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[3,3]-Sigmatropic Shifts and Retro-ene Rearrangements in Cyanates, Isocyanates, Thiocyanates, and Isothiocyanates of the Form RX-YCN and RX-NCY†

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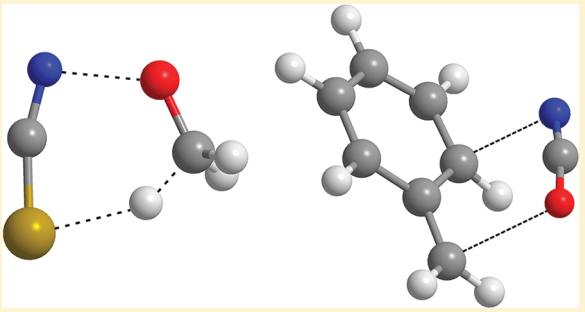
Supporting Information

ABSTRACT: Retro-ene type [$2\pi + 2\pi + 2\sigma$] and [3,3]-sigmatropic shift reactions involving the substituent groups R in heteroatom-substituted cyanates and thiocyanates RX-YCN and the isomeric isocyanates and isothiocyanates of the type RX-NCY (X = CR_2, NR′, O, or S; Y = O or S) have been investigated computationally at the B3LYP/6-311++G(d,p) level. Retro-ene reactions of alkyl derivatives of the title compounds afford alkenes, imines, carbonyl and thiocarbonyl compounds together with HNCO (HNCS) or HOCN (HSCN). [3,3]-Sigmatropic shifts (hetero-Cope rearrangements) of the corresponding allyl, propargyl, benzyl, and aryl derivatives causes allylic rearrangements, propargyl−allenyl rearrangement, conversion of benzyl cyanates to *o*-isocyanatotoluenes, and conversion of *N*-cyanatoarylamines to *o*-isocyanatoanilines, etc. The corresponding rearrangements of allyl thiocyanates, arylamino thiocyanates and isothiocyanates, and arylsulfenyl thiocyanates and isothiocyanates are also described.



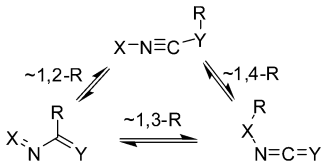
INTRODUCTION

Cyanates, thiocyanates, isocyanates, and isothiocyanates have widespread uses in preparative chemistry.[1−5] The heteroatom-substituted compounds of the types RX-Y-CN and RX-NCY (X = NR′, O, or S; Y = O or S; R, R′ = H, alkyl, or aryl) are often unstable compounds with the characteristics of reactive intermediates, which can, nevertheless, be employed synthetically in situ. Several amino isocyanates R_2N-NCO,[6,7] alkoxy isocyanates RO-NCO,[6] sulfenyl isocyanates RS-NCO,[8] and alkoxy isothiocyanates RO-NCS[9,10] have been prepared and isolated in low-temperature matrices. Amino isothiocyanates R_2N-NCS are in some cases persistent at room temperature for a short time, thus allowing their chemical reactions to be investigated.[11,12] Sulfenyl isothiocyanates RS-NCS have not been characterized securely,[13] but many sulfenyl thiocyanates RS-SCN are known.[14]

Recently, the potential occurrence of 1,4-shifts of substituent groups R of the type R-Y-CNX → R-X-N═C═Y; 1,3-shifts R-C(═Y)-N═X → R-X-N═C═Y; and 1,2-shifts R-C(═Y)-N═X → R-Y-CNX (Scheme 1) was evaluated computationally. The activation energies for several of these reactions would be accessible under conditions of flash vacuum thermolysis (FVT), thus making them good candidates for experimental observation.[15]

The observation of several elimination and rearrangement reactions[16] of carbamoyl azides (R_2N-CO-N_3), alkoxy isothiocyanates (RO-NCS), and related compounds motivated us to investigate the potential occurrence of other rearrangements, particularly the retro-ene and [3,3]-sigmatropic shift reactions described herein.

Scheme 1. 1,2-, 1,3-, and 1,4-Shifts in Iso(thio)cyanates and Nitrile Oxides (Sulfides)



COMPUTATIONAL DETAILS

All calculations were performed with the program package Gaussian 03[17] using the B3LYP[18] density functional with the 6-311++G(d,p)[19] basis set. The nature of all stationary points as true minima or as first-order transition states was confirmed by calculating harmonic frequencies. Scaled zero-point vibrational energy corrections have been taken into account.[20,21]

B3LYP has proved to be a reliable method for the study of systems related to the title compounds, e.g., isocyanates,[15] ketenes,[22] and iminopropadienones.[23] With the development of new DFT methods, several functionals with either an increased amount of exact exchange

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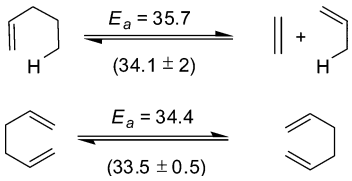
or dispersion corrections have been trialled (see the Supporting Information for details), together with a triple-ζ basis set with diffuse functions which is necessary to correctly treat the weak interactions in loose complexes between cumulenes and nucleophiles (such as amines) and the zwitterions formed therefrom.[22] Although most functionals give similar results for the activation barriers of the retro-ene reaction ([$2\pi + 2\pi + 2\sigma$] cycloreversion) and the Cope rearrangement ([3,3]-sigmatropic shift), which are of particular interest for the present paper, those derived from the B3LYP/6-311+G(d,p) calculations (Scheme 2) are closest to the reference data, within 1−2 kcal/mol of available experimental values.[15,24] All of the calculated transition states at this level are shown in the Supporting Information.

Scheme 2. Activation Barriers at the B3LYP/6-311+G(d) Level in kcal/mol (Experimental Values in Parentheses)

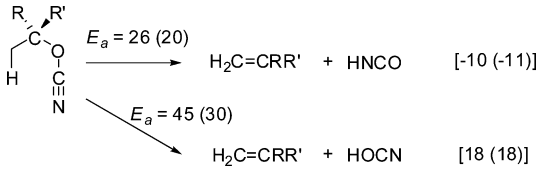


RESULTS AND DISCUSSION

1. Retro-ene Type Reactions. *Alkyl Cyanates ROCN.* Alkyl cyanates R-OCN isomerize to the lower energy isocyanates R-NCO at or above room temperature, probably via an ion-pair mechanism in solution.[25] The rearrangement of primary and secondary alkyl cyanates to isocyanates is much slower but still occurring in the gas phase, probably via bimolecular[26] or wall-catalyzed mechanisms. In addition, elimination of HOCN/HNCO to form alkenes occurs when alkyl cyanates are heated in the gas phase.[25b,27] Secondary and tertiary alkyl cyanates decompose to mixtures of the corresponding isocyanate, HNCO and alkene in solution and in the gas phase. *tert*-Butyl cyanate is very short-lived in solution due to its facile decomposition to isobutene and isocyanic acid.[25d]

The calculated retro-ene activation barriers for formation of HNCO from ethyl and *tert*-butyl cyanates (Scheme 3) are 26 and 20 kcal/mol, respectively, in agreement with the fact that ethyl cyanate is just isolable at room temperature for a short time, but *tert*-butyl cyanate is not. The bond dissociation energy for the homolytic cleavage of the C−O bond is around 61 kcal/mol and hence not responsible for the observed decomposition.

Scheme 3. Elimination of Alkenes from Alkyl Cyanates H_3C-CRR′-OCN[a]

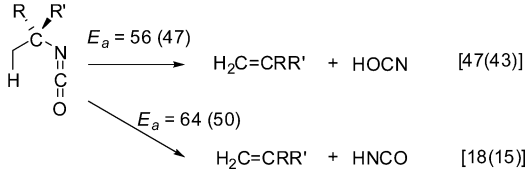


[a]Activation barriers and reaction energies (in brackets) are in kcal/mol; the first numbers refer to R = R′ = H and the values in parentheses to R = R′ = Me. The calculated energy difference between HOCN and HNCO is 28 kcal/mol.

A 1,2-elimination of HOCN has a higher activation energy of 45 (Et) and 30 (*t*-Bu) kcal/mol, and this reaction has not been observed.

Alkyl Isocyanates RNCO. Gas-phase thermolysis of alkyl isocyanates, particularly secondary and tertiary ones, affords alkenes and isocyanic acid, HNCO. The measured activation energies were 53.3 and 52.4 kcal/mol for isopropyl and *tert*-butyl isocyanates, respectively.[28a] Similar activation energies were obtained in a second study,[28b] 55.2, 51.8, and 51.6 ± 0.5 kcal/mol, for ethyl, isopropyl, and *tert*-butyl isocyanates, respectively, and it was determined that the unimolecular decompositions of ethyl and isopropyl isocyanates (but not *tert*-butyl isocyanate) are accompanied by parallel, autocatalytic free radical chain reactions.[28b] Photolysis of ethyl isocyanate also produces HNCO among other products.[29] Cyanic acid, HOCN, could in principle be formed in retro-ene type reactions on FVT of these alkyl isocyanates, but only HNCO was detected by us in millimeterwave and matrix-isolation IR spectroscopy experiments on the FVT of *tert*-butyl isocyanate because of either a direct formation of isocyanic acid in a 1,2-elimination process or tautomerization of cyanic acid. The latter reaction is very likely to take place on collisions with the hot quartz wall in FVT and static pyrolysis experiments. Our calculations on the decomposition of the ethyl and *tert*-butyl isocyanates (Scheme 4) to HNCO reveal barriers for the 1,2-eliminations of 64 (Et) and 50 (*t*-Bu) kcal/mol. The barriers for the retro-ene reactions leading to HOCN formation are lower with 56 and 47 kcal/mol for ethyl and *tert*-butyl isocyanates, respectively, and thus in better agreement with experiment, but the difference is small for *t*-Bu. The transition states for the *tert*-butyl isocyanate reactions are given in Figure 1. It is noted that the C−N bond breakage is very advanced in the transition state for the retro-ene raction (2.8 A). However, simple homolysis does not play any role, as the calculated bond dissociation energy of the C−N bond is 86−90 kcal/mol.

Scheme 4. Elimination of Alkenes from Alkyl Isocyanates H_3C-CRR′-NCO[a]



[a]Activation barriers and reaction energies (in brackets) are in kcal/mol; the first numbers refer to R = R′ = H and the values in parentheses to R = R′ = Me. The calculated energy difference between HOCN and HNCO is 28 kcal/mol.

The differences between Schemes 3 and 4 can be rationalized as follows: in Scheme 3, the starting point is the high energy cyanate (ca. 25−28 kcal/mol above the corresponding isocyanate in Scheme 4), and the formation of HNCO is the most favorable (exothermic) reaction, which indeed has the lowest activation barrier. In Scheme 4, in contrast, the starting point is the low energy isocyanate, and the otherwise preferred retro-ene reaction leads to the high-energy HOCN, 28 kcal/mol above HNCO. This allows the formation of HNCO to be almost competitive.

Alkylamino and imino cyanates. Alkylamino and imino cyanates R_2N-OCN and RR′C═N-OCN are little known compounds that have not been fully characterized.[30−33] We have

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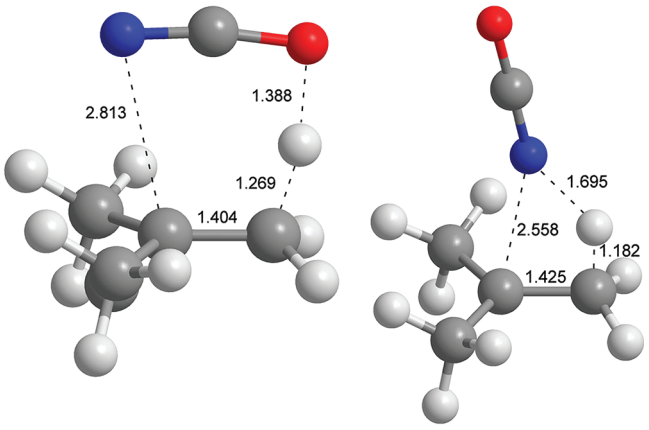
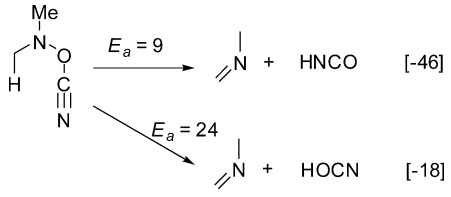


Figure 1. Transition states for the reactions of *tert*-butyl isocyanate shown in Scheme 4: retro-ene rearrangement (left) and 1,2-elimination (right) (bond distances in A).

calculated the activation energy for the retro-ene reaction of dimethylamino cyanate to HNCO and *N*-methylmethanimine

Scheme 5. Fragmentation of *N*-Dimethylamino Cyanate[a]



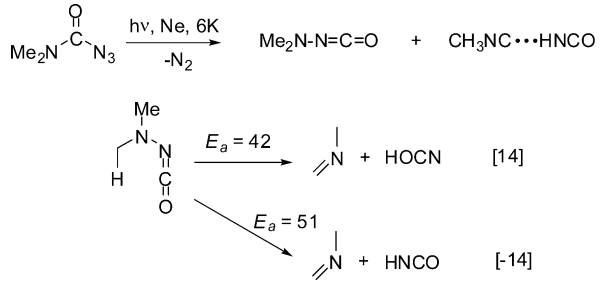
[a]Activation barriers and reaction energies (in brackets) are in kcal/mol.

(Scheme 5) to be as little as 9 kcal/mol, and even the 1,2 elimination of HOCN possesses a feasible barrier of only 24 kcal/mol. However, the energy required for breaking the N−O bond in dimethylamino cyanate is only 23 kcal/mol, so that homolytic fragmentation of amino cyanates may also be a potential pathway to cyanic acid under high-temperature conditions.

Amino Isocyanates R_2N-NCO. Generation of dimethylamino isocyanate by photolysis of dimethylcarbamoyl azide in a neon matrix at 6 K is accompanied by IR bands assigned to HNCO and a molecular complex between CH_3NC and HNCO.[34] Dimethylamino isocyanate and HNCO are also formed on FVT of the azide at 350−600 °C and detected by Ar-matrix IR (2218 and 2259 cm^{-1}, respectively) and mass spectrometry.[35]

Under matrix photolysis conditions, it is likely that HNCO is formed directly rather than by tautomerization of HOCN, but both paths are potentially possible in the gas phase FVT reaction. Both paths are computationally feasible, and the transition states are shown in Figure 2. The retro-ene type elimination of HOCN is favored over the 1,2-elimination to HNCO by ca. 9 kcal/mol, and the N−N bond breakage is very advanced in both transition states (2.4 A). The formation of *N*-methylmethanimine and HOCN is slightly endothermic, but the formation of *N*-methylmethanimine and HNCO is exothermic by 14 kcal/mol. The differences between the cyanate and isocyanate reactions in Schemes 5 and 6 can be

Scheme 6. Fragmentation of *N*-Dimethylamino Isocyanate[a]



[a]Activation barriers and reaction energies (in brackets) are in kcal/mol.

understood in the same way as described for Schemes 3 and 4 above.

It must be noted that the calculated N−N bond dissociation energy in Me_2N-NCO is ca. 56 kcal/mol, and therefore free radical processes are probably not responsible for the formation of HNCO.[36]

Alkoxy Isocyanates RO-NCO. Monomeric methoxy isocyanate has been prepared in Ne and Ar matrices by photolysis

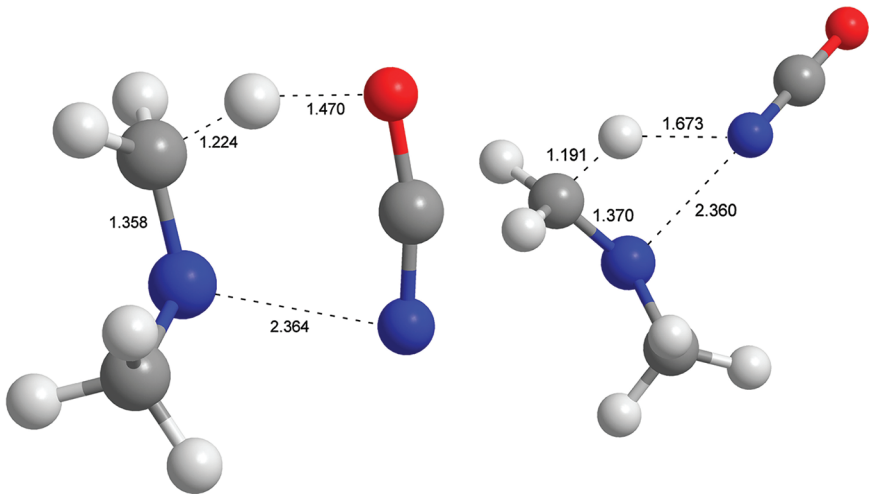


Figure 2. Transition states for the reactions of dimethylamino isocyanate shown in Scheme 6: retro-ene rearrangement (left) and 1,2-elimination (right) (bond distances in Å).

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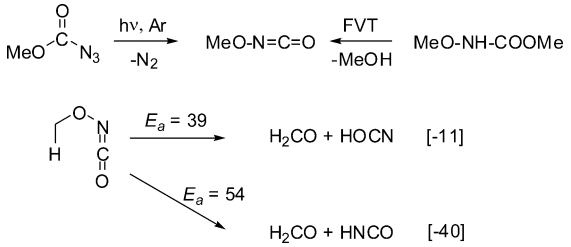
of methyl azidoformate and by FVT of *N*-methoxycarbonyl-*O*-methylhydroxylamine (together with some HNCO and formaldehyde) (Scheme 7).[37,6] It is also formed on FVT of methyl azidoformate, but only in trace amounts, the major products being formaldehyde, HNCO, carbon dioxide, and methanimine.[6] Several mechanisms for formation of the byproduct have been discussed, including pericyclic fragmentations of *N*-methoxycarbonyl-*O*-methylhydroxylamine.[6] The potential retro-ene fragmentation H_3CO-NCO → HOCN + $H_2C{=}O$ was not considered. We calculate an activation barrier of 39 kcal/mol for this reaction (Scheme 7). Such a reaction would be very feasible under FVT conditions, whereas the direct 1,2-elimination of HNCO requires a much higher activation energy of 54 kcal/mol. As mentioned above, FVT experiments in our laboratories indicate that cyanic acid, HOCN, isomerizes very easily to the lower energy isocyanic acid, HNCO, during collisions with the hot wall of the quartz tube. The N−O bond dissociation energy of 44 kcal/mol makes a radical fragmentation pathway less likely but not impossible in this case.

Scheme 7. Formation and Fragmentation of Methoxy Isocyanate[a]

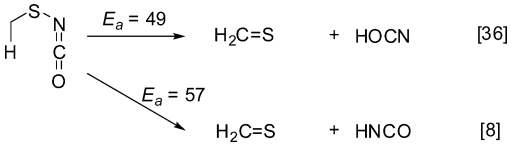


[a]Activation barriers and reaction energies (in brackets) are in kcal/mol.

Alkoxy cyanates (percyanates) RO-OCN are not known. They are expected to be highly unstable compounds that easily undergo both retro-ene and free radical fragmentation reactions.

Sulfenyl Isocyanates RS-NCO. Several halogenated alkylsulfenyl isocyanates have been prepared,[38,39] but simple alkylsulfenyl isocyanates are unknown. We calculate a barrier of 49 kcal/mol for the retro-ene reaction of CH_3S-NCO, which is lower by 8 kcal/mol than the barrier of the direct 1,2-elimination. Radical fragmentation requires 62 kcal/mol and is hence unlikely to occur (Scheme 8). Thus, alkylsulfenyl isocyanates should be potentially isolable compounds.

Scheme 8. Fragmentation of Methylsulfenyl Isocyanate[a]

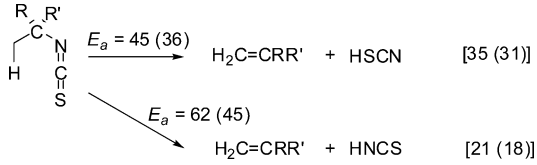


[a]Activation barriers and reaction energies (in brackets) are in kcal/mol.

Sulfenyl cyanates RS-OCN are unknown, but comparison with the other reactions described herein makes it very likely that retro-ene fragmentations will occur easily (see further under [3,3]-rearrangements).

Alkyl isothiocyanates R-NCS. Alkyl isothiocyanates R-NCS undergo pyrolytic fragmentation to alkenes and isothiocyanic acid, HNCS, with activation barriers ca. 13 kcal/mol lower than those for the corresponding fragmentation of isocyanates RNCO with large alkyl groups (Scheme 9).[28] Our calculated barriers for 1,2-elimination of HNCS in ethyl and *tert*-butyl isothiocyanates are 62 and 45 kcal/mol, respectively, which are in fact a little lower than those in RNCO. The preferred pathway remains the retro-ene type elimination of HSCN with activation energies of 45 (Et) and 36 (*t*-Bu) kcal/mol (about 11 kcal/mol lower than for the isocyanates described above). Simple homolysis is unimportant with calculated C−N bond dissociation energies of 70−74 kcal/mol.

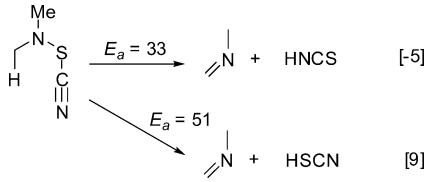
Scheme 9. Fragmentation of Alkyl Isothiocyanates[a]



[a]Activation barriers and reaction energies (in brackets) are in kcal/mol; the first numbers refer to R = R′ = H and the values in parentheses to R = R′ = Me.

Amino Thiocyanates RR′N-SCN. Amino Thiocyanates RR′N-SCN are known compounds.[40] Me_2N-SCN, MeN-$(SCN)_2$, and $N(SCN)_3$ are obtained as unstable liquids which can be stored for some time at −78 to −20 °C.[41] *N*-Thiocyanatobenzylamines have also been prepared.[42] Retro-ene reactions have not been reported for these compounds, but a barrier of 33 kcal/mol is calculated for Me_2N-SCN, thus making this a very likely route to HNCS (Scheme 10). The direct 1,2-elimination requires 51 kcal/mol, which is even more than the bond dissociation energy (43 kcal/mol), and thus it is unlikely to be observed.

Scheme 10. Fragmentation of *N*-Dimethylamino Thiocyanate[a]



[a]Activation barriers and reaction energies (in brackets) are in kcal/mol.

Amino Isothiocyanates R_2N-NCS. Several dialkylamino isothiocyanates have been prepared as transient intermediates, which can be trapped in low temperature reactions and stored at liquid air temperature.[11] Retro-ene reactions have not been reported, but the calculated barrier of only 32 kcal/mol for the conversion of Me_2N-NCS to HSCN and *N*-methylmethanimine would make this reaction very feasible. We calculate 46 kcal/mol for the unlikely 1,2-elimination, which is in the same range as homolysis (the N−N bond dissociation energy is 43 kcal/mol).

The energetics for the fragmentations of amino thiocyanates and amino isothiocyanates (Schemes 10 and 11) are much more similar than those for cyanates and isocyanates (Schemes 5 and 6). This can be ascribed largely to the fact that the

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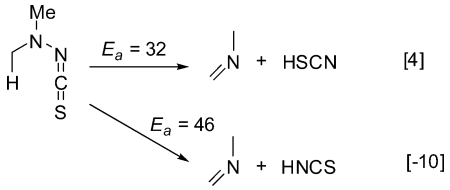
Scheme 11. Fragmentation of *N*-Dimethylamino Isothiocyanate[a]

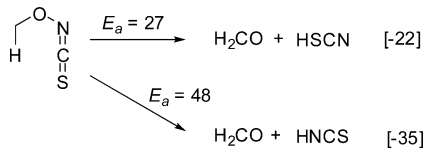


[a]Activation barriers and reaction energies (in brackets) are in kcal/mol.

calculated energy differences between thiocyanates and isothiocyanates is very small (0−5 kcal/mol), and the difference between HSCN and HNCS is only 14 kcalmol (cf. 28 kcal/mol for HOCN/HNCO).

Alkoxy isothiocyanates RO-NCS. Alkoxy isothiocyanates RO-NCS have been found to undergo a thermal pericyclic retro-ene type elimination of aldehyde to form HSCN (Scheme 12).[10]

Scheme 12. Fragmentation of Methoxy Isothiocyanate[a]



[a]Activation barriers and reaction energies (in brackets) are in kcal/mol.

The calculated activation barriers at the B3LYP/6-311++G(d,p) level are 27 and 48 kcal/mol for HSCN and HNCS formation, respectively. This is in good agreement with previous calculations (barriers to HSCN formation at the B3LYP/6-31G(d,p) and MP2/cc-pVDZ levels are 32 and 27 kcal/mol; the 1,2-elimination requires an additional 25 kcal/mol).[10] The HSCN formed tautomerizes to the more stable HNCS. The facile retro-ene reaction explains why EtO-NCS was not observable in the FVT reaction.[10]

The calculated N−O bond dissociation energy in 1-methyl-3-methoxythiourea is ca. 48 kcal/mol[10] However, it is lowered to a mere 30 kcal/mol in the case of MeO-NCS. Therefore, in this case, free-radical fragmentation may compete with retro-ene process forming HSCN but not with the molecular elimination of HNCS.

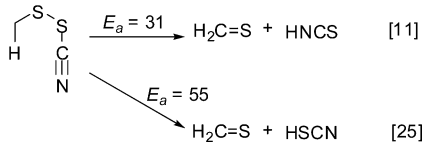
Alkoxy thiocyanates RO-SCN. Alkoxy thiocyanates RO-SCN are unknown, but a comparison with the other compounds described herein makes retro-ene fragmentations very likely.

Sulfenyl thiocyanates RS-SCN are in many cases isolable but somewhat labile compounds.[14] These compounds have not been reported to isomerize to the isothiocyanates, RS-NCS. Such isomerization is a common reaction for secondary and tertiary alkyl, allylic, and benzylic thiocyanates.[5]

We calculate an activation barrier of 31 kcal/mol for the retro-ene reaction of methylsulfenyl thiocyanate to HNCS, which is therefore a very likely reaction (Scheme 13). The calculated barriers for the 1,2-elimination leading to HSCN and the homolysis of the S−S bond are 55 and 47 kcal/mol, respectively, and these reactions are, therefore, unlikely to compete.

The calculated data for the retro-ene type reactions are summarized in Table 1 for easy direct comparison.

Scheme 13. Fragmentation of Methylsulfenyl Thiocyanate[a]



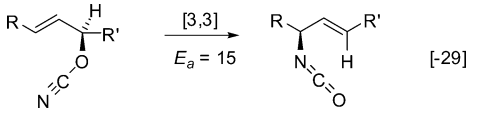
[a]Activation barriers and reaction energies (in brackets) are in kcal/mol.

Table 1. Activation and Reaction Energies (kcal/mol) for Retro-ene Rearrangements and 1,2-Elimination Discussed in Schemes 3−13

reactant	E_a (ΔE_R) retro-ene rearrangement	E_a (ΔE_R) 1,2-elimination
CH_3-CR_2-OCN (Scheme 3)	$H_2C{=}CR_2$ + HNCO	$H_2C{=}CR_2$ + HOCN
R = H	26 (−10)	45 (18)
R = Me	20 (−11)	30 (18)
CH_3-CR_2-NCO (Scheme 4)	$H_2C{=}CR_2$ + HOCN	$H_2C{=}CR_2$ + HNCO
R = H	56 (47)	64 (18)
R = Me	47 (43)	50 (15)
$N(CH_3)_2$-OCN (Scheme 5)	$H_2C{=}$NMe + HNCO	$H_2C{=}$NMe + HOCN
	9 (−46)	24 (−18)
$N(CH_3)_2$-NCO (Scheme 6)	$H_2C{=}$NMe + HOCN	$H_2C{=}$NMe + HNCO
	42 (14)	51 (−14)
CH_3O-NCO (Scheme 7)	$H_2C{=}O$ + HOCN	$H_2C{=}O$ + HNCO
	39 (−11)	54 (−40)
CH_3S-NCO (Scheme 8)	$H_2C{=}S$ + HOCN	$H_2C{=}S$ + HNCO
	49 (36)	57 (8)
CH_3-CR_2-NCS (Scheme 9)	$H_2C{=}CR_2$ + HSCN	$H_2C{=}CR_2$ + HNCS
R = H	45 (35)	62 (21)
R = Me	36 (31)	45 (18)
$N(CH_3)_2$-SCN (Scheme 10)	$H_2C{=}$NMe + HNCS	$H_2C{=}$NMe + HSCN
	33 (−5)	51 (9)
$N(CH_3)_2$-NCS (Scheme 11)	$H_2C{=}$NMe + HSCN	$H_2C{=}$NMe + HNCS
	32 (4)	46 (−10)
CH_3O-NCS (Scheme 12)	$H_2C{=}O$ + HSCN	$H_2C{=}O$ + HNCS
	27 (−22)	48 (−35)
CH_3S-SCN (Scheme 13)	$H_2C{=}S$ + HNCS	$H_2C{=}S$ + HSCN
	31 (11)	55 (25)

2. [3,3]-Sigmatropic Shifts. *Allyl and Propargyl Cyanates.* Allylic cyanates RR′C=CH−CHR″-OCN isomerize very rapidly to the isocyanates OCN-CRR′-CH=CHR″[43] with conservation of chirality[43c] by means of a [3,3]-sigmatropic shift of the OCN group (Scheme 14). The allylic cyanates are

Scheme 14. Rearrangement of Allylic Cyanates[a]



[a]Activation barriers and reaction energies (in brackets) are in kcal/mol.

only rarely detectable, but one highly substituted and conjugated example has been isolated (ethyl 3-cyanato-5,5-diphenyl-2,4-pentadienoate), and the activation enthalpy for

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the [3,3]-sigmatropic rearrangement to the isocyanate (ethyl 5-isocyanato-5,5-diphenyl-2,3-pentadienoate) was measured as 19 kcal/mol with an entropy of activation of −30 cal K^{-1} mol^{-1}.[43e] This is in good accord with our calculations, which predict a barrier of only 15 kcal/mol for the unhindered 3-cyanato-1-propen (the transition state is shown in Figure 3). Thus, simple allylic cyanates are practically unisolable.

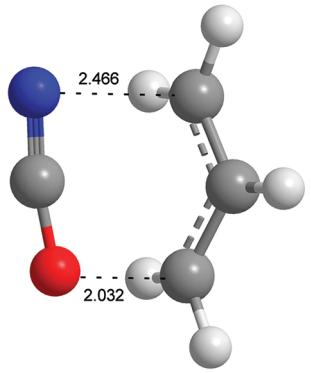
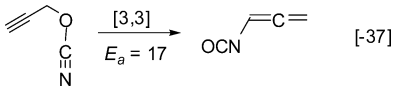


Figure 3. Transition state for the 3,3-sigmatropic rearrangement of 3-cyanato-1-propene shown in Scheme 14 (bond distances in Å).

Similarly, propargyl cyanates $R^1CC\text{-}CR^2R^3\text{-}OCN$ undergo the [3,3]-sigmatropic rearrangement to allenyl isocyanates $R^2R^3C{=}C{=}CR^1\text{-}NCO$ at 20 °C.[43f] The [3,3]-rearrangement of allylic cyanates is faster than that of the propargylic ones[43e] In agreement with this, we calculate an activation barrier of 17 kcal/mol for the parent reaction $HCC\text{-}CH_2\text{-}OCN \rightarrow O{=}C{=}N\text{-}CH{=}C{=}CH_2$ (Scheme 15).

Scheme 15. Rearrangement of Propargyl Cyanate to Allenyl Isocyanate[a]



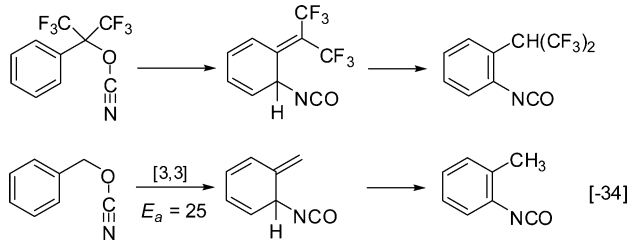
[a]Activation barriers and reaction energies (in brackets) are in kcal/mol.

Benzyl Cyanates. The attempted preparation of α,α-bis(trifluoromethyl)benzyl cyanate, $Ph\text{-}C(CF_3)_2\text{-}OCN$, from the alcohol, ClCN, and base led instead to the [3,3]-rearrangement product *o*-isocyanato-α,α-bis(trifluoromethyl)toluene (Scheme 16).[44]

Benzyl cyanate $PhCH_2\text{-}OCN$ is also a very unstable compound. Although it can be detected by IR spectroscopy in solution at −25 °C, it rearranges almost explosively to benzyl isocyanate if heated above 0 °C.[25d] The isocyanate then trimerizes to tribenzyl isocyanurate. However, the decomposition products have not been fully characterized.[25d] We calculated the barrier for the [3,3]-rearrangement of benzyl cyanate according to Scheme 16 as 25 kcal/mol in agreement with the unstable nature of the compound.

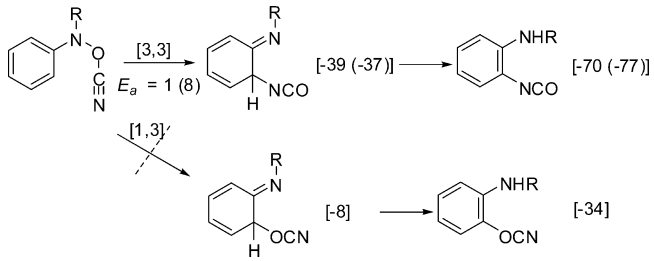
Arylamino Cyanates. *N*-Cyanates have calculated energies some 30 kcal/mol higher than the *N*-isocyanates; e.g., the unknown $Ph_2N\text{-}OCN$ is 34 kcal/mol above $Ph_2N\text{-}NCO$. Being so high in energy, it is no surprise that its [3,3]-sigmatropic rearrangement is almost barrierless (0.6 kcal/mol) (Scheme 17). The intermediate product, isocyanophenyliminocyclohexadiene, and the final product, *o*-anilinophenyl isocyanate, are

Scheme 16. Benzyl Cyanate Rearrangements[a]



[a]Activation barriers and reaction energies (in brackets) are in kcal/mol.

Scheme 17. Rearrangement of *N*-Diphenylamino Cyanate, R = Ph (*N*-Acetyl-*N*-phenylamino cyanate, R = C(O)Me)[a]



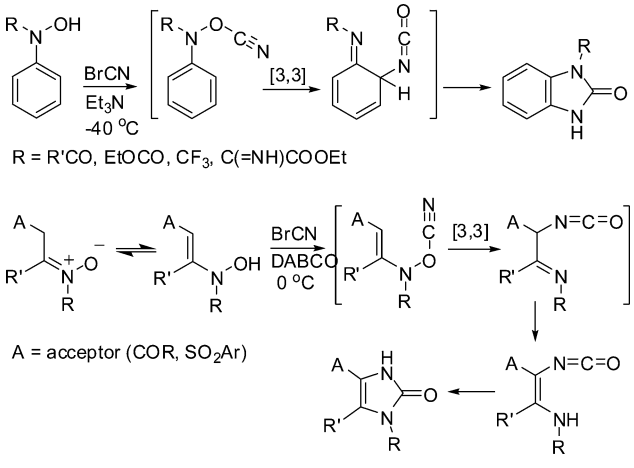
[a]Activation barriers and reaction energies (in brackets) are in kcal/mol.

both clearly favored thermodynamically by about 39 and 70 kcal/mol, respectively. The formal 1,3-H shift to *o*-anilinophenyl isocyanate is unlikely to occur intramolecularly; instead, this product will be formed by intermolecular tautomerization in solution.

Similarly to the results for the rearrangements of *N*-diphenylamino cyanate, the calculated [3,3]-sigmatropic rearrangement of *N*-acetyl-N-phenylamino cyanate possesses a very low activation barrier of 8 kcal/mol, with reaction energies of −37 and −77 for the two steps (Scheme 17). Thus, the *N*-cyanates are found to be highly unstable, short-lived reactive intermediates.

Lobo and co-workers have described syntheses of benzimidazolones, imidazolones, and related compounds by treatment of hydroxylamines or nitrones with BrCN and base at low temperatures.[45] The reactions are believed to proceed via

Scheme 18. *N*-Arylamino Cyanate Rearrangements



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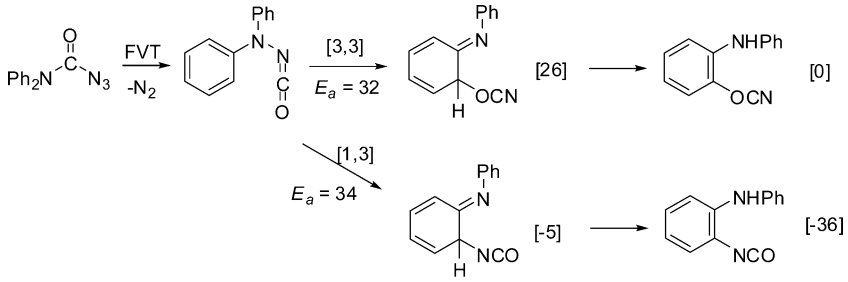
Scheme 19. Rearrangement of *N*-Diphenylamino Isocyanate[a]



[a]Activation barriers and reaction energies (in brackets) are in kcal/mol.

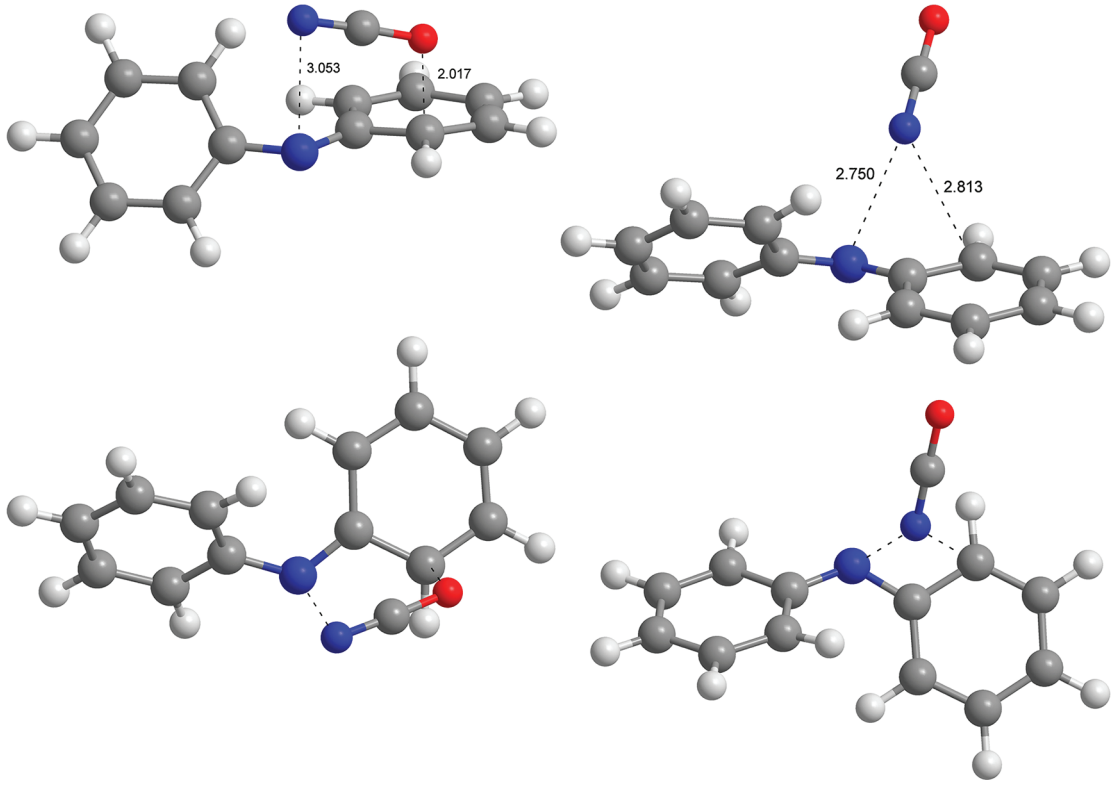


Figure 4. Transition states in different orientations for the reactions of diphenylamino isocyanate shown in Scheme 19: 3,3-sigmatropic rearrangement (left) and 1,3-shift (right) (bond distances in Å).

transient *N*-cyanatoamines, which undergo rapid [3,3]-sigmatropic shifts to enamino isocyanates prior to cyclization (Scheme 18).

Arylamino Isocyanates. Diphenylamino isocyanate (ν_{max} 2220 cm^{-1} in Ar matrix) is obtained on FVT of *N,N*-diphenylcarbamoyl azide at 370−650 °C with low-temperature isolation of the product as well as by matrix photolysis (254 nm) of the azide.[35] Diphenylamino isocyanate would be able to rearrange to *o*-anilinophenyl cyanate in a [3,3]-sigmatropic shift (Scheme 19). The calculated activation barrier for this reaction is 32 kcal/mol at the B3LYP/6-311++G(d,p) level, which indicates that it is difficult to prevent the reaction from occurring under FVT conditions. However, an unusual 1,3-sigmatropic shift of the NCO group in diphenylamino isocyanate to form the corresponding isocyanate has virtually the same calculated activation barrier, 34 kcal/mol, and this reaction is thermodynamically advantageous, since isocyanates are of lower energy than cyanates (Scheme 19). Figure 4 shows the structures of the calculated transition states for both reactions.

The calculated N−N bond dissociation energy in Ph_2N-NCO is only 38 kcal/mol. Therefore, the molecular rearrangements illustrated in Scheme 19 are energetically preferred, but free radical processes cannot be excluded under FVT conditions, where, in fact, diphenylamine, carbazole, and HNCO have been detected by IR and mass spectrometry.[35] It is also noted that the N−N bond breakage is very advanced in both of the transition states shown in Figure 4 (3.1 and 2.8 A, respectively).

The difference in barrier heights for the [3,3]-rearrangements of diphenylamino cyanate and diphenylamino isocyanate (30 kcal/mol, Schemes 17 and 19) is approximately equal to the ground-state energy difference between the cyanate and the isocyanate.

Sulfenyl Cyanates. RS-OCN compounds are not known, but it should be possible to generate them as reactive

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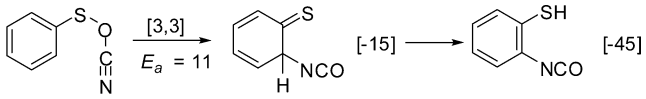
intermediates. The calculated rearrangement barrier for phenylsulfenyl cyanate is only 11 kcal/mol, and the reaction is highly exothermic (Scheme 20), probably due to the instability of the

Scheme 20. Rearrangement of Phenylsulfenyl Cyanate[a]

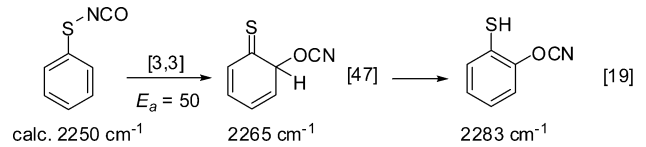


[a]Activation barriers and reaction energies (in brackets) are in kcal/mol.

S−O bond in the sulfenyl cyanates. The calculated bond dissociation energy of the S−O bond is 31 kcal/mol.

Arylsulfenyl Isocyanates. Arylsulfenyl isocyanates have been described as polymeric, although the nature of both the monomeric and the polymeric materials remains obscure.[46,47] The reaction of 2,4,6-tri-*tert*-butylphenylsulfenyl chloride with metal cyanates was reported to give rise to a new absorption at 1940 cm^{-1} in the IR spectrum, which was ascribed to 2,4,6-tri-*tert*-butylphenylsulfenyl isocyanate;[47] however, it is very unlikely that an isocyanate would absorb at such a low frequency, and the calculated absorption is in fact at 2250 cm^{-1} for phenylsulfenyl isocyanate (Scheme 21).

Scheme 21. Rearrangement of Phenylsulfenyl Isocyanate[a]

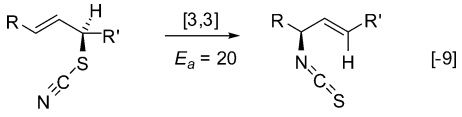


[a]Activation barriers and reaction energies (in brackets), calculated at the B3LYP/6-311++G(d,p) level, are in kcal/mol. Wavenumbers at the B3LYP/6-31G(d) level, scaled by a factor 0.9613.

Our calculated activation barrier for the [3,3]-sigmatropic rearrangement of phenylsulfenyl isocyanate is 50 kcal/mol (Scheme 21). Thus, this reaction will not take place easily, and with an S−N bond homolysis energy of 61 kcal/mol, phenylsulfenyl isocyanate should be an isolable compound under suitable reaction conditions. Further investigation of the formation and chemistry of arylsulfenyl isocyanates is indicated.

Allyl Thiocyanates. [3,3]-Sigmatropic rearrangements of allyl thiocyanates to allyl isothiocyanates have been reported.[48] The calculated barrier of 20 kcal/mol for the rearrangement of 3-thiocyanato-1-propene (Scheme 22) is in agreement with

Scheme 22. Rearrangement of Allylic Thiocyanates[a]

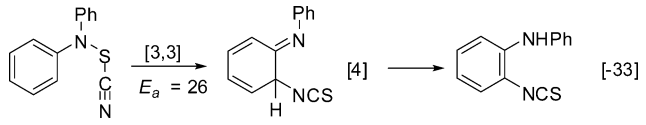


[a]Activation barriers and reaction energies (in brackets) are in kcal/mol.

the ready occurrence of this reaction. The barrier is 5 kcal/mol higher than that for the corresponding cyanate rearrangement (Scheme 14), but the allylic thiocyanates will still be very unstable compounds. For the analogous allyl selenocyanate to allyl isoselenocyanate rearrangement, see Banert et al.[49]

Amino Thiocyanates R_2N-SCN. Amino Thiocyanates R_2N-SCN should also rearrange easily: the barrier is predicted to be 26 kcal/mol for the *N*-diphenylamino thiocyanate (Scheme 23).

Scheme 23. Rearrangement of *N*-Diphenylamino Thiocyanate[a]

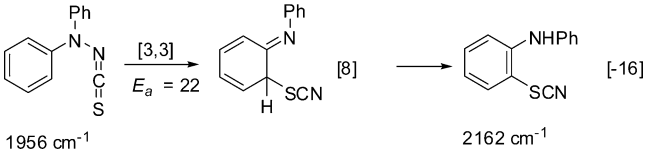


[a]Activation barriers and reaction energies (in brackets) are in kcal/mol.

However, the N−S bond energy is comparable (29 kcal/mol), so that homolysis is also feasible.

Arylamino Isothiocyanates. *N*-Diphenylamino isothiocyanate was obtained by treating diphenyldithiocarbazic acid with dicyclohexylcarbodiimide at −80 °C. The IR absorption at 1956 cm^{-1} disappeared rapidly on warming to room temperature, to be replaced by a band at 2162 cm^{-1} due to a rearrangement to *o*-thiocyanatodiphenylamine (Scheme 24).[12]

Scheme 24. Rearrangement of *N*-Diphenylamino Isothiocyanate[a]



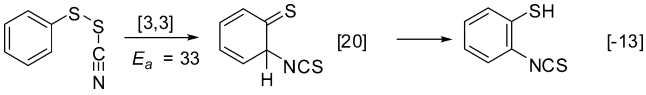
[a]Activation barriers and reaction energies (in brackets) are in kcal/mol.

We calculate a barrier of only 22 kcal/mol for this [3,3]-sigmatropic shift. This is only slightly less than the N−N bond dissociation energy of 25 kcal/mol, so that homolysis is a possibility in the higher temperature regime.

Aryloxy isothiocyanates ArO-NCS are currently not known, but they are expected to be very unstable compounds, rearranging very easily in a similar manner.

Arylsulfenyl Thiocyanates. PhSSCN has been reported to decompose at 70 °C with formation of PhSCN,[50] but no analytical details were provided. It seems more likely that the computationally facile [3,3]-sigmatropic rearrangement to *o*-(HS)-C_6H_4-NCS was taking place (Scheme 25). Obviously, this

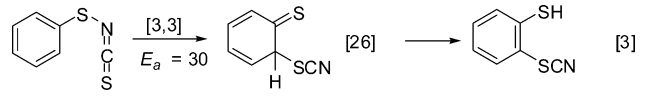
Scheme 25. Rearrangement of Phenylsulfenyl Thiocyanate[a]



[a]Activation barriers and reaction energies (in brackets) are in kcal/mol.

reaction needs reinvestigation. We calculate an activation energy of 33 kcal/mol. Homolytic fragmentation does not play a role, as the cleavage of the S−S bond requires 48 kcal/mol.

Scheme 26. Rearrangement of Phenylsulfenyl Isothiocyanate[a]



[a]Activation barriers and reaction energies (in brackets) are in kcal/mol.

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Table 2. Activation and Reaction Energies (kcal/mol) for [3,3] and [1,3] Sigmatropic Rearrangements Described in Schemes 14−26

reaction	E_a (ΔE_R) [3,3] sigmatropic shift	E_a (ΔE_R) [1,3] sigmatropic shift
H_2C═CH-CH_2-OCN → H_2C═CH-CH_2-NCO (Scheme 14)	15 (−29)	
HC≡C-CH_2-OCN → H_2C═C═CH-NCO (Scheme 15)	17 (−37)	
PhCH_2-OCN → *o*-CH_3-Ph-NCO (Scheme 16)	25 (−34)	
Ph_2N-OCN → *o*-NHPh-Ph-NCO (3,3) or *o*-NHPh-Ph-OCN (1,3) (Scheme 17)	1 (−70)	
PhAcN-OCN → *o*-NHAc-Ph-NCO (3,3) or *o*-NHPh-Ph-OCN (1,3) (Scheme 17)	8 (−77)	
Ph_2N-NCO → *o*-NHPh-Ph-OCN (3,3) or *o*-NHPh-Ph-NCO (1,3) (Scheme 19)	32 (0)	34 (−36)
PhS-OCN → *o*-SH-Ph-NCO (Scheme 20)	11 (−45)	
PhS-NCO → *o*-SH-Ph-OCN (Scheme 21)	50 (19)	
H_2C═CH-CH_2-SCN → H_2C═CH-CH_2-NCS (Scheme 22)	20 (−9)	
Ph_2N-OCN → *o*-NHPh-Ph-NCO (Scheme 23)	26 (−33)	
Ph_2N-NCS → *o*-NHPh-Ph-SCN (Scheme 24)	22 (−16)	
PhS-SCN → *o*-SH-Ph-NCS (Scheme 25)	33 (−13)	
PhS-NCS → *o*-SH-Ph-SCN (Scheme 26)	30 (3)	

Sulfenyl Isothiocyanates RS-NCS. There are no reliable reports on sulfenyl isothiocyanates, RS-NCS,[13] but our calculations indicate that the [3,3]-sigmatropic shift would be facile for the unknown PhS-NCS with an activation barrier of 30 kcal/mol (Scheme 26). Again, the S−N bond dissociation energy is too high to be relevant at 47 kcal/mol .

The computed data are summarized in Table 2 for ease of comparison.

CONCLUSION AND OUTLOOK

All the pericyclic retro-ene and [3,3]-rearrangements considered here are energetically feasible, mostly with modest and sometimes with very low activation energies. Most of the cyanates and thiocyanates are potentially isolable compounds, at least at low temperatures, but some of them have activation barriers so low that they are practically unobservable reactive intermediates under ordinary reaction conditions. This is the case for example with the *N*-cyanates, RR′N-OCN and *S*-cyanates RS-OCN (activation barriers 1−11 kcal/mol for retro-ene and [3,3]-sigmatropic shifts (Schemes 5, 17, 18, and 20). Nevertheless, such compounds should be observable under suitable matrix isolation conditions.

The six-centered transition state for retro-ene reactions is always favored for these decompositions, but in some cases the alternative four-centered 1,2-elimination has a (nearly) competitive activation energy. Isocyanates are about 30 kcal/mol more stable than the corresponding cyanates, whereas there is only a very small calculated energy difference between thiocyanates and isothiocyanates. Alkoxy isocyanates RO-NCO and amino isocyanates RR′N-NCO, are unstable compounds isolable at low temperatures, and they rearrange with activation barriers of ca. 30−44 kcal/mol (Schemes 6, 7 and 19). A comparison of the energy data for dimethylamino cyanate and the corresponding isocyanate (Schemes 5 and 6) reveals that in the former case a very low activation energy of 9 kcal/mol can be ascribed to the high-lying cyanate as the starting point, and formation of the low-lying HNCO as the product, which makes the reaction exothermic by 59 kcal/mol. The corresponding reaction of dimethylamino isocyanate (Scheme 6) has a more substantial barrier of 44 kcal/mol, which can be ascribed to the low-lying isocyanate as the starting point and the formation of the high-lying HOCN as the product, thereby making the reaction essentially thermoneutral.[51] As a consequence, a lower difference in barrier heights for the retro-ene and 1,2-eliminations is calculated (44 and 51 kcal/mol). A similar comparison can be made for the reactions of alkyl cyanates and isocyanates in Schemes 3 and 4. While the retro-ene reaction is favored in all cases, the 1,2-elimination becomes almost competitive for *tert*-butyl isocyanate.

[3,3]-Sigmatropic shifts are usually favored substantially over the alternative 1, 3-shifts, but in the case of diphenylamino isocyanate there is only a 2 kcal/mol energy difference between the two reaction paths (Scheme 19). This may be ascribed to the exothermicity of the 1,3-shift and a pseudopericyclic nature of this reaction.

Homolytic fragmentation of the RX-YCN or RX-NCY bonds is usually not competitive with the pericyclic reactions, but they may play a role in high temperature reactions of amino isocyanates (Schemes 6 and 19), alkoxy isothiocyanates (Scheme 12), and amino thiocyanates and isothiocyanates (Schemes 23 and 24).

The computational data are largely in good accord with the available experimental data, but some reactions require experimental reinvestigation, for example the formation and chemistry of the poorly characterized sulfenyl isocyanates RS-NCO (Scheme 21), sulfenyl thiocyanates RS-SCN (Scheme 25), and sulfenyl isothiocyanates RS-NCS (Scheme 26).

In spite of their high intramolecular reactivities, many of the compounds described herein are expected to have considerable synthetic potential as reactive intermediates, which has only been exploited in selected cases.[11,12,43,45]

ASSOCIATED CONTENT

Supporting Information

Selection of computational method. ZPVE-corrected calculated activation energies for reference reactions using different methods (B3LYP, MPW1K, BMK, B97D, M06-2X, PCM-B3LYP with the 6-311++G(d,p) basis set. Tables of Cartesian coordinates and calculated energies for all structures described herein. Imaginary frequencies for all calculated transition states. Figures showing all calculated transition states. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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■ DEDICATION

†Dedicated to Prof. Ernst Anders on the occasion of his 70th birthday.

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