Hz, 1 H, 2-H). − ^{13}C NMR ($CDCl_3$): δ = 28.42 (t), 34.77 (t), 47.01 (d, C-5), 72.31 (d, C-7), 78.10 (s, C-6), 115.71 (t, C-1), 134.91 (d, C-2), 136.56 (s, br., NCS). − GC MS (70 eV); *m*/*z* (%): 151 (11) [M^+], 91 (93), 77 (61), 41 (82), 39 (100).

Monitoring of the reaction **6l** → **3l** by ^{1}H NMR spectroscopy furnished data for the corresponding azide and the iminophosphorane.

5-Azidohept-1-en-6-yne: ^{1}H NMR ([D$_6$]DMSO): δ = 1.70 (m, 2 H, 4-H), 2.13 (m, 2 H, 3-H), 3.78 (d, ^4J = 2.1 Hz, 1 H, 7-H), 4.41 (td, ^3J = 6.7 Hz, ^4J = 2.1 Hz, 1 H, 5-H), 4.98 (dm, $^3J_{cis}$ = 10.3 Hz, 1 H, 1-H), 5.05 (dm, $^3J_{trans}$ = 17.2 Hz, 1 H, 1-H), 5.80 (ddt, $^3J_{trans}$ = 17.2 Hz, $^3J_{cis}$ = 10.3 Hz, ^3J = 6.7 Hz, 1 H, 2-H).

***N*-(1-Ethynyl-pent-4-enyl)triphenyliminophosphorane:** ^{1}H NMR ([D$_6$]DMSO): δ = 1.61 (m, 2 H, 2-H), 2.12 (m, 2 H, 3-H), 2.79 (d, ^4J = 2.2 Hz, 1 H, 2′-H), 3.68 (dtd, $^3J(^{31}P,^1H)$ = 19.5 Hz, ^3J = 6.6 Hz, ^4J = 2.2 Hz, 1 H, 1-H), 4.80 (dm, $^3J_{cis}$ = 10.1 Hz, 1 H, 5-H), 4.85 (dm, $^3J_{trans}$ = 17.3 Hz, 1 H, 5-H), 5.67 (ddt, $^3J_{trans}$ = 17.3 Hz, $^3J_{cis}$ = 10.1 Hz, ^3J = 6.7 Hz, 1 H, 4-H). The signals due to the phenyl groups and those of the excess PPh_3 overlapped.

1,4-Diisothiocyanatobut-2-yne (3m) from 5m (Method A): The product was prepared as a yellow oil (2.21 g, 55%), in analogy to a known[9] procedure, starting with diamine **5m**[22] (2.00 g, 23.8 mmol). − IR ($CDCl_3$): $\tilde{\nu}$ = 2042 cm^{-1}, br. (NCS). − ^{1}H NMR ($CDCl_3$): δ = 4.31 (s). − ^{13}C NMR ($CDCl_3$): δ = 35.01 (t), 77.32 (s), 138.17 (br. s, NCS). − GC MS (70 eV); *m*/*z* (%): 168 (15) [M^+], 141 (16), 84 (31), 58 (36), 51 (100). − $C_6H_4N_2S_2$ (168.2): calcd. C 42.84, H 2.40, N 16.65, S 38.12; found C 43.02, H 2.34, N 16.97, S 38.22.

1,4-Diisothiocyanatobut-2-yne (3m) from 6m (Method B): The ditosylate **6m**[23] (10.00 g, 25.4 mmol) was treated with NaN_3 in DMSO, a phosphorus(III) compound, and CS_2 according to the procedure described for the synthesis of **3c**. However, $P(OMe)_3$ was used instead of PPh_3, in order to facilitate the separation of **3m** and the phosphorus compounds. After the usual workup, these phosphorus compounds were evaporated at 40 °C/0.001 Torr, and **3m** was recondensed by short-path distillation at 90 °C/0.001 Torr with a yield of 940 mg (22%). The product proved to be identical to **3m** synthesized from **5m**.

Monitoring of the reaction **6m** → **3m** by ^{1}H NMR spectroscopy afforded data for the corresponding azide and the iminophosphate.

1,4-Diazidobut-2-yne: ^{1}H NMR ([D$_6$]DMSO): δ = 4.25 (s).

***N*,*N*′-(But-2-yne-1,4-diyl)bis(trimethyliminophosphate):** ^{1}H NMR ([D$_6$]DMSO): δ = 3.63 (d, $^3J(^{31}P,^1H)$ = 10.5 Hz, 18 H, OMe), 3.75 (d, $^3J(^{31}P,^1H)$ = 26.3 Hz, 4 H, CH_2).

2,5-Diisothiocyanatohex-3-yne (3n): The ditosylate **6n**[24] (5.00 g, 11.8 mmol) was treated with NaN_3 in DMSO, $P(OMe)_3$, and CS_2 according to the procedure described for the synthesis of **3m**. After the usual workup, however, the product was isolated by flash chromatography (Et_2O/hexane, 1:1) instead of by short path distillation, to yield 210 mg (9%) of **3n** as a yellow oil. − IR ($CDCl_3$): $\tilde{\nu}$ = 2063 cm^{-1} (NCS). − ^{1}H NMR ($CDCl_3$): δ = 1.61 (d, ^3J = 6.9 Hz, 6 H, Me), 4.57 (qd, ^3J = 6.9 Hz, J = 0.8 Hz, 2 H, CHNCS), $A_3A'_3XX'$ system. − ^{13}C NMR ($CDCl_3$): δ = 23.42 (Me), 44.33 (CH), 80.78, 137.85 (NCS). − $C_8H_8N_2S_2$ (196.3): calcd. C 48.95, H 4.11, N 14.27, S 32.67; found C 49.00, H 4.16, N 14.81, S 32.65.

Compound **3n** is probably composed of *meso* and *rac* isomers, since ditosylate **6n** was prepared from the commercial mixture of the corresponding diastereomeric diols.

4-Isothiocyanatobut-2-ynyl Thiocyanate (3o): A solution of **3i** (1.91 g, 13.1 mmol) and NH_4SCN (1.56 g, 20.5 mmol) in DMSO (50 mL) was stirred at 50 °C for 6 h. The mixture was then diluted with water and extracted three times with *tert*-butyl methyl ether. The combined organic layers were washed with water and dried with $MgSO_4$. The solvent was removed in vacuo to give 0.81 g (37%) of **3o** as a viscous yellowish oil. − ^{1}H NMR ($CDCl_3$): δ = 3.78 (t, ^5J = 2.0 Hz, 2 H, 1-H), 4.32 (t, ^5J = 2.0 Hz, 2 H, 4-H). − ^{13}C NMR ($CDCl_3$): δ = 22.70 (C-1), 35.16 (C-4), 77.56, 79.08, 110.45 (SCN), 138.35 (NCS). − $C_6H_4N_2S_2$ (168.2): calcd. C 42.84, H 2.40, N 16.65, S 38.12; found C 42.76, H 2.36, N 16.97, S 38.33.

Equilibration of (3-Isothiocyanatooct-4-ynyl)benzene (3a) and 5-Phenyl-1-propylpenta-1,2-dienyl Thiocyanate (4a): When the synthesis of **3a** was performed as described in ref.,[6] but without purification by kugelrohr distillation, the thiocyanate **4a**, containing only a trace of **3a**, was obtained (92% yield) and thus characterized for the first time. On heating in solution ($CDCl_3$, 60 °C), both **3a** and **4a** produced the equilibrium mixture, with **3a**/**4a** = 90:10. These isomeric compounds could be separated by flash chromatography (Et_2O/hexane, 1:50, order of elution: **3a**, **4a**).

Compound 3a: Light yellow oil. − IR (CCl_4): $\tilde{\nu}$ = 2028 cm^{-1} (NCS). − ^{1}H NMR ($CDCl_3$): δ = 1.02 (t, ^3J = 7.5 Hz, 3 H, 8-H), 1.57 (sext, ^3J = 7.3 Hz, 2 H, 7-H), 2.09−2.19 (m, 2 H, 2-H), 2.23 (td, ^3J = 7.1 Hz, ^5J = 2.1 Hz, 2 H, 6-H), 2.41−2.51 (m, 2 H, 1-H), 4.38 (tt, ^3J = 6.7 Hz, ^5J = 2.1 Hz, 1 H, 3-H), 7.20−7.32 (m, 5 H, Ph). − ^{13}C NMR ($CDCl_3$): δ = 13.48 (q, C-8), 20.54 (t), 21.89 (t), 31.74 (t), 38.81 (t), 48.67 (d, C-3), 75.63 (s), 86.95 (s), 126.21 (d), 128.34 (d), 128.45 (d), 135.97 (br. s, NCS), 139.75 (s).

Compound 4a: Light yellow oil. − IR (CCl_4): $\tilde{\nu}$ = 2155 cm^{-1} (SCN). − ^{1}H NMR ($CDCl_3$): δ = 0.92 (t, ^3J = 7.4 Hz, 3 H, 3′-H), 1.46 (sext, ^3J = 7.3 Hz, 2 H, 2′-H), 2.25 (td, ^3J = 7.3 Hz, ^5J = 3.0 Hz, 2 H, 1′-H), 2.45 (m, 2 H, 4-H), 2.78 (t, ^3J = 7.1 Hz, 2 H, 5-H), 5.60 (m, 1 H, 3-H), 7.17−7.34 (m, 5 H, Ph). − ^{13}C NMR ($CDCl_3$): δ = 13.16 (q, C-3′), 20.71 (t, C-2′), 29.95 (t, C-1′), 34.63 (t, C-5), 35.56 (t, C-4), 93.94 (s, C-1), 97.53 (d, C-3), 110.68 (s, SCN), 126.06 (d, Ph), 128.33 (d, Ph), 128.35 (d, Ph), 140.60 (s, Ph), 202.49 (s, C-2). The assignments of the signals were based on ^{13}C-^{1}H shift correlation.

Equilibration of 1-(Pent-1-ynyl)cyclobutyl Isothiocyanate (3b) and 1-(Cyclobutylidenemethylene)butyl Thiocyanate (4b): When the synthesis of **3b** was performed as described in ref.,[6] but without purification by kugelrohr distillation, a mixture containing **3b**/**4b** = 75:25 (84% yield of the crude products) was obtained. It could be separated by flash chromatography or HPLC (Et_2O/hexane, 1:50, order of elution: **4b**, **3b**). Thus, **4b** could be isolated and characterized for the first time. On heating in solution ($CDCl_3$, 60 °C), both

pure **3b** and **4b** produced the equilibrium mixture, with **3b/4b** = 99.5:0.5 (94% yield, ^{1}H NMR standard). The ratio was determined by integration of the ^{1}H NMR signals of **4b** relative to those of the ^{13}C satellites of **3b**. Flash vacuum pyrolysis of a mixture of **3b** and **4b** at 450 °C gave 3-methyleneoct-1-en-4-yne (92% yield), by elimination followed by electrocyclic ring-opening.

Compound 3b: Yellow oil. − IR (CCl_4): $\tilde{\nu}$ = 2048 cm^{-1} (NCS), 2225 (C≡C). − ^{1}H NMR ($CDCl_3$): δ = 0.98 (t, ^3J = 7.4 Hz, 3 H, Me), 1.53 (sext, ^3J = 7.4 Hz, 2 H, 4′-H), 1.93−2.04 (m, 2 H, 3-H), 2.19 (t, ^3J = 7.1 Hz, 2 H, 3′-H), 2.51 (br. t, ^3J = 7.8 Hz, 4 H, 2-H). − ^{13}C NMR ($CDCl_3$): δ = 13.40 (q, Me), 15.15 (t, C-3), 20.56 (t, C-3′), 21.88 (t, C-4′), 39.04 (t, C-2), 54.01 (s, C-1), 79.56 (s), 84.56 (s), 134.19 (s, NCS). The assignments of the signals were based on ^{13}C-^{1}H shift correlation. − GC MS (70 eV); *m*/*z* (%): 179 (3) [M$^+$], 151 (100), 93 (51), 91 (48), 77 (73).

The spectroscopic data of the product were compatible to those reported in ref.[6]

Compound 4b: Yellow oil. − IR (CCl_4): $\tilde{\nu}$ = 2154 cm^{-1} (SCN). − ^{1}H NMR ($CDCl_3$): δ = 0.94 (t, ^3J = 7.4 Hz, 3 H, Me), 1.55 (sext, ^3J = 7.3 Hz, 2 H, 3-H), 1.95−2.08 (m, 2 H, 3′′-H), 2.29 (t, ^3J = 7.3 Hz, 2 H, 2-H), 2.91−3.01 (m, 4 H, 2′′-H/4′′-H). − ^{13}C NMR ($CDCl_3$): δ = 13.14 (q, Me), 17.43 (t), 20.95 (t), 30.02 (t, C-2′′), 36.22 (t), 95.45 (s), 110.71 (s), 110.93 (s), 193.55 (s, C-1′).

General Procedure for Flash Vacuum Pyrolysis and Workup of Unstable Products: The scale of the flash vacuum pyrolyses was normally in the range of 100−500 mg. In the case of **3f**, pyrolyses on larger scales (≥ 1.0 g) were also performed. The starting material was deposited in a 10 mL flask, which was connected to a glass tube (about 45 × 1.5 cm), arranged horizontally and filled with Raschig rings (3 × 3 mm or 4 × 4 mm, freshly heat-dried in vacuo). The other tube joint and a rotary slide valve oil pump (final vacuum 0.001 Torr) were connected through two traps cooled by liquid nitrogen. In the case of less volatile starting materials, such as **3m**, **3n**, and **3o**, an oil diffusion pump (final vacuum at least 10^{-5} Torr) was used. The glass tube was heated to 200−450 °C by a pipe still (e.g., type 12/38/400, Firma Carbolite). Flash vacuum pyrolyses at higher temperatures (500−550 °C) were performed with the aid of quartz tubes and quartz Raschig rings. If necessary, the flask with the starting material was heated by a hot air generator or a heating bath (for example, 40 °C for **3i** and 90 °C for **3l** or **3m**) in order to drive the vapor of the substrate through the hot pyrolysis tube without carrier gas. In the case of unstable products like **9**, **10**, or **21o**, it was useful to minimize polymerization by dilution of the collected substance with a weighed quantity of an inert solvent before thawing the trap. Several other products, such as **18**, were also very unstable as neat substances at room temperature. Nevertheless, they could be handled conveniently in solution. Some of them, like **14a** and **15a**, could even be separated and purified by chromatography. In these cases, however, solvent removal had to be performed in vacuo at low temperature (< 0° C), and dilution with a solvent appropriate for spectroscopic characterization had to be carried out as soon as possible. In some cases, renewed flash vacuum pyrolyses of separated thiocyanates, such as unstable **14a**, gave lower yields. When low stability was accompanied with low volatility, flash vacuum pyrolysis was difficult or even impossible (starting with **18**, for example).

1-Propylpropa-1,2-dienyl Thiocyanate (4c) by Thermolysis of 3c: Flash vacuum pyrolysis of **3c** (130 mg, 0.93 mmol) was performed at 400 °C (see Table 1) to yield 100 mg (total yield 77%) of a mixture of **3c** and **4c** as a colorless liquid. Nearly the same results were obtained when **3c** was pyrolyzed at 350 or 450 °C. The two compounds could be partially separated by flash chromatography (CH_2Cl_2/hexane, 1:1, order of elution: **3c**, **4c**). − **Compound 4c:** IR ($CDCl_3$): $\tilde{\nu}$ = 2156 cm^{-1} (SCN). − ^{1}H NMR ($CDCl_3$): δ = 1.00 (t, ^3J = 7.2 Hz, 3 H, 3′-H), 1.67 (sext, ^3J = 7.2 Hz, 2 H, 2′-H), 2.35 (tt, ^3J = 7.2 Hz, ^5J = 3.3 Hz, 2 H, 1′-H), 5.13 (t, ^5J = 3.3 Hz, 2 H, 3-H). − ^{13}C NMR ($CDCl_3$): δ = 13.25 (C-3′), 20.75, 35.19, 80.79 (C-3), 93.12 (C-1), 109.98 (SCN), 206.68 (C-2). − The spectroscopic data for the product were compatible to those reported in ref.[6]

1-Propylpenta-1,2-dienyl Thiocyanate (4d) by Thermolysis of 3d: Flash vacuum pyrolysis of **3d** (500 mg, 2.99 mmol) was performed at 300 °C (see Table 1) to produce 480 mg (total yield 96%) of a two-component mixture of **3d/4d** = 86:14, as a light yellow liquid. A mixture enriched in thiocyanate **4d** could be obtained by flash chromatography (Et_2O/hexane, 1:10, order of elution: **3d**, **4d**). Pyrolysis of **3d** at 400 °C gave a mixture of **3d** (59% recovered), **4d** (12% yield), (*E*)-oct-2-en-4-yne (17%), and (*Z*)-oct-2-en-4-yne (12%). On heating in solution ($CDCl_3$, 60 °C), both **3d** and **4d** yielded the equilibrium mixture with **3d/4d** = 93:7.

Compound 4d: IR ($CDCl_3$): $\tilde{\nu}$ = 2154 cm^{-1} (SCN). − ^{1}H NMR ($CDCl_3$): δ = 0.98 (t, ^3J = 7.4 Hz, 3 H, Me), 1.06 (t, ^3J = 7.4 Hz, 3 H, Me), 1.55 (sext, ^3J = 7.2 Hz, 2 H, 2′-H), 2.10 (qd, ^3J = 7.3 Hz, ^3J = 6.2 Hz, 2 H, 4-H), 2.32 (td, ^3J = 7.2 Hz, ^5J = 3.0 Hz, 2 H, 1′-H), 5.64 (tt, ^3J = 6.2 Hz, ^5J = 3.0 Hz, 1 H, 3-H). − ^{13}C NMR ($CDCl_3$): δ = 12.85 (q, Me), 13.23 (q, Me), 20.91 (t), 21.88 (t), 35.74 (t), 94.10 (s, C-1), 100.17 (d, C-3), 110.77 (s, SCN), 201.99 (s, C-2). − The spectroscopic data for the product were in agreement with those reported in ref.[6]

Equilibration of 2-Isothiocyanato-2-methylhept-3-yne (3e) and 3-Methyl-1-propylbuta-1,2-dienyl Thiocyanate (4e): When the synthesis of **3e** was performed as described in ref.,[6] but without purification by kugelrohr distillation, a mixture with **3e/4e** = 41:59 (60% yield) was obtained and could be separated by flash chromatography (Et_2O/hexane, 1:50, order of elution: **3e**, **4e**). Thus, **4e**, which had only been observed by thin layer chromatography in ref.,[6] could be isolated and characterized for the first time. Flash vacuum pyrolysis of a mixture of **3e** and **4e** at 400 °C exclusively gave 2-methylhept-1-en-3-yne (92% yield). On heating in solution ($CDCl_3$, 60 °C), both **3e** and **4e** afforded the equilibrium mixture, with **3e/4e** = 62:38.

Compound 3e: Colorless oil. − IR ($CDCl_3$): $\tilde{\nu}$ = 2052 cm^{-1} (NCS), 1992. − ^{1}H NMR ($CDCl_3$): δ = 0.97 (t, ^3J = 7.3 Hz, 3 H, 7-H), 1.51 (sext, ^3J = 7.2 Hz, 2 H, 6-H), 1.63 (s, 6 H, 2 × Me), 2.16 (t, ^3J = 7.0 Hz, 2 H, 5-H). − ^{13}C NMR ($CDCl_3$): δ = 13.43 (q, C-7), 20.44 (t), 21.92 (t), 31.90 (q, 2 × Me), 54.46 (C-2), 80.85 (s), 83.23 (s), 135.27 (br. s, NCS).

Compound 4e: Yellow oil. − IR ($CDCl_3$): $\tilde{\nu}$ = 2152 cm^{-1} (SCN). − ^{1}H NMR ($CDCl_3$): δ = 0.94 (t, ^3J = 7.3 Hz, 3 H, 3′-H), 1.53 (sext, ^3J = 7.3 Hz, 2 H, 2′-H), 1.79 (s, 2 × Me), 2.28 (t, ^3J = 7.2 Hz, 2 H, 1′-H). − ^{13}C NMR ($CDCl_3$): δ = 13.19 (q, C-3′), 20.45 (q, 2 × Me), 20.92 (t), 36.12 (t), 91.14 (s), 104.34 (s), 111.20 (s, SCN), 200.29 (s, C-2).

Propa-1,2-dienyl Thiocyanate (4f) by Thermolysis of 3f: Flash vacuum pyrolyses of **3f** (1.01 g, 10.4 mmol) were performed at 400 °C/0.001 Torr (see Table 1) and also at 470 °C/0.001 Torr or 400 °C/14 Torr, giving 0.98 g (total yield 97%) of a mixture with **3f/4f** = 1:2 in each case. Thermolysis of **3f** in solution at 60 °C resulted in a multicomponent mixture containing only a small amount of **4f**. The separation of **3f** and **4f** by distillation under vacuum was difficult. Therefore, the mixture of **3f** and **4f** was stirred with an excess

of MeOH at room temperature for 3 d in order to transform the isothiocyanate into methyl *N*-prop-2-ynylthiocarbamate. Afterwards, **4f** could be isolated by vacuum distillation. Furthermore, the thiocyanate could be purified with the help of preparative GC (3-m silicon OV 101, 100 °C) to afford **4f** as a colorless liquid. − ^{1}H NMR ($CDCl_3$): δ = 5.30 (d, ^4J = 6.3 Hz, 2 H, 3-H), 5.81 (t, ^4J = 6.3 Hz, 1 H, 1-H). − ^{13}C NMR ($CDCl_3$): δ = 78.20 (d, C-1), 82.64 (t, C-3), 110.17 (SCN), 209.35 (s, C-2). − GC MS (70 eV); *m*/*z* (%): 97 (34) [M^+], 70 (47), 45 (49), 39 (100), 38 (32).

The NMR spectra of the product were identical to those of **4f** synthesized by another method.[40] This route to preparing allenyl thiocyanate was only described for a case starting with a mixture of tetraorganotin compounds, which produced a mixture of **4f** and 3-thiocyanatoprop-1-yne, most probably just on NMR tube scale. We repeated the synthesis on a preparative scale and obtained pure **4f** in 86% yield by treatment of pure prop-2-ynyltriphenyltin[41] in CCl_4 with $(SCN)_2$ [42] at 0 °C.

3-Methylbuta-1,2-dienyl Thiocyanate (4g) by Thermolysis of 3g: Flash vacuum pyrolysis of **3g** (700 mg, 5.59 mmol) was performed at 400 °C (Table 1) as well as at 200, 300, and 450 °C. Compound **4g**[7c−7d] (270 mg, 2.16 mmol) was treated similarly at 200, 300, and 400 °C. In all cases, mixtures of **3g** and **4g** were recovered in high yields (90−100%). At 200 °C, the equilibration of **3g** and **4g** was incomplete: **3g**/**4g** = 85:15 from **3g** and **3g**/**4g** = 9:91 from **4g**. Flash vacuum pyrolysis performed in the range of 300−450 °C, however, always gave rise to nearly the same ratio of **3g**/**4g** = 15:85. Furthermore, the slow equilibration of **3g** ⇄ **4g** can also be observed in solution at room temperature.

Compound 4g: ^{1}H NMR ($CDCl_3$): δ = 1.82 (d, ^5J = 3.0 Hz, 6 H, Me), 5.62 (sept, ^5J = 3.0 Hz, 1 H, 1-H). The ^{1}H NMR spectroscopic data were identical to those of **4g** synthesized from **6g** (X = Br) and NaSCN.[7c−7d]

1-Methylpropa-1,2-dienyl Thiocyanate (4h) by Thermolysis of 3h: Flash vacuum pyrolysis of **3h** (290 mg, 2.61 mmol) was performed at 400 °C (see Table 1) to give 270 mg (total yield 93%) of a mixture of **3h** and **4h** as a colorless liquid. The mixture could be enriched in thiocyanate **4h** by liquid chromatography (CH_2Cl_2/hexane, 3:2, order of elution: **3h**, **4h**). − IR ($CDCl_3$): $\tilde{\nu}$ = 2158 cm^{-1} (SCN). − ^{1}H NMR ($CDCl_3$): δ = 2.13 (t, ^5J = 3.2 Hz, 3 H, Me), 5.09 (q, ^5J = 3.2 Hz, 2 H, 3-H). − ^{13}C NMR ($CDCl_3$): δ = 20.08 (Me), 79.99 (C-3), 88.67 (C-1), 109.83 (SCN), 207.10 (C-2).

1-(Chloromethyl)propa-1,2-dienyl Thiocyanate (4i) by Thermolysis of 3i: Flash vacuum pyrolysis of **3i** (460 mg, 3.16 mmol) was performed at 400 °C (see Table 1) to yield 420 mg (total yield 91%) of a mixture of **3i** and **4i**. The thiocyanate **4i** was isolated by flash chromatography (CH_2Cl_2/hexane, 3:2, order of elution: **3i**, **4i**) as a colorless liquid. − IR ($CDCl_3$): $\tilde{\nu}$ = 2159 cm^{-1} (SCN), 1952 (C=C=C). − ^{1}H NMR ($CDCl_3$): δ = 4.30 (t, ^5J = 2.0 Hz, 2 H, 1′-H), 5.35 (t, ^5J = 2.0 Hz, 2 H, 3-H). − ^{13}C NMR ($CDCl_3$): δ = 44.18 (C-1′), 82.25 (C-3), 91.45 (C-1), 109.28 (SCN), 208.47 (C-2). − GC MS (70 eV); *m*/*z* (%): 147 (5) [M^+, ^{37}Cl], 145 (11) [M^+, ^{35}Cl], 87 (22), 51 (100). − C_5H_4ClNS (145.6): calcd. C 41.24, H 2.77, N 9.62, S 22.02; found C 41.32, H 2.59, N 9.94, S 22.24.

3-Phenylpropa-1,2-dienyl Thiocyanate (4j) by Thermolysis of 3j: A solution of **3j** (780 mg, 4.50 mmol) in CH_2Cl_2 was kept for 24 h at room temperature. Removal of the solvent gave **4j** in quantitative yield. The product was purified by flash chromatography (CH_2Cl_2/hexane, 1:1) to furnish a yellowish liquid. − IR ($CDCl_3$): $\tilde{\nu}$ = 2160 cm^{-1} (SCN). − ^{1}H NMR ($CDCl_3$): δ = 6.21 (d, ^4J = 5.9 Hz, 1 H), 6.68 (d, ^4J = 5.9, 1 H), 7.30−7.45 (m, 5 H, Ph). − ^{13}C NMR ($CDCl_3$): δ = 82.29 (C-1), 102.53 (C-3), 110.06 (SCN), 127.86, 128.90, 130.73 (Ph, *para*), 133.81 (Ph, *ipso*), 205.96 (C-2). − GC MS (70 eV); *m*/*z* (%): 173 (11) [M^+], 115 (100), 89 (23), 63 (29), 39 (25). − $C_{10}H_7NS$ (173.2): calcd. C 69.33, H 4.07, N 8.09, S 18.51; found C 68.67, H 4.12, N 8.25, S 18.64.

1-Isopropenylpropa-1,2-dienyl Thiocyanate (4k) and 2-Methyl-4-methylenecyclobut-1-enyl Thiocyanate (7) by Thermolysis of 3k: Flash vacuum pyrolyses of **3k** (100 mg, 0.73 mmol) were performed at 300, 400, and 450 °C (see Table 3) to produce mixtures of **3k**, **4k**, and **7** as colorless liquids.

Compound 4k: ^{1}H NMR ($CDCl_3$): δ = 1.92 (br. dd, ^4J = 1.6 Hz, ^4J = 1.4 Hz, 3 H, Me), 5.21 (br. q, ^4J = 1.6 Hz, 1 H, 2′-H), 5.23 (br. q, ^4J = 1.4 Hz, 1 H, 2′-H), 5.39 (br. s, 2 H, 3-H).

The compound **7** could be separated by flash chromatography (CH_2Cl_2/hexane, 1:1) as a colorless liquid. − IR ($CDCl_3$): $\tilde{\nu}$ = 2162 cm^{-1} (SCN), 1597 (C=C). − ^{1}H NMR ($CDCl_3$): δ = 2.08 (s, 3 H, Me), 3.01 (s, 2 H, 3-H), 4.65 (s, 1 H, C=CH_2), 4.91 (s, 1 H, C=CH_2). − ^{13}C NMR ($CDCl_3$): δ = 14.85 (q, Me), 41.03 (t, C-3), 97.71 (t, =CH_2), 108.28 (s, SCN), 116.16 (s), 143.26 (s), 161.43 (s). − GC MS (70 eV); *m*/*z* (%): 137 (91) [M^+], 110 (62), 79 (32), 77 (100). − C_7H_7NS (137.2): calcd. C 61.28, H 5.14, N 10.21, S 23.37; found C 60.81, H 5.22, N 10.26, S 23.56.

Hepta-1,2,6-trienyl Thiocyanate (4l) and 2-Ethenylpenta-1,4-dienyl Thiocyanate (11) by Thermolysis of 3l: Flash vacuum pyrolysis of **3l** (256 mg, 1.69 mmol) was performed at 300, 400, 470, and 500 °C. Besides the starting material **3l** (8%), a mixture of **4l** (47% yield) and **11** (16%, geometrical isomers 1:1.1), which could not be separated by HPLC or preparative GC, was produced at 300 °C. Pyrolysis at higher temperatures led to more complex mixtures of products.

Compound 4l: ^{1}H NMR ($CDCl_3$): δ = 2.25 (m, 4 H, 4-H, 5-H), 5.04 (d, $^3J_{cis}$ = 10.0 Hz, 1 H, 7-H), 5.07 (d, $^3J_{trans}$ = 17.0 Hz, 1 H, 7-H). The signals due to 1-H, 3-H, and 6-H and those of **11** overlapped. − ^{13}C NMR ($CDCl_3$): δ = 27.35 (t), 32.38 (t), 78.83 (d, C-1), 99.51 (d, C-3), 110.63 (s, SCN), 115.86 (t, C-7), 136.78 (d, C-6), 205.24 (s, C-2).

Compounds (*E*)-11 and (*Z*)-11: ^{1}H NMR ($CDCl_3$): δ = 3.08 (dt, ^3J = 6.4 Hz, ^4J = 1.6 Hz, 2 H, 3-H), 3.12 (dt, ^3J = 6.4 Hz, ^4J = 1.6 Hz, 2 H, 3-H), 5.08−5.18 (5-H, signals and those of **4l** overlapped), 5.24 (d, $^3J_{cis}$ = 10.1 Hz, 1 H, 2′-H), 5.38 (d, $^3J_{trans}$ = 17.5 Hz, 1 H, 2′-H), 5.70−5.90 (4-H, signals and those of **4l** overlapped), 5.98 (s, 1 H, 1-H), 6.27 (s, 1 H, 1-H), 6.35 (dd, $^3J_{trans}$ = 17.5 Hz, $^3J_{cis}$ = 10.1 Hz, 1 H, 1′-H), 6.67 (dd, $^3J_{trans}$ = 17.5 Hz, $^3J_{cis}$ = 10.1 Hz, 1 H, 1′-H). − ^{13}C NMR ($CDCl_3$): δ = 32.12 (t, C-3), 37.20 (t, C-3), 100.43 (d), 113.75 (d), 116.84 (t), 117.06 (t), 118.18 (t), 119.74 (t), 130.53 (d), 132.58 (d), 133.68 (d), 135.45 (d). Signals due to C-2 and SCN could not be observed.

1-(Isothiocyanatomethyl)propa-1,2-dienyl Thiocyanate (4m) and 2,3-Dithiocyanate 21m by Thermolysis of 3m: Flash vacuum pyrolysis of **3m** (100 mg, 0.59 mmol) at 250 °C afforded a mixture of nearly equal amounts of **3m**, **4m**, and **21m** (43% total yield). On heating a very dilute solution of **3m** in toluene for 7 h at 70 °C, a mixture with **3m**/**4m**/**21m** = 3:24:73 was quantitatively produced. Flash vacuum pyrolysis of **3m** (480 mg, 2.85 mmol) at 400 °C exclusively gave **21m**; however, the yield was limited to 210 mg (44%) since the precursor **3m** could not be vaporized without decomposition when an oil diffusion pump and a pyrolysis tube filled with Raschig rings were used. However, pyrolysis at 500 °C, performed in a tube without Raschig rings, permitted the vaporization of **3m** without de-

composition, due to a lower pressure gradient. Thus, a two-component mixture with **3m/21m** = 1:9 was obtained quantitatively. At higher temperatures (550 °C), the ratio **3m/21m** was nearly unchanged; however, the yield of recovered compounds was smaller (77%).

Compound 4m: ^{1}H NMR ($CDCl_3$): δ = 4.36 (t, ^5J = 2.8 Hz, 2 H, 1′-H), 5.44 (t, ^5J = 2.8 Hz, 2 H, 3-H). − ^{13}C NMR ($CDCl_3$): δ = 46.72 (C-1′), 83.82 (C-3), 88.64 (C-1), 108.72 (SCN), 136.80 (NCS), 208.42 (C-2).

Compound 21m: Colorless solid, m.p. 65−66 °C (Et_2O/hexane). − IR ($CDCl_3$): $\tilde{\nu}$ = 2164 cm^{-1} (SCN). − ^{1}H NMR ($CDCl_3$): δ = 6.13 (d, ^2J = 2.0 Hz, 2 H), 6.18 (d, ^2J = 2.0 Hz, 2 H). − ^{13}C NMR ($CDCl_3$): δ = 108.16 (s, SCN), 127.21 (t, C-1/C-4), 130.16 (s, C-2/C-3). − GC MS (70 eV); *m*/*z* (%): 168 (15) [M$^+$], 141 (17), 110 (14), 84 (38), 60 (43), 51 (100). − $C_6H_4N_2S_2$ (168.2): calcd. C 42.84, H 2.40, N 16.65, S 38.12; found C 42.85, H 2.46, N 16.71, S 37.84.

1-(1-Isothiocyanatoethyl)buta-1,2-dienyl Thiocyanate (4n) and 3,4-Dithiocyanates 22 by Thermolysis of 3n: Flash vacuum pyrolysis of **3n** (150 mg, 0.76 mmol) was performed at 300, 400, and 450 °C to yield mixtures of (*E*,*E*)-**22**, (*E*,*Z*)-**22**, and (*Z*,*Z*)-**22**. For the pyrolyses at 400 and 450 °C, the ratio of the three geometrical isomers of **22** was nearly constant. When the flash vacuum pyrolysis was performed at 300 °C, besides (*E*,*E*)-**22** (9% yield), (*E*,*Z*)-**22** (43%), and (*Z*,*Z*)-**22** (9%), the starting material **3n** (5%) and the allene **4n** (15%) were obtained. Thermolysis of **3n** could conveniently be induced by heating a solution of **3n** in toluene at 90 °C (see Figure 1). Prolonged reaction times (≥ 50 h) did not lead to subsequent isomerization of the C=C bonds [i.e., constant ratio of (*E*,*E*)-**22**, (*E*,*Z*)-**22**, and (*Z*,*Z*)-**22**]; however, **22** was slowly degraded. Separation of the three geometrical isomers of **22** by chromatography was difficult, but necessary in order to assign the isomers: i.e., to distinguish between (*E*,*Z*)-**22** on the one hand and (*E*,*E*)-**22** and (*Z*,*Z*)-**22**, which were always produced in equal quantities, on the other hand. A mixture of (*E*,*Z*)-**22** and (*Z*,*Z*)-**22** could be isolated by HPLC (CH_2Cl_2/hexane, 2:1) as a colorless oil.

Compound 4n: ^{1}H NMR ($CDCl_3$): δ = 1.58 (d, ^3J = 6.9 Hz, 3 H, Me), 1.88 (d, ^3J = 6.9 Hz, 3 H, Me), 4.50 (m, 1 H, 1′-H), 5.80 (qd, ^3J = 6.9 Hz, ^5J = 2.4 Hz, 1 H, 3-H). − ^{13}C NMR ($CDCl_3$): δ = 13.95 (Me), 21.26 (Me), 55.40 (C-1′), 93.53 (C-1), 96.83 (C-3), 109.12 (SCN), 203.82 (C-2). The signal due to NCS could not be observed. Compound **4n** is probably composed of two diastereomers (compare **3n**); however, only one set of NMR signals was observed.

Compound (*E*,*E*)-22: ^{1}H NMR ($CDCl_3$): δ = 1.86 (d, ^3J = 6.9 Hz, 6 H, Me), 6.52 (q, ^3J = 6.9 Hz, 2 H, 2-H/5-H). − ^{13}C NMR ($CDCl_3$): δ = 16.75 (Me), 109.00 (SCN), 119.58 (C-3/C-4), 142.25 (C-2/C-5).

Compound (*E*,*Z*)-22: ^{1}H NMR ($CDCl_3$): δ = 1.91 (d, ^3J = 6.9 Hz, 3 H, Me), 2.06 (d, ^3J = 6.9 Hz, 3 H, Me), 6.27 (q, ^3J = 6.9 Hz, 1 H), 6.47 (q, ^3J = 6.9 Hz, 1 H). − ^{13}C NMR ($CDCl_3$): δ = 16.25 (Me), 16.90 (Me), 108.59 (SCN), 109.70 (SCN), 120.60 (C-4), 123.30 (C-3), 140.60 (CH), 141.86 (CH).

Compound (*Z*,*Z*)-22: ^{1}H NMR ($CDCl_3$): δ = 2.08 (d, ^3J = 6.9 Hz, 6 H, Me), 6.56 (q, ^3J = 6.9 Hz, 2 H, 2-H/5-H). − ^{13}C NMR ($CDCl_3$): δ = 16.80 (Me), 109.12 (SCN), 124.73 (C-3/C-4), 140.37 (C-2/C-5).

4-Methylpent-4-en-2-ynyl Thiocyanate (8): Compound **6k**[12] (X = Br, 1.27 g, 7.99 mmol) was added to a solution of NH_4SCN (1.22 g, 16.0 mmol) in H_2O (10 mL) and MeOH (10 mL). The resulting mixture was stirred, with protection from light, at room temperature for 6 h. The organic phase was then separated, and the aqueous phase was extracted three times with Et_2O. The combined organic layers were dried with $MgSO_4$. After removal of the solvent in vacuo, the residue was recondensed by short-path distillation at 30 °C/0.015 Torr to yield **8** (0.68 g, 62%) as a colorless oil. − IR (CCl_4): $\tilde{\nu}$ = 3100 cm^{-1} (C=CH_2), 2231 (C≡C), 2159 (SCN), 1613 (C=C). − ^{1}H NMR ($CDCl_3$): δ = 1.90 (t, *J* = 1.4 Hz, 3 H, Me), 3.89 (s, 2 H, 1-H), 5.32 (m, 1 H, 5-H), 5.39 (m, 1 H, 5-H). − ^{13}C NMR ($CDCl_3$): δ = 23.01 (Me), 23.81 (C-1), 79.69, 88.29, 110.85 (SCN), 123.68 (C-5), 125.37 (C-4). − GC MS (70 eV); *m*/*z* (%): 137 (53) [M$^+$], 79 (71), 77 (100), 39 (64).

1-(1-Methylethenyl)propa-1,2-dienyl Isothiocyanate (9) and 2-Methyl-4-methylenecyclobut-1-enyl Isothiocyanate (10) by Thermolysis of 8: Flash vacuum pyrolysis of **8** was performed at 200, 270, 290, 300, 320, and 400 °C. Because of the instability of the products, it was useful to start with a solution of **8** in chloroform, which was vaporized and passed through the pyrolysis tube, or to dilute the contents of the trap before thawing. When **8** (360 mg, 2.62 mmol) was converted at 400 °C, the sole product was **10** (310 mg, 86%), which was collected in a trap with a weighed quantity of $CDCl_3$ (ca. 2 mL). − IR ($CDCl_3$): $\tilde{\nu}$ = 2040 cm^{-1}, br. (NCS). − ^{1}H NMR ($CDCl_3$): δ = 1.96 (s, 3 H, Me), 2.66 (s, 2 H, 3-H), 4.58 (s, 1 H, C=CH_2), 4.79 (s, 1 H, C=CH_2). − ^{13}C NMR ($CDCl_3$): δ = 14.2 (q, Me), 35.8 (t, C-3), 96.5 (t, =CH_2), 122.6 (s), 136.5 (br. s, NCS), 142.7 (s), 144.3 (s). − GC MS (70 eV); *m*/*z* (%): 137 (96) [M$^+$], 79 (65), 77 (100), 39 (73).

Thermolysis at 200 °C afforded unchanged starting material **8**. In the range of 270−320 °C, flash vacuum pyrolysis of **8** produced mixtures of **8**, **9**, and **10**, such as with **8/9/10** = 79:16:5 at 270 °C, **8/9/10** = 19:43:38 at 290 °C, and **8/9/10** = 7:8:85 at 320 °C. If a solution containing nearly equal amounts of **8**, **9**, and **10** generated by thermolyses of **8** was used as starting material for flash vacuum pyrolysis at 400 °C, **10** was again the exclusive product.

Compound 9: ^{1}H NMR ($CDCl_3$): δ = 1.78 (s, 3 H, Me), 5.07 (s, 1 H, 2′-H), 5.32 (s, 1 H, 2′-H), 5.55 (s, 2 H, 3-H). − GC MS (70 eV); *m*/*z* (%): 137 (53) [M$^+$], 79 (67), 77 (100), 53 (51), 39 (69).

Pent-2-en-4-ynyl Thiocyanate (12a): Pent-1-en-4-yn-3-ol was treated with PBr_3 according to a general procedure,[14,32] to furnish (*E*)-1-bromopent-2-en-4-yne,[32] (*Z*)-1-bromopent-2-en-4-yne,[32] and 3-bromopent-1-en-4-yne (total yield 66% after recondensation by short-path distillation, ratio about 45:30:25 and 45:25:30 in two different batches). The mixture of these bromides (0.50 g, 3.45 mmol), NH_4SCN (0.28 g, 3.7 mmol), and MeOH (20 mL) was stirred at 40 °C for 19 h, then diluted with water and extracted three times with *tert*-butyl methyl ether. The combined organic layers were repeatedly washed with water and dried with $MgSO_4$. The solvent was removed in vacuo to yield 0.29 g (68%) of a two-component mixture with (*E*)-**12a**/(*Z*)-**12a** = 2:1. − IR ($CDCl_3$): $\tilde{\nu}$ = 2159 cm^{-1} (SCN). − C_6H_5NS (123.2): calcd. C 58.51, H 4.09, N 11.37, S 26.03; found C 58.31, H 4.28, N 11.30, S 26.32. − The two diastereomeric thiocyanates could be separated by flash chromatography (Et_2O/hexane, 1:10).

Compound (*E*)-12a: Yellowish liquid. − ^{1}H NMR ($CDCl_3$): δ = 3.01 (d, ^4J = 2.1 Hz, 1 H, 5-H), 3.61 (d, ^3J = 7.8 Hz, 2 H, 1-H), 5.80 (dd, $^3J_{trans}$ = 15.6 Hz, ^4J = 2.1 Hz, 1 H, 3-H), 6.26 (dt, $^3J_{trans}$ = 15.6 Hz, ^3J = 7.8 Hz, 1 H, 2-H). − ^{13}C NMR ($CDCl_3$): δ = 35.00 (C-1), 79.25 (C-5), 84.68 (C-4), 110.20 (SCN), 114.30, 135.20.

Compound (*Z*)-12a: Yellowish liquid. − ^{1}H NMR ($CDCl_3$): δ = 3.31 (d, ^4J = 2.1 Hz, 1 H, 5-H), 3.86 (d, ^3J = 7.8 Hz, 2 H, 1-H),

5.81 (dd, $^3J_{cis}$ = 10.5 Hz, ^4J = 2.1 Hz, 1 H, 3-H), 6.15 (dt, $^3J_{cis}$ = 10.5 Hz, ^3J = 7.8 Hz, 1 H, 2-H). − ^{13}C NMR ($CDCl_3$): δ = 31.60 (C-1), 79.36 (C-5), 84.68 (C-4), 111.00 (SCN), 113.43, 134.61.

Thermal Equilibration of (*E*)-12a, (*Z*)-12a, Penta-1,2,4-trienyl Thiocyanate (14a), and Thiocyanate 15a: Flash vacuum pyrolysis of (*E*)-**12a**, (*Z*)-**12a**, and **14a** was performed at 250, 400, and 420 °C (see Table 4). In all cases, the contents of the trap were shown to consist exclusively of (*E*)-**12a**, (*Z*)-**12a**, **14a**, and **15a**, which could be partially separated by flash chromatography [Et_2O/hexane, 1:10, order of elution: **15a**, **14a**, (*Z*)-**12a**, (*E*)-**12a**]. Solvent removal from those fractions that contained **14a** or **15a** (ca. 100 mg) was performed in vacuo at low temperature, since the neat compounds were very unstable. Thus, flash vacuum pyrolysis of **14a** resulted in lower yields of products, and a nonvolatile residue remained even on vaporization of the starting material **14a** at 10^{-5} Torr. A mixture with (*E*)-**12a**/(*Z*)-**12a** = 2:1 (400 mg, 3.25 mmol) was pyrolyzed analogously at 250, 300, 400, and 450 °C.

Compound 14a: Yellowish liquid. − IR ($CDCl_3$): $\tilde{\nu}$ = 2159 cm^{-1} (SCN). − ^{1}H NMR ($CDCl_3$): δ = 5.28 (d, $^3J_{cis}$ = 9.2 Hz, 1 H, 5-H), 5.44 (d, $^3J_{trans}$ = 16.1 Hz, 1 H, 5-H), 5.97 (d, ^4J = 6.0 Hz, 1 H, 1-H), 6.19 (dt, ^3J = 16.8 Hz, $^3J \approx {}^3J_{cis} \approx$ 10.0 Hz, 1 H, 4-H), 6.32 (dd, ^3J = 10.0 Hz, ^4J = 6.0 Hz, 1 H, 3-H). − ^{13}C NMR ($CDCl_3$): δ = 80.08 (d, C-1), 102.00 (d, C-3), 110.12 (s, SCN), 121.48 (t, C-5), 129.35 (d, C-4), 207.42 (s, C-2). − GC MS (70 eV); *m*/*z* (%): 123 (6) [M^+], 122 (31), 65 (82), 39 (100).

Compound 15a (major geometrical isomer): ^{1}H NMR ($CDCl_3$): δ = 3.12 (br. dd, *J* = 2.2 Hz, *J* = 0.9 Hz, 2 H, 4-H), 5.65 (q, *J* = 0.6 Hz, 1 H, CHSCN), 6.30 (dt, *J* = 2.6 Hz, *J* = 0.7 Hz, 1 H, 1-H), 6.81 (dq, *J* = 2.6 Hz, *J* = 0.9 Hz, 1 H, 2-H). − **15a** (minor geometrical isomer): ^{1}H NMR ($CDCl_3$): δ = 3.04 (q, *J* = 0.8 Hz, 2 H, 4-H), 5.45 (t, *J* = 0.7 Hz, 1 H, CHSCN), 6.51 (dq, *J* = 2.7 Hz, *J* = 0.7 Hz, 1 H, 1-H), 6.90 (dq, *J* = 2.7 Hz, *J* = 0.9 Hz, 1 H, 2-H). − ^{13}C NMR (both isomers, $CDCl_3$): δ = 36.71 (t, C-4), 37.94 (t, C-4), 92.17 (d, *C*−SCN), 93.15 (d, *C*−SCN), 111.26 (s, SCN), 111.59 (s, SCN), 134.73 (d), 136.27 (d), 144.15 (d), 146.02 (d), 152.56 (s, C-3), 153.44 (s, C-3).

(*Z*)-3-Methylpent-2-en-4-ynyl Thiocyanate [(*Z*)-12b]: The known[15] starting material (*Z*)-1-bromo-3-methylpent-2-en-4-yne was prepared from 3-methylpent-2-en-4-yn-1-ol and PBr_3, according to a general literature procedure,[14,32] in 77% yield. This bromide was transformed into (*Z*)-**12b** as described for the synthesis of **12a**. The product (*Z*)-**12b** was isolated as a yellowish liquid in 84% yield. − ^{1}H NMR ($CDCl_3$): δ = 1.95 (s, 3 H, Me), 3.30 (s, 1 H, 5-H), 3.81 (d, ^3J = 7.7 Hz, 2 H, 1-H), 5.90 (t, ^3J = 7.7 Hz, 1 H, 2-H). − ^{13}C NMR ($CDCl_3$): δ = 22.96 (Me), 33.59 (C-1), 80.89 (C-4), 84.47 (C-5), 111.76 (SCN), 124.74 (C-3), 129.59 (C-2). − GC MS (70 eV); *m*/*z* (%): 137 (7) [M^+], 79 (91), 75 (100), 51 (44).

(*E*)-3-Methylpent-2-en-4-ynyl Thiocyanate [(*E*)-12b], 3-Methylpenta-1,2,4-trienyl Thiocyanate (14b), and Thiocyanate 15b by Thermolysis of (*Z*)-12b: Flash vacuum pyrolysis of (*Z*)-**12b** (200 mg, 1.46 mmol) was performed at 300, 400, and 450 °C (see Table 5) to yield mixtures of (*Z*)-**12b**, (*E*)-**12b**, **14b**, and **15b**. The allene **14b** was isolated by flash chromatography (Et_2O/hexane, 1:5); the other products could not be separated. The assignments of the geometrical configurations of (*Z*)-**12b** and (*E*)-**12b** were proven by their ^{13}C NMR spectroscopic data, including the γ effect, which induced a shielding effect on the signal of the methyl group of (*E*)-**12b** with Δδ = 5.47 ppm. The attribution of the geometrical isomers (*E*)-**15b** (major isomer) and (*Z*)-**15b** (minor isomer) was based on homonuclear NOE difference spectra. The assignments of the NMR signals of **15b** were verified by ^{13}C-^{1}H shift correlation.

Compound (*E*)-12b: ^{1}H NMR ($CDCl_3$): δ = 1.95 (s, 3 H, Me), 2.97 (s, 1 H, 5-H), 3.68 (d, ^3J = 7.7 Hz, 2 H, 1-H), 6.01 (t, ^3J = 7.7 Hz, 1 H, 2-H). − ^{13}C NMR ($CDCl_3$): δ = 17.49 (Me), 31.59 (C-1), 77.86 (C-4), 84.63 (C-5), 110.70 (SCN), 124.66 (C-3), 129.19 (C-2).

Compound 14b: Yellowish liquid. − IR ($CDCl_3$): $\tilde{\nu}$ = 2158 cm^{-1} (SCN). − ^{1}H NMR ($CDCl_3$): δ = 1.94 (d, ^5J = 2.3 Hz, 3 H, Me), 5.27 (d, $^3J_{cis}$ = 10.6 Hz, 1 H, 5-H), 5.35 (d, $^3J_{trans}$ = 17.1 Hz, 1 H, 5-H), 5.87 (m, 1 H, 1-H), 6.31 (dd, $^3J_{trans}$ = 17.1 Hz, $^3J_{cis}$ = 10.6 Hz, 1 H, 4-H). − ^{13}C NMR ($CDCl_3$): δ = 14.40 (q, Me), 77.91 (d, C-1), 109.15 (s), 110.67 (s), 117.74 (t, C-5), 132.37 (d, C-4), 207.56 (s, C-2). − GC MS (70 eV); *m*/*z* (%): 137 (34) [M^+], 79 (81), 77 (100).

Compound (*E*)-15b: ^{1}H NMR ($CDCl_3$): δ = 1.70 (td, *J* = 2.5 Hz, *J* = 1.5 Hz, 3 H, Me), 2.92 (m, 2 H, 3-H), 5.53 (br. s, 1 H, CHSCN), 6.44 (m, 1 H, 2-H). − ^{13}C NMR ($CDCl_3$): δ = 11.81 (q, Me), 33.94 (t, C-3), 90.77 (d, *C*−SCN), 111.50 (s, SCN), 137.16 (d, C-2), 145.60 (s), 155.36 (s).

Compound (*Z*)-15b: ^{1}H NMR ($CDCl_3$): δ = 1.93 (m, 3 H, Me), 2.80 (qt, *J* = 2.5 Hz, *J* = 0.8 Hz, 2 H, 3-H), 5.43 (br. s, 1 H, CHSCN), 6.54 (m, 1 H, 2-H). − ^{13}C NMR ($CDCl_3$): δ = 14.36 (q, Me), 35.36 (t, C-3), 91.58 (d, *C*−SCN), 111.66 (s, SCN), 140.12 (d, C-2), 145.35 (s), 153.65 (s).

3-Ethynylcyclohex-2-enyl Thiocyanate (16b): A solution of **16a**[16] (0.76 g, 5.41 mmol) and NH_4SCN (0.82 g, 10.8 mmol) in DMSO (10 mL) was stirred at room temperature for 16 h. The mixture was then poured into ice/water and extracted three times with Et_2O. The combined organic layers were washed with water and dried with $MgSO_4$. After removal of the solvent in vacuo, the residue was purified by flash chromatography (Et_2O/hexane, 1:3) to yield 0.21 g (24%) of **16b** as a light yellow oil. − IR ($CDCl_3$): $\tilde{\nu}$ = 3304 cm^{-1} (C≡CH), 2154 (SCN), 1624 (C=C). − ^{1}H NMR ($CDCl_3$): δ = 1.75 (m, 1 H), 1.90 (m, 1 H), 2.08 (m, 2 H), 2.22 (m, 2 H), 3.01 (s, 1 H, C≡CH), 4.16 (m, 1 H, 1-H), 6.14 (m, 1 H, 2-H). − ^{13}C NMR ($CDCl_3$): δ = 18.72 (CH_2), 28.67 (CH_2), 28.88 (CH_2), 46.02 (C-1), 78.80 (C≡*C*H), 83.13 (*C*≡CH), 111.50 (SCN), 127.00 (C-3), 130.60 (C-2). − C_9H_9NS (163.2): calcd. C 66.22, H 5.56, N 8.58, S 19.64; found C 66.43, H 5.64, N 8.56, S 19.37.

Thiocyanate 18 by Thermolysis of 16b: Flash vacuum pyrolysis of **16b** was performed at 300, 350, and 400 °C. Pyrolysis of **16b** (120 mg, 0.735 mmol) at 300 °C afforded a mixture (50 mg, total yield 42%) with **16b/18** ≈ 1:4, as a brown liquid. The reaction of **16b** at higher temperatures (350 and 400 °C) led to complex multicomponent mixtures. The allene **18** was very unstable; however, it could be isolated by flash chromatography (CH_2Cl_2/hexane, 1:1). − IR ($CDCl_3$): $\tilde{\nu}$ = 2160 cm^{-1} (SCN). − ^{1}H NMR ($CDCl_3$): δ = 1.80 (m, 2 H), 2.18 (m, 2 H), 2.48 (m, 2 H), 5.85 (s, 1 H), 6.01 (br. s, 2 H). − ^{13}C NMR ($CDCl_3$): δ = 21.64 (t), 24.85 (t), 26.82 (t), 78.25 (d, CH−S), 109.82 (s), 110.96 (s), 122.00 (d), 134.20 (d), 204.13 (s, =C=).

Isothiocyanate 20a: The bromide **19a**[17] (1.66 g, 12.5 mmol) was treated with NaN_3 in DMSO, PPh_3, and CS_2 according to the procedure described for the synthesis of **3c** (Method B). The product was recondensed by short-path distillation at 30 °C/0.001 Torr to yield **20a** (70%) as a colorless liquid. − IR ($CDCl_3$): $\tilde{\nu}$ = 2078 cm^{-1}, br. (NCS). − ^{1}H NMR ($CDCl_3$): δ = 4.08 (dt, ^3J = 7.4 Hz, ^5J = 2.8 Hz, 2 H, 4-H), 4.98 (dt, ^4J = 6.4 Hz, ^5J = 2.8 Hz, 2 H, 1-H), 5.25 (m, 1 H, 3-H). − ^{13}C NMR ($CDCl_3$): δ = 43.45 (t, C-4), 78.98 (t, C-1), 85.04 (d, C-3), 132.54 (s, NCS), 208.31 (s, C-2). − GC MS (70 eV); *m*/*z* (%): 111 (54) [M^+], 72 (36), 58 (42), 53

(100), 51 (34), 39 (20). − C_5H_5NS (111.2): calcd. C 54.02, H 4.53, N 12.60, S 28.84; found C 54.04, H 4.44, N 12.85, S 27.95.

Monitoring of the reaction **19a** → **20a** by ^{1}H NMR spectroscopy furnished the data for the corresponding azide and the iminophosphorane.

4-Azidobuta-1,2-diene: ^{1}H NMR ([D$_6$]DMSO): δ = 3.82 (dt, ^3J = 7.4 Hz, ^5J = 2.8 Hz, 2 H, 4-H), 5.02 (dt, ^4J = 6.4 Hz, ^5J = 2.8 Hz, 2 H, 1-H), 5.40 (m, 1 H, 3-H).

***N*-(Buta-2,3-dienyl)triphenyliminophosphorane:** ^{1}H NMR ([D$_6$]-DMSO): δ = 3.68 (ddt, $^3J(^{31}P,^1H)$ = 21.7 Hz, ^3J = 7.4 Hz, ^5J = 2.8 Hz, 2 H, 1-H), 4.59 (dt, ^4J = 6.4 Hz, ^5J = 2.8 Hz, 2 H, 4-H), 5.16 (m, 1 H, 2-H). The signals due to the phenyl groups overlapped with those of the excess PPh_3.

Isothiocyanate 20b: The chloride **19b**[18] (1.28 g, 12.5 mmol) was treated with NaN_3 in DMSO, PPh_3, and CS_2 according to the procedure described for the synthesis of **3c** (Method B). The product was recondensed by short-path distillation at 30 °C/0.001 Torr to give 340 mg (22%) of **20b** as a colorless liquid. − IR ($CDCl_3$): $\tilde{\nu}$ = 2089 cm^{-1}, br. (NCS). − ^{1}H NMR ($CDCl_3$): δ = 1.77 (t, ^5J = 3.2 Hz, 3 H, Me), 4.01 (t, ^5J = 3.2 Hz, 2 H, 4-H), 4.85 (sext, ^5J = 3.2 Hz, 2 H, 1-H). − ^{13}C NMR ($CDCl_3$): δ = 15.08 (Me), 47.24 (C-4), 76.59 (C-1), 93.33 (C-3), 131.23 (NCS), 205.22 (C-2). − GC MS (70 eV); *m*/*z* (%): 125 (29) [M$^+$], 85 (34), 67 (53), 65 (45), 41 (100), 39 (67). − C_6H_7NS (125.2): calcd. C 57.57, H 5.64, N 11.19, S 25.61; found C 57.73, H 5.68, N 10.88, S 25.85.

Monitoring of the reaction **19b** → **20b** by ^{1}H NMR spectroscopy afforded the data for the corresponding azide and the iminophosphorane.

4-Azido-3-methylbuta-1,2-diene: ^{1}H NMR ([D$_6$]DMSO): δ = 1.70 (br. s, Me), 3.82 (br. s, 4-H), 4.91 (br. s, 1-H).

***N*-(2-Methylbuta-2,3-dienyl)triphenyliminophosphorane:** ^{1}H NMR ([D$_6$]DMSO): δ = 1.60 (t, ^5J = 3.2 Hz, 3 H, Me), 3.59 (br. d, $^3J(^{31}P,^1H)$ = 20.1 Hz, 2 H, 1-H), 4.48 (br. q, ^5J = 3.2 Hz, 2 H, 4-H). The signals due to the phenyl groups overlapped with those of the excess PPh_3.

Diisothiocyanate 20o and 1-Methylene-2-isothiocyanatoprop-2-enyl Thiocyanate (21o) by Thermolysis of 3o: Flash vacuum pyrolysis of **3o** (190 mg, 1.13 mmol) was performed at 400 °C to produce exclusively the very unstable product **21o** (100 mg, 53%), which could only be characterized in solution. − IR ($CDCl_3$): $\tilde{\nu}$ = 2153 cm^{-1} (SCN), 2061, br. (NCS). − ^{1}H NMR ($CDCl_3$): δ = 5.55 (br. s, 1 H), 5.67 (m, 1 H), 6.06 (br. s, 1 H), 6.18 (m, 1 H). − ^{13}C NMR ($CDCl_3$): δ = 108.52 (s, SCN), 115.56 (t), 125.40 (t), 128.50 (s), 132.26 (s), 137.75 (s, NCS).

On heating a solution of **3o** (50 mg, 0.30 mmol) in toluene (5 mL) at 90 °C for 2.5 h, a two-component mixture with **3o**/**20o** = 1:1 was generated. This was shown by ^{1}H NMR spectroscopy after removal of the toluene at 0.001 Torr and low temperature. Furthermore, the reaction **3o** → **20o** → **21o** could be monitored with the help of NMR spectroscopy, by heating a dilute solution of **3o** in [D$_8$]toluene or $CDCl_3$ at 60 °C. Whereas the formation of **20o** (yield ≤ 19%) was observed easily, **21o** was detected only in traces (≤ 3.5%), due to the very low stability of this compound.

Compound 20o: ^{1}H NMR ($CDCl_3$): δ = 4.20 (t, ^5J = 2.0 Hz, 2 H, 4-H), 5.50 (t, ^5J = 2.0 Hz, 2 H, 1-H).

1-Methyleneprop-2-enyl Thiocyanate (21a): Flash vacuum pyrolysis of **20a** (0.47 g, 4.2 mmol) at 400 °C gave **21a** (0.44 g, 94%) as a colorless liquid. − IR ($CDCl_3$): $\tilde{\nu}$ = 2162 cm^{-1} (SCN). − ^{1}H NMR ($CDCl_3$): δ = 5.45 (d, $^3J_{cis}$ = 10.5 Hz, 1 H, 3-H), 5.57 (d, $^3J_{trans}$ = 17.1 Hz, 1 H, 3-H), 5.75 (s, 1 H, 1′-H), 5.81 (s, 1 H, 1′-H), 6.50 (dd, $^3J_{trans}$ = 17.1 Hz, $^3J_{cis}$ = 10.5 Hz, 1 H, 2-H). − ^{13}C NMR ($CDCl_3$): δ = 109.48 (s, SCN), 119.48 (t), 122.68 (t), 132.20 (s, C-1), 133.15 (d, C-2). − GC MS (70 eV); *m*/*z* (%): 111 (24) [M$^+$], 71 (22), 58 (24), 53 (100), 51 (22). − C_5H_5NS (111.2): calcd. C 54.02, H 4.53, N 12.60, S 28.84; found C 53.93, H 4.39, N 12.93, S 28.06.

2-Methyl-1-methyleneprop-2-enyl Thiocyanate (21b): Flash vacuum pyrolysis of **20b** (0.40 g, 3.2 mmol) at 400 °C yielded **21b** (0.38 g, 95%) as an unstable colorless liquid. − IR ($CDCl_3$): $\tilde{\nu}$ = 2161 cm^{-1} (SCN). − ^{1}H NMR ($CDCl_3$): δ = 2.03 (s, Me), 5.30 (s, 1 H), 5.41 (s, 1 H), 5.76 (s, 1 H), 5.82 (s, 1 H). − ^{13}C NMR ($CDCl_3$): δ = 20.07 (q, Me), 109.32 (s, SCN), 117.32 (t), 118.70 (t), 133.68 (s), 137.93 (s). − GC MS (70 eV); *m*/*z* (%): 125 (15) [M$^+$], 85 (23), 67 (42), 65 (31), 41 (100), 39 (68).

Dithiocyanate 21m from 4i: A solution of NH_4SCN (108 mg, 1.42 mmol) and **4i** (170 mg, 1.17 mmol) in DMSO (10 mL) was stirred for 8 h at room temperature. The reaction mixture was poured into ice/water and extracted three times with *tert*-butyl methyl ether. The combined organic layers were washed with water and dried with $MgSO_4$. Removal of the solvent gave 75 mg (38%) of **21m**, which proved identical to the product obtained by thermolysis of **3m**.

2-Chloro-1-methyleneprop-2-enyl Thiocyanate (21p): A solution of LiCl (60 mg, 1.4 mmol) and **4i** (200 mg, 1.37 mmol) in DMSO (10 mL) was stirred for 8 h at room temperature. After workup as described for the reaction **4i** → **21m**, the product **21p** (70 mg, 35%) was isolated as a colorless oil. − IR ($CDCl_3$): $\tilde{\nu}$ = 2164 cm^{-1} (SCN). − ^{1}H NMR ($CDCl_3$): δ = 5.76 (m, 1 H), 5.95 (m, 1 H), 6.06 (s, 1 H), 6.31 (s, 1 H). − ^{13}C NMR ($CDCl_3$): δ = 109.00 (SCN), 118.87 (t), 127.04 (t), 129.60, 134.53. − C_5H_4ClNS (145.6): calcd. C 41.24, H 2.77, N 9.62, S 22.02; found C 40.95, H 2.80, N 9.69, S 22.40.

2,5-Dimethyl-3,4-dithiocyanatohexa-2,4-diene (24): Compound **23**[26] (1.02 g, 3.8 mmol) was added to a melt of hexadecyltributylphosphonium thiocyanate[27,28] (6.24 g, 12.8 mmol) at 40 °C. The reaction mixture was stirred for 3 d at 40 °C and then extracted with pentane/Et_2O. Removal of the solvent yielded **24** (470 mg, 55%) as a solid, which could be purified by recrystallization (pentane/Et_2O) and sublimation (120 °C/0.001 Torr), m.p. 72 °C. − IR (CCl_4): $\tilde{\nu}$ = 2160 cm^{-1} (SCN), 1605, 1435, 1368. − UV/Vis (cyclohexane): λ_{max} (lg ε) = 231 nm (4.03). − ^{1}H NMR ($CDCl_3$): δ = 1.90 (s, 6 H, Me), 2.10 (s, 6 H, Me). − ^{13}C NMR ($CDCl_3$): δ = 22.22 (q, Me), 23.04 (q, Me), 109.61 (s, SCN), 115.67 (s), 148.70 (s). − MS (70 eV); *m*/*z* (%): 224 (33) [M$^+$], 108 (66), 107 (100), 93 (38), 91 (43). − $C_{10}H_{12}N_2S_2$ (224.3): calcd. C 53.54, H 5.39, N 12.49; found C 53.37, H 5.35, N 12.67.

4-Thiocyanatocyclohex-4-ene-1,1,2,2-tetracarbonitrile (25a): A solution of **21a** (190 mg, 1.71 mmol) and TCNE (280 mg, 2.19 mmol) in THF (10 mL) was stirred for 4 d at room temperature. After evaporation of the solvent, the excess of TCNE was removed by sublimation (60 °C/0.001 Torr). The residue consisted of **25a** (370 mg, 90%) as a yellowish powder, m.p. 184 °C. − IR (KBr): $\tilde{\nu}$ = 2157 cm^{-1} (SCN). − ^{1}H NMR ([D$_6$]acetone): δ = 3.72 (m, 2 H), 3.89 (m, 2 H), 6.71 (m, 1 H, 5-H). − ^{13}C NMR ([D$_6$]acetone): δ = 32.58 (t), 34.28 (t), 37.73 (s), 39.00 (s), 107.76 (SCN), 110.40 (CN), 110.73 (CN), 118.66 (C-4), 129.00 (C-5). − GC MS (70 eV); *m*/*z* (%): 239 (24) [M$^+$], 111 (60), 71 (67), 53 (100). − $C_{11}H_5N_5S$ (239.2): calcd. C 55.23, H 2.11, N 29.27, S 13.39; found C 55.06, H 2.29, N 29.25, S 13.93.

4-Methyl-5-thiocyanatocyclohex-4-ene-1,1,2,2-tetracarbonitrile (25b): The diene **21b** (170 mg, 1.36 mmol) was treated with TCNE in THF according to the procedure for the synthesis of **25a**. After workup, **25b** (310 mg, 90%) was isolated as a brownish powder; m.p. 173 °C. − IR (KBr): $\tilde{\nu}$ = 2262 cm^{-1} (CN), 2162 (SCN). − ^{1}H NMR ([D$_6$]acetone): δ = 2.27 (s, 3 H, Me), 3.78 (m, 2 H), 3.90 (m, 2 H). − ^{13}C NMR ([D$_6$]acetone): δ = 21.01 (Me), 36.08 (t), 37.12 (t), 38.34 (s), 38.78 (s), 108.92 (SCN), 110.43 (CN), 110.64 (CN), 120.07 (C-5), 136.76 (C-4). − GC MS (70 eV); *m/z* (%): 253 (62) [M^+], 125 (60), 85 (100), 67 (98), 39 (62). − $C_{12}H_7N_5S$ (253.3): calcd. C 56.91, H 2.79, N 27.65, S 12.66; found C 56.41, H 2.61, N 27.69, S 11.94.

1,4,5,6,7,8,9,10-Octahydrobenzocycloocten-2-yl Thiocyanate (26a) and 5,6,7,8,9,10-Hexahydrobenzocycloocten-2-yl Thiocyanate (27): A solution of **21a** (350 mg, 3.15 mmol) and cyclooctyne[43] (175 mg, 1.62 mmol) in Et_2O (15 mL) was stirred for 4 d at room temperature. After reaction times of 24, 48, and 72 h, further portions of cyclooctyne (each 175 mg, 1.62 mmol) were added. After 4 d, the solvent and volatile compounds were removed in vacuo, and the residue was purified by flash chromatography (Et_2O/hexane, 1:10) to afford **26a** (220 mg, 32%) as a colorless liquid, which already contained small amounts of **27**. − IR ($CDCl_3$): $\tilde{\nu}$ = 2157 cm^{-1} (SCN). − ^{1}H NMR ($CDCl_3$): δ = 1.31−1.72 (m, 8 H), 2.15 (m, 4 H, 5-H, 10-H), 2.78 (m, 2 H), 2.94 (m, 2 H), 6.17 (m, 1 H, 3-H). − ^{13}C NMR ($CDCl_3$): δ = 25.42 (t), 25.44 (t), 27.43 (t), 27.53 (t), 29.57 (t), 30.84 (t), 32.15 (t), 33.80 (t), 109.13 (SCN), 119.59 (C-2), 126.96 (s), 127.32 (s), 131.61 (C-3). − $C_{13}H_{17}NS$ (219.4): calcd. C 71.18, H 7.81, N 6.39, S 14.62; found C 71.29, H 7.81, N 6.27, S 14.63.

Upon prolonged exposure to air (about 0.5 year), **26a** was completely oxidized to **27**. − ^{1}H NMR ($CDCl_3$): δ = 1.33−1.37 (m, 4 H), 1.63−1.73 (m, 4 H), 2.78 (m, 4 H, 5-H, 10-H), 7.17 (d, ^3J = 7.9 Hz, 1 H, 4-H), 7.28 (d, ^4J = 2.0 Hz, 1 H, 1-H), 7.29 (dd, ^3J = 7.9 Hz, ^4J = 2.0 Hz, 1 H, 3-H). − ^{13}C NMR ($CDCl_3$): δ = 25.75 (t), 25.77 (t), 31.92 (t), 32.04 (t), 32.06 (t), 32.23 (t), 111.20 (s, SCN), 120.70 (s), 128.30 (d), 130.75 (d), 130.79 (d), 143.50 (s), 143.80 (s).

1,4,5,6,7,8,9,10-Octahydrobenzocycloocten-2,3-diyl Dithiocyanate (26m): A solution of **21m** (100 mg, 0.59 mmol) and cyclooctyne[43] (130 mg, 1.20 mmol) in chloroform (2 mL) was stirred at room temperature for 24 h. The solvent and volatile compounds were then removed in vacuo, and the residue was purified by flash chromatography (Et_2O/hexane, 1:9) to yield **26m** (52 mg, 32%) as a white solid, m.p. 63 °C. − IR ($CDCl_3$): $\tilde{\nu}$ = 2162 cm^{-1} (SCN). − ^{1}H NMR ($CDCl_3$): δ = 1.48−1.57 (m, 8 H), 2.19 (t, *J* = 5.4 Hz, 4 H, 5-H, 10-H), 3.20 (s, 4 H, 1-H, 4-H). − ^{13}C NMR ($CDCl_3$): δ = 26.27 (t), 28.34 (t), 30.24 (t), 38.27 (t), 107.40 (SCN), 126.75 (s), 127.12 (s). − $C_{14}H_{16}N_2S_2$ (276.4): calcd. C 60.83, H 5.83, N 10.13, S 23.20; found C 60.54, H 6.00, N 9.85, S 23.17.

Methyl 3,4-Dithiocyanatocyclohex-3-enecarboxylate (28m): A solution of **21m** (80 mg, 0.48 mmol) in methyl acrylate (freshly distilled, 4 mL) was stirred under argon for 7 d at room temperature. Volatile compounds were then removed at 20 °C/0.001 Torr, and the residue was extracted with chloroform. Removal of the solvent gave **28m** (60 mg, 50%) as a colorless oil. − IR ($CDCl_3$): $\tilde{\nu}$ = 2162 cm^{-1} (SCN), 1734 (C=O). − ^{1}H NMR ($CDCl_3$): δ = 1.90−2.04 (m, 1 H), 2.14−2.24 (m, 1 H), 2.56−2.88 (m, 5 H), 3.66 (s, 3 H, OMe). − ^{13}C NMR ($CDCl_3$): δ = 24.96 (t), 31.64 (t), 34.50 (t), 38.89 (d, C-1), 52.35 (q, OMe), 107.17 (s, SCN), 107.32 (s, SCN), 126.50 (s), 130.30 (s), 172.89 (s, C=O). − $C_{10}H_{10}N_2O_2S_2$ (254.3): calcd. C 47.23, H 3.96, N 11.01, S 25.22; found C 47.51, H 4.06, N 10.97, S 25.19.

4-Ethoxycyclohex-1-ene-1,2-diyl Dithiocyanate (29m): A solution of **21m** (80 mg, 0.48 mmol) in ethyl vinyl ether (freshly distilled, 4 mL) was stirred under argon for 28 d at room temperature. Volatile compounds were then removed at 20 °C/0.001 Torr, and the residue was extracted with chloroform. Removal of the solvent yielded **29m** (80 mg, 70%) as a colorless oil. − IR ($CDCl_3$): $\tilde{\nu}$ = 2162 cm^{-1} (SCN). − ^{1}H NMR ($CDCl_3$): δ = 1.12 (t, ^3J = 7.0 Hz, 3 H, Me), 1.82−2.10 (m, 2 H), 2.53−2.90 (m, 4 H), 3.53 (q, ^3J = 7.0 Hz, 2 H, OCH_2), 3.80 (m, 1 H, 4-H). − ^{13}C NMR ($CDCl_3$): δ = 15.46 (q, Me), 27.12 (t), 29.69 (t), 38.58 (t), 64.13 (t, OCH_2), 71.50 (C-4), 107.42 (s, SCN), 107.51 (s, SCN), 125.83 (s), 129.41 (s). − $C_{10}H_{12}N_2OS_2$ (240.4): calcd. C 49.97, H 5.03, N 11.66, S 26.68; found C 50.56, H 5.11, N 11.68, S 27.58.

(*E*)-3-Thiocyanatomethylenecyclohex-4-ene-1,1,2,2-tetracarbonitrile (30): A solution of the equilibrium mixture of **12a** and **14a** (450 mg, 3.66 mmol including 202.5 mg, 1.64 mmol of **14a**) and TCNE (1.00 g, 7.81 mmol) in THF (2 mL) was stirred at room temperature for 2 d. After evaporation of the solvent, unchanged **12a** and then the excess of TCNE were removed at 80 °C/0.001 Torr. The residue consisted of **30** (320 mg, 77% based on **14a**) as a brown powder, m.p. 139−141 °C. − IR ($CDCl_3$): $\tilde{\nu}$ = 2170 cm^{-1} (SCN). − ^{1}H NMR ([D$_6$]acetone): δ = 3.37 (m, 2 H, 6-H), 6.55 (dtd, ^3J = 10.4 Hz, ^3J = 4.2 Hz, ^5J = 1.7 Hz, 1 H, 5-H), 6.84 (dtd, ^3J = 10.4 Hz, ^4J = 2.1 Hz, ^4J = 0.9 Hz, 1 H, 4-H), 7.85 (m, CHSCN). − ^{13}C NMR ([D$_6$]acetone): 33.48 (t, C-6), 41.86 (s), 45.95 (s), 108.76 (s, SCN), 110.60 (s, CN), 112.06 (s, CN), 120.52 (d), 125.37 (s, C-3), 126.27 (d), 129.47 (d). The *E* configuration of **30** was assigned on the basis of homonuclear NOE difference ^{1}H NMR spectra.

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