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Rearrangements of Acyl, Thioacyl, and Imidoyl (Thio)cyanates to Iso(thio)cyanates, Acyl Iso(thio)cyanates to (Thio)acyl Isocyanates, and Imidoyl Iso(thio)cyanates to (Thio)acyl Carbodiimides, RCX-YCN ⇌ RCX-NCY ⇌ RCY-NCX ⇌ RCY-XCN (X and Y = O, S, NR′)

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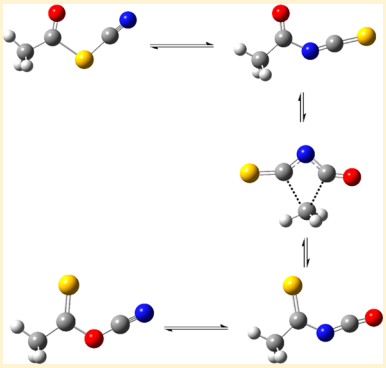
Supporting Information

ABSTRACT: Two types of rearrangements have been investigated computationally at the B3LYP/6-311+G(d,p) level. The activation barriers for rearrangement of acyl thiocyanates RCO−SCN to the corresponding isothiocyanates RCO−NCS are 30−31 kcal/mol in agreement with the observation that the thiocyanates are in some cases isolable albeit very sensitive compounds. Alkoxycarbonyl-, (alkylthio)carbonyl- and carbamoyl thiocyanates are isolable and have higher calculated barriers (ca. 40 kcal/mol) toward rearrangement to isothiocyanates, whereas all thioacyl thiocyanate derivatives are rather unstable compounds with barriers in the range 20−30 kcal/mol for rearrangement to the isothiocyanates. Acyl-, alkoxycarbonyl-, and carbamoyl cyanates R−CO−OCN are predicted to be in some cases isolable compounds with barriers up to ca. 40 kcal/mol for rearrangement to the isocyanates RCO−NCO. All of the rearrangements of this type involve the HOMO of a nearly linear (thio)cyanate anion and the LUMO of the acyl cation, in particular the acyl C═X π^* orbital. The second type of rearrangement involves 1,3-shifts of the groups R attached to the (thio)acyl groups, that is, acyl isothiocyanate−thioacyl isocyanate and imidoyl isothiocyanate−thioacyl carbodiimide rearrangements. These reactions involve four-membered cyclic, zwitterionic transition states facilitated by lone pair−LUMO interactions between the migrating R group and the neighboring iso(thio)cyanate function. Combination of the two rearrangements leads to the general reaction scheme RCX−YCN ⇌ RCX−NCY ⇌ RCY−NCX ⇌ RCY−XCN (X and Y = O, S, NR′).



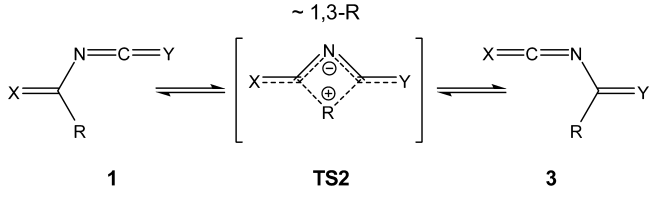
INTRODUCTION

Thanks to their high reactivities, cyanates, thiocyanates, isocyanates and isothiocyanates have widespread uses in preparative chemistry[1] and attract the interest of physical-organic and theoretical chemists as well. These compounds can also undergo several fascinating rearrangements.

A number of 1,2-, 1,3-, and 1,4-shifts of substituent groups of the types R−C(═Y)−N═X → R−Y−CNX, R−C(═Y)−N═X → R−X−N═C═Y, and R−Y−CNX → R−X−N═C═Y were evaluated theoretically,[2] and several [3,3]-sigmatropic shifts and retro-ene type reactions of (thio)-cyanates and iso(thio)cyanates were described recently.[3] Another rearrangement involving the thermal 1,3-shift of substituents R in acyl isocyanates **1a** (degenerate rearrangement) and acyl isothiocyanates **1b** proceeds via the transition state **TS2**.[4,5] The analogous degenerate rearrangement of thioacyl isothiocyanates **1c** (Scheme 1) will be described in this paper.

Thus, the reactions of **1a** and **1b** in Scheme 1 have calculated activation barriers between ca. 20 and 50 kcal/mol. These reactions are formally "forbidden", thermal 1,3-shifts, but they become "allowed" due to the presence of orthogonal orbitals on the cumulene moieties. The energies of the transition states **TS2** are lowered drastically when the migrating groups R possess a lone pair that can interact with the LUMO of the

Scheme 1. 1,3-Rearrangements of Acyl Isocyanates, Acyl Isothiocyanates and Thioacyl Isothiocyanates



a: X = Y = O
b: X = O; Y = S
c: X = Y = S

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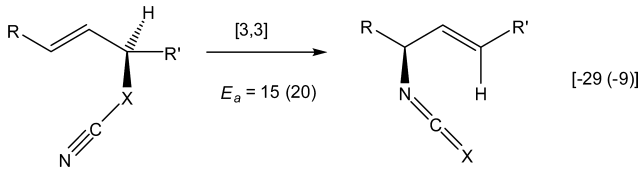
cumulene, which lies in the plane of the molecule (i.e., R = halogen, alkoxy, alkylthio, and amino groups). These and related 1,3-shifts of the R groups in compounds of the type R−CX−CR′═C═Y, namely, acylketenes, imidoylketenes, acylthioketenes and acylallenes, have been reviewed.[6]

Due to the ambident nature of the thiocyanate ion, SCN^-, reactions between alkyl halides and inorganic thiocyanates can lead to either thiocyanates (rhodanides) RSCN or isothiocyanates (mustard oils) RNCS. Moreover, there are many reports on rearrangements of thiocyanates to isothiocyanates in the literature. Several studies indicate that benzylic thiocyanates (including diphenylmethyl thiocyanate) rearrange via an ion pair mechanism in solution,[7] and this also appears to be the case for the rearrangement of alkyl (especially *tert*-butyl) thiocyanates.[8] An ion pair mechanism has also been advanced for the isomerization of alkyl cyanates ROCN to isocyanates RNCO.[9] Alkyl thiocyanates that do not form carbenium ions readily tend not to isomerize.[8,10] Methyl thiocyanate rearranges to the isothiocyanate in a sealed tube at 180−185 °C,[11] and it has also been reported to rearrange slowly at its boiling point, 131 °C.[8]

Allylic thiocyanates are extremely unstable, because they undergo facile [3,3]-sigmatropic rearrangements, which have been investigated by several authors.[8,12−16] The enthalpy of activation has been determined as 18−22 kcal/mol, depending on the solvent used.[15] In excellent agreement with this, our calculations for the gas-phase yielded an activation barrier of 20 kcal/mol (Scheme 2).[3] Thus, most allylic thiocyanates are very fragile compounds. The computed barrier for the corresponding [3,3]-sigmatropic shift in allyl cyanate is only 15 kcal/mol.[3] Related rearrangements of allenyl thiocyanates to propargyl isothiocyanates[17] and of propargyl thiocyanates to allenyl isothiocyanates[18] have also been described.

Scheme 2. Rearrangement of Allylic Cyanates (X = O) and Thiocyanates (X = S, Values in Parentheses)[a]



[a]Calculated activation barriers and reaction energies [in brackets] are in kcal/mol.

Reactions of acyl halides with thiocyanate ion usually lead to the exclusive formation of acyl isothiocyanates, R−CO−NCS, and the corresponding thiocyanates R−CO−SCN are little-known compounds (see below). This is true generally of acyl, thioacyl, and imidoyl thiocyanates, RCX−SCN (X = O, S, or NR′). In this paper we report a theoretical investigation of these rearrangements, which indicates that all acyl- and thioacyl thiocyanates should be isolable or at least detectable at room temperature, although they are all prone to rearrangement to the corresponding isothiocyanates. Acyl cyanates RCX−OCN are unknown, but, as we will show, the calculated activation barriers indicate that some of them should be isolable compounds.

COMPUTATIONAL DETAILS

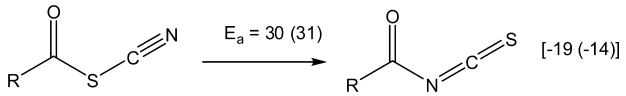
All calculations were performed with the program package Gaussian 03[19] using the B3LYP[20] density functional with the 6-311+G(d,p)[21] basis set. The nature of all stationary points as true minima or as first-order transition states was confirmed by calculating harmonic frequencies. Scaled zero-point vibrational energy corrections have been taken into account.[22,23] The wave function stability of selected transition states and their open shell character has been examined; however, no instability or diradical character could be found. B3LYP has proved itself as a reliable approach in the study of systems related to the title compounds, for example, isocyanates,[2] ketenes[24] and iminopropadienones.[25,26]

RESULTS AND DISCUSSION

1. Thiocyanates. *Acyl and Aroyl Thiocyanates R−CO−SCN.* The reaction of acid halides with metal or ammonium thiocyanate is a standard method for the synthesis of acyl/aroyl isothiocyanates, R−CO−NCS.[1d-e,27−29] The corresponding thiocyanates R−CO−SCN are not usually detectable in these reactions,[8,27] but Goerdeler has mentioned that benzoyl thiocyanate was observable at −30 °C.[30] Acyl thiocyanates are supposed to rearrange rapidly to the isothiocyanates, if formed at all. There are, however, two methods of synthesis of acyl/aroyl thiocyanates, (i) by thermal decomposition of 5-acyl/5-arylthio-1,2,3,4-thiatriazoles,[31,32] and (ii) reaction of thiocarboxylates $Ar-CO-S^-$ with BrCN.[32] The aliphatic derivatives are mostly very unstable, rearranging to the isothiocyanates at or below room temperature, but several aroyl thiocyanates can be isolated. Benzoyl thiocyanate Ph−CO−SCN rearranges to benzoyl isothiocyanate at room temperature,[31−33] but 2,4,6-tribromo- and 2,4,6-triiodobenzoyl thiocyanates are stable compounds, and 3,4,5-trimethoxybenzoyl- and 2,6-dimethyl-4-nitrobenzoyl thiocyanates are isolable but unstable toward thermal rearrangement.[32]

Our calculated activation barriers for the unimolecular gas-phase rearrangements of acetyl and benzoyl thiocyanates to the corresponding isothiocyanates are 31 and 30 kcal/mol, respectively. The reactions are highly exothermic rearrangements (Scheme 3; Table 1). This is in keeping with the detectability but instability of Ph−CO−SCN at room temperature. The transition states for acetyl and benzoyl thiocyanate rearrangements are presented in Figure 1; they are prototypical for all related transition states. The orbitals involved in the shift are the HOMO of the thiocyanate moiety, a π orbital, interacting with one of the two C═O π^* LUMOs of the benzoyl cation (Figure 2). The orthogonal arrangement of the SCN^- moiety relative to the carbonyl type group allows the best overlap between the above-mentioned frontier orbitals. Although there is a second (near degenerate) C═O π^* benzoyl cation LUMO which is orthogonal to the first and lies (almost) in plane with the aromatic ring, no interaction between this orbital and the thiocyanate anion could be found. For this reason the reaction cannot be classified as pseudopericyclic.

Scheme 3. 1,3-Shifts of Benzoyl Thiocyanate (R = Ph) and Acetyl Thiocyanate (R = Me, Values in Parentheses)[a]



[a]Calculated activation barriers and reaction energies [in brackets] are in kcal/mol.

Attempts to find a transition state for the rearrangement of tribromobenzoyl thiocyanate were foiled because of an

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Table 1. Activation and Reaction Energies (kcal/mol) for 1,3-Rearrangements of Thiocyanates and Cyanates Discussed in Schemes 3−12

reactant	E_a	ΔE_R
R−CO−SCN (Scheme 3)		
R = Ph (benzoyl thiocyanate)	31	−14
R = Me (acetyl thiocyanate)	30	−19
R = 2,4-Br_2Ph (2,4-dibromobenzoyl thiocyanate)	30	−16
EtX−CO−SCN (Scheme 4)		
X = O	42	−15
X = S	40	−15
R_2N−CO−SCN (Scheme 5)		
R = Ph	40	−16
R = Me	34	−19
Ph−CS−SCN (Scheme 6)	34	−19
EtX−CS−SCN (Scheme 7)		
X = O	39	−15
X = S	36	−15
RR′N−CS−SCN (Scheme 8)		
R = R′ = Me	29	−19
R = Ph, R′ = Me	29	−19
R−C(=NR′)−SCN (Scheme 9)		
R = Ph, R′ = Me	19	−17
R = NMe_2, R′ = H	31	−17
Ph−C(=N−NH_2)−SCN (Scheme 10)	25	−18
R−CO−OCN (Scheme 11)		
R = Ph	28	−34
R = EtO	39	−32
R = NPh_2	36	−30
R−CS−OCN (Scheme 12)		
R = Ph	26	−38
R = Me	32	−35

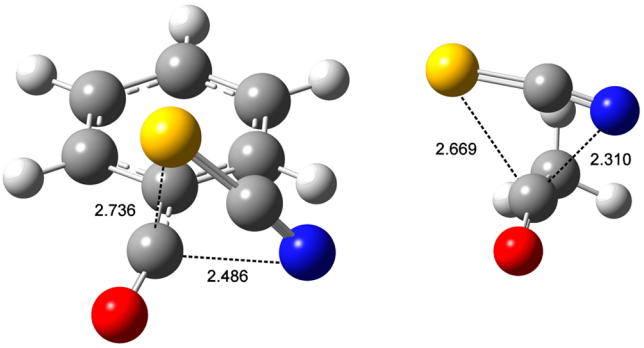

Figure 1. Transition states for the 1,3-shifts of benzoyl (left) and acetyl thiocyanate (right). Bond lengths are in Å.

interaction with the neighboring Br atom in the *ortho*-position of the phenyl ring. Its steric and electronic bulkiness prevents an orientation of the thiocyanates moiety relative to the rest of the molecule common to all these 1,3-shifts. This is best illustrated by the corresponding transition state for the 1,3-shift of 2,4-dibromobenzoyl thiocyanate (Figure 3), which possesses the same calculated activation barrier as for benzoyl thiocyanate. Replacing the hydrogen atom in the second *ortho* position with a bromine atom repels the NCS^- moiety out of its orthogonal and slightly tilted orientation above the C=O group. Depending on the starting structure, this leads to either the original thiocyanate or the corresponding isothiocyanates The further rearrangement of benzoyl isothiocyanate to thiobenzoyl isocyanate will be described in Section 3 below.

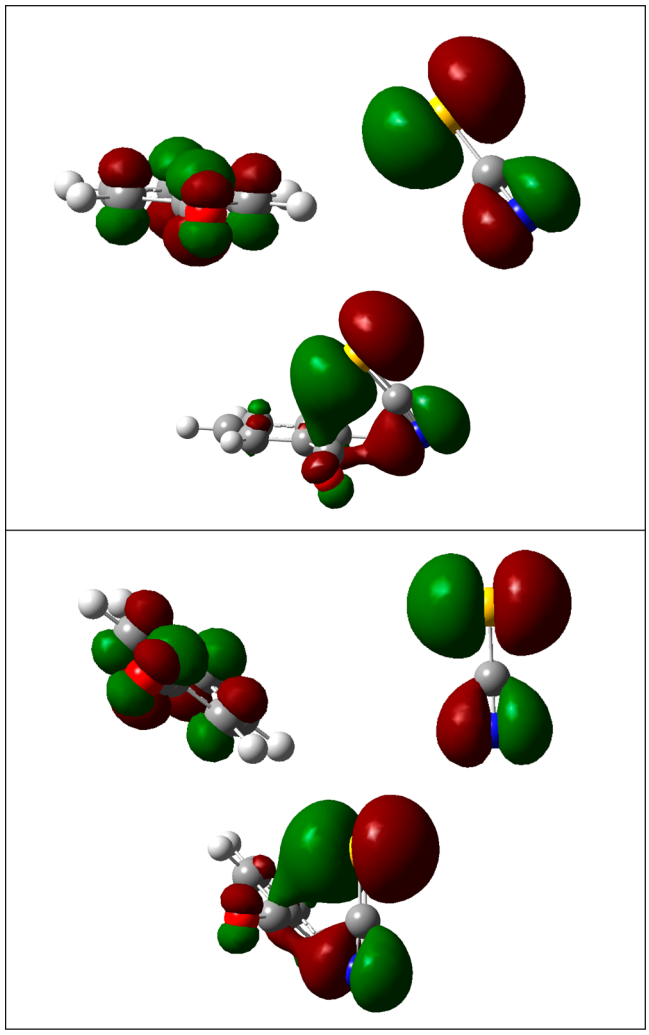

Figure 2. Orbitals involved in the 1,3-shifts of thiocyanates are shown in two different orientaions: benzoyl cation LUMO (left), SCN^- HOMO (right) and HOMO of the TS (bottom).

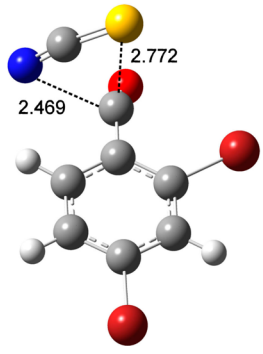

Figure 3. Transition state for the 1,3-shift of SCN in 2,4-dibromobenzoyl thiocyanate. Bond lengths are in Å.

Ethoxycarbonyl Thiocyanate EtO−CO−SCN and (Ethylthio)carbonyl Thiocyanate EtS−CO−SCN. Ethoxycarbonyl thiocyanate is a distillable compound (41−42 °C/2 mmHg), but the corresponding (ethylthio)carbonyl thiocyanate was not isolable under similar reaction conditions.[34,35] Goerdeler and Chuen-Huei Ho also found that only the isothiocyanates RS−CO−NCS were obtainable from the acyl chlorides and NaSCN.[36] However, we calculate very similar

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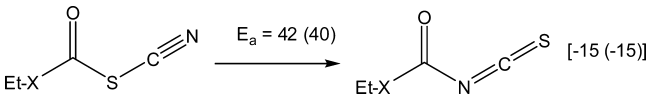
activation barriers for the isomerization of the two compounds, 42 and 40 kcal/mol, respectively (Scheme 4). Therefore, both should be isolable under suitable reaction conditions.

Scheme 4. 1,3-Shifts of Ethoxycarbonyl Thiocyanate (X = O) and Thioethoxycarbonyl Thiocyanate (X = S, Values in Parentheses)[a]

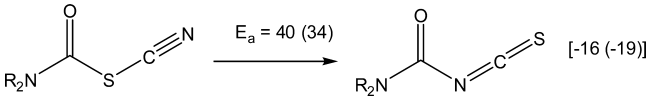


[a]Calculated activation barriers and reaction energies [in brackets] are in kcal/mol.

Carbamoyl Thiocyanates, $R_2N-CO-SCN$. *N,N*-Diphenylcarbamoyl thiocyanate $Ph_2N-CO-SCN$ is obtainable from the carbamoyl chloride with KSCN in refluxing acetonitrile, and it rearranges to the isothiocyanate on melting at 140 °C.[37] In contrast, the *N,N*-dimethyl analogue, $Me_2N-CO-SCN$, could not be obtained in a pure state; it isomerized to the isothiocyanate slowly at room temperature and more rapidly in refluxing acetone.[37]

Our calculated activation barriers are 40 and 34 kcal/mol, respectively, in agreement with the observed relative stabilities (Scheme 5). Yet, the dimethyl compound should be isolable under appropriate, mild conditions.

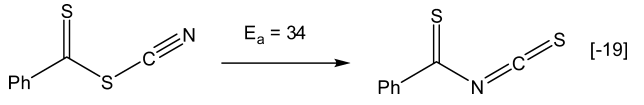
Scheme 5. 1,3-Shifts of *N,N*-Diphenylcarbamoyl Thiocyanate (R = Ph) and *N,N*-Dimethylcarbamoyl Thiocyanate (R = Me, Values in Parentheses)[a]



[a]Calculated activation barriers and reaction energies [in brackets] are in kcal/mol.

Thioaroyl Thiocyanates Ar–CS–SCN. Aromatic thioacyl thiocyanates have been prepared from thioaroyl chloride and sodium thiocyanate at room temperature (Ar = Ph, *o*-tolyl, 2,4-dimethylphenyl, and mesityl).[38] They can be stored at −18 °C but decompose to a black mass at room temperature. They rearrange in solution to form thioaroyl isothiocyanates Ar–CS–NCS. Thiobenzoyl thiocyanate Ph–CS–NCS (Scheme 6) possesses a computed activation barrier of 34 kcal/mol, in line with the experimentally observed stability.

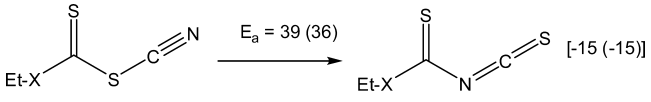
Scheme 6. 1,3-Shift of Thiobenzoyl Thiocyanate[a]



[a]Calculated activation barrier and reaction energy [in brackets] are in kcal/mol.

Alkoxythiocarbonyl Thiocyanates RO–CS–SCN and [Alkyl(aryl)thio]thicarbonyl Thiocyanates RS–CS–SCN. The former are unknown, but compounds of the type RS–CS–SCN were prepared by Goerdeler and Hohage and reported to be stable at 0 °C (R = *inter alia* Me, Ph, $PhCH_2$). Rearrangement to the isothiocyanates RS–CS–NCS was difficult and proceeded in low yield.[39] Our calculated barriers for this process are 39 and 36 kcal/mol for the ethoxy and thioethoxy thioacyl thiocyanates, respectively, and indicate a certain stability of both compound types (Scheme 7).

Scheme 7. 1,3-Shifts of Ethoxy Thioacyl Thiocyanate (X = O) and Thioethoxy Thioacyl Thiocyanate (X = S, Values in Parentheses)[a]



[a]Calculated activation barriers and reaction energies [in brackets] are in kcal/mol.

Thiocarbamoyl Thiocyanates, $R_2N-CS-SCN$. The treatment of *N,N*-dialkylthiocarbamoyl chlorides in ethyl acetate with sodium thiocyanate affords thiocarbamoyl isothiocyanates, $R_2N-CS-NCS$. The corresponding thiocyanates $R_2N-CS-SCN$ were detectable as intermediates by IR spectroscopy, but not isolated (R = *inter alia* Me, Et, iPr, $PhCH_2$).[40] However, Cambron reported strong evidence for the formation and isolation of *N*-ethyl-*N*-phenyl- and *N*-methyl-*N*-phenylthiocarbamoyl thiocyanates R(Ph)N–CS–SCN by reaction of thiocarbamoyl chlorides with potassium thiocyanate in absolute ethanol at room temperature.[41] These compounds rearrange to the corresponding thiocarbamoyl isothiocyanates at their melting points (75–114 °C) or on heating to 100–110 °C. This is in agreement with our predicted activation barriers of 29 kcal/mol for both the dimethylamino and the methyl(phenyl)-amino derivative (Scheme 8).

Scheme 8. 1,3-Shifts of *N,N*-Dimethylthioarbamoyl Thiocyanate (R = R′ = Me) and *N*-Methyl-*N*-phenyl Thiocarbamoyl Thiocyanate (R = Me, R′ = Ph, Values in Parentheses)[a]

[a]Calculated activation barriers and reaction energies [in brackets] are in kcal/mol.

Imidoyl Thiocyanates, R–C(=NR′)–SCN. The reaction of imidoyl and carbimidoyl chlorides with metal thiocyanates has only yielded imidoyl isothiocyanates, R–C(=NR′)–NCS.[42] Our calculated activation barrier for the rearrangements of the imidoyl thiocyanate Ph–C(=N–CH_3)–SCN and carbimidoyl thiocyanate $Me_2N-C(=NH)-SCN$ are 19 and 31 kcal/mol, respectively (Scheme 9). Thus, both of these compounds are capable of existence, and the carbimidoyl thiocyanates should be detectable and potentially isolable at ordinary temperatures.

A hydrazonyl thiocyanate Ph–CO–C(=N–NHAr)–SCN is implicated as an intermediate in the reaction of the corresponding hydrazonyl bromide with KSCN in EtOH–H_2O at room temperature, which yields a 2-benzoyl-5-imino-1,3,4-thiadiazole as a cyclization product.[43] This indicates that hydrazonyl thiocyanates are capable of existence. Accordingly, we have calculated the barrier for the rearrangement of Ph–C(=N–NH_2)–SCN (Scheme 10). The moderate activation energy of 25 kcal/mol indicates that these compounds will be sensitive but at least observable at low temperatures.

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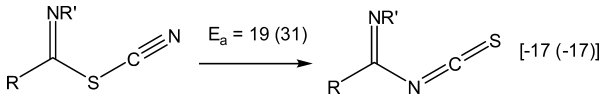
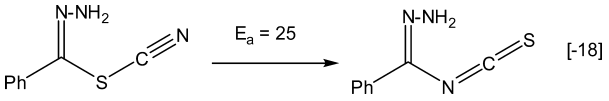
Scheme 9. 1,3-Shifts of Phenyl *N*-Methyl-imidoyl Thiocyanate (R = Ph, R′ = Me) and *N,N*-Dimethylaminocarbimidoyl Thiocyanate (R = NMe_2, R′ = H, Values in Parentheses)[a]



[a]Calculated activation barriers and reaction energies [in brackets] are in kcal/mol.

Scheme 10. 1,3-Shift of Phenyl Hydrazonyl Thiocyanate[a]

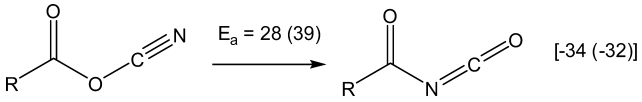


[a]Calculated activation barrier and reaction energy [in brackets] are in kcal/mol.

The thiocyanate rearrangements are summarized in Table 1.

2. Cyanates. *Acyl and Aroyl Cyanates, R−CO−OCN.* Cyanates of this type are unknown, but our calculations predict reasonably high activation barriers for isomerization (Scheme 11), thus indicating they should be stable, isolable compounds. The carbamoyl cyanate $Ph_2N−CO−OCN$ has a barrier of 36 kcal/mol.

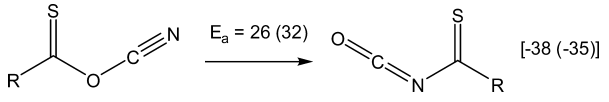
Scheme 11. 1,3-Shifts of Benzoyl Cyanate (R = Ph) and Ethoxycarbonyl Cyanate (R = EtO, Values in Parentheses)[a]



[a]Calculated activation barriers and reaction energies [in brackets] are in kcal/mol. For *N,N*-diphenylcarbamoyl cyanate $Ph_2N−CO−OCN$ the barrier is 36 kcal/mol.

Thioacyl cyanates can in principle undergo the same types of 1,3-rearrangements as discussed in Section 1, that is, formation of thioacyl isocyanates. The latter are thermodynamically substantially more stable, and the required barriers are moderate, so the reactions will yield thioacyl isocyanates (Scheme 12), although the thioacyl cyanates should be detectable if not isolable.

Scheme 12. 1,3-Shifts of Thiobenzoyl Cyanate (R = Ph) and Thioacetyl Cyanate (R = Me, Values in Parentheses)[a]



[a]Calculated activation barriers and reaction energies [in brackets] are in kcal/mol.

The cyanate rearrangements are also summarized in Table 1, and Figure 4 shows a representative transition state for these reactions.

3. 1,3-Shifts of R in Acyl, Thioacyl and Imidoyl Isocyanates, Isothiocyanates, and Carbodiimides. The 1,3-rearrangements described in this section (Schemes 14−22) are depicted in terms of the *s-E* conformers of the *α*-(thi)oxo- and *α*-imidoyl-cumulenes, in which the R-groups are correctly oriented for the migration to take place. It should be noted, however, that these cumulenes can exist as *s-E* and *s-Z* conformers (see Scheme 13).

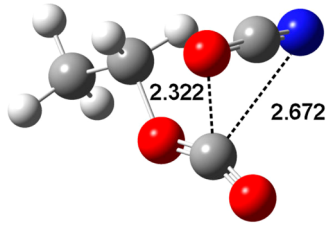
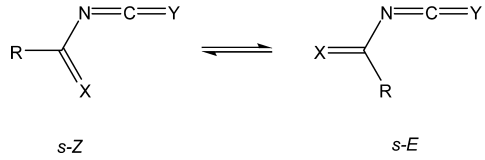


Figure 4. Transition state for the cyanate-isocyanate isomerization of ethoxycarbonyl cyanate, EtO−CO−OCN. Bond lengths are in Å.

Scheme 13. *s-Z*−*s-E* Interconversion



Usually, the *s-Z* conformers have the lowest energies, but the differences are small (a 2−3 kcal/mol range).[5] This also applies to the thoroughly investigated *α*-oxoketenes[44] and their thio analogs[45] as well as the *α*-imidoylketenes and *α*-oxoketenimines.[46] In the latter case, the rotational barriers for *s-Z*−*s-E* interconversion are on the order of 15 kcal/mol.[46a] Moreover, when amino groups R are undergoing migration, they first have to rotate about the C−R single bonds in order to bring the amine lone pair into a position syn-periplanar with the cumulene moiety in order that it can interact with the LUMO. This rotation has an energy barrier of the order of 5−8 kcal/mol.[46] Because this conformation leads to the 1,3-shift, the *s-E* isomers are not always found to be energy minima.[5] Accordingly, several isothiocyanates in this study exist only in their *s-Z* form (mainly those with amino or aromatic groups).

In this paper, the activation energies for the 1,3-shifts of R pertain to the lowest-energy forms, that is, the *s-Z* conformation. The energy difference between the two conformers is again usually less than 2−3 kcal/mol. The corresponding conformations also exist in case of the initial (thio)cyanates for which the *s-E* and *s-Z* conformers possess more or less the same energy (typically within 1 kcal/mol). The rearrangements of thioacyl isocyanates to the corresponding acyl isothiocyanates discussed in the following are exothermic; those of thioacyl isothiocyanates are of course degenerate. Schemes 14−20 and Table 2 describe these reactions.

The rearrangement of thiobenzoyl isocyanate to benzoyl isothiocyanate takes place via a 1,3-shift of the phenyl group (Scheme 1 and Scheme 13).[5] The calculated activation barrier is high, ca. 58 kcal/mol, and the reaction is exothermic by 3 kcal/mol. The barrier of the degenerate reaction of thioacyl isothiocyanate is predicted to be similar, 62 kcal/mol. The data for the 2,4-dibromobenzoyl isothiocyanate are also similar (E_a = 50 kcal/mol; Scheme 14 and Table 2). Therefore, reactions involving the rearrangement of aroyl thiocyanates to aroyl isothiocyanates at or near room temperature are not expected to lead to significant amounts of thiobenzoyl isocyanates. The 1,3-shift converting thioacetyl isocyanate to acetyl isothiocyanate possesses an even larger barrier as expected for a methyl group migration[6] (71 kcal/mol; Table 2). It is generally found

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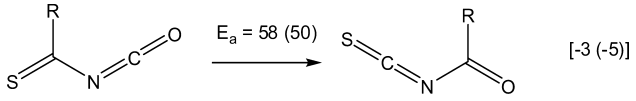
Scheme 14. 1,3-Shifts of Thiobenzoyl Isocyanate (R = Ph) and 2,4-Dibromothiobenzoyl Isocyanate (R = 2,4-$Br_2C_6H_3$, Values in Parentheses) to the Acyl Isothiocyanates[a]



[a]Calculated activation barriers and reaction energies [in brackets] are in kcal/mol.

Table 2. Activation and Reaction Energies (kcal/mol) for 1,3-Rearrangements of Isothiocyanates and Isocyanates discussed in Schemes 14−21

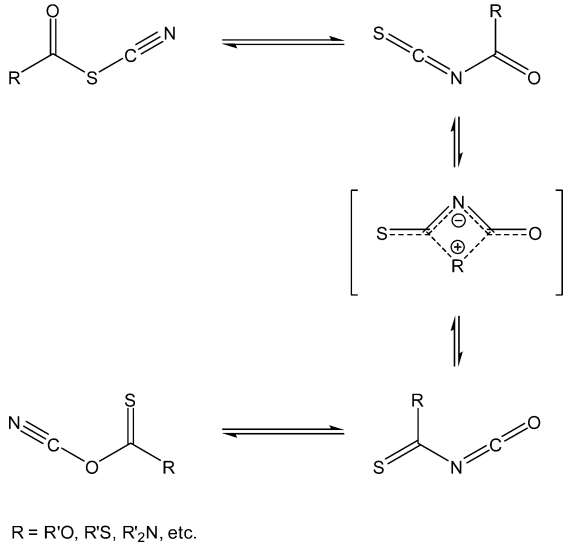
reactant	E_a	ΔE_R
Thioacyl isocyanate ⇌ Acyl isothiocyanate		
R−CS−NCO ⇌ R−CO−NCS (Scheme 14)		
R = Ph	58	−3
R = Me	71	−4
R = 2,4-Br_2Ph (2,4-dibromobenzoyl thiocyanate)	50	−5
EtX−CS−NCO ⇌ EtX−CO−NCS (Scheme 16)		
X = O	37	−5
X = S	29	−4
R_2N−CS−NCO ⇌ R_2N−CO−NCS (Scheme 17)		
R = Ph	33	−5
R = Me	31	−3
Ph−CS−NCS ⇌ Ph−CS−NCS	62	Degen.
EtX−CS−NCS ⇌ EtX−CS−NCS		
X = O	44	Degen.
X = S	34	Degen.
RR′N−CS−NCS ⇌ RR′N−CS−NCS (Scheme 18)		
R = R′ = Me	34	Degen.
R = Ph, R′ = Me	35	Degen.
R−CS−NCNR′ ⇌ R−C(=NR′)−NCS (Scheme 19)		
R = Ph, R′ = Me	59	−11
R = NMe_2, R′ = H	33	−4
Ph−CS−NCN−NH_2 ⇌ Ph−C(=N−NH_2)−NCS	54	−23
Guanyl isocyanate ⇌ Acyl carbodiimide (Scheme 20)		
NMe_2−C(=NMe)−NCO ⇌ NMe_2−CO−NCNMe	32	−2
Acyl isocyanate ⇌ Acyl isocyanate (Scheme 21)		
R = Ph	57	Degen.
R = EtO	35	Degen.

that 1,3-migration of aryl groups have much higher activation barriers than those of groups carrying lone pairs (e.g., NMe_2), the latter being favored by the lone-pair LUMO interaction (cf. Introduction and Scheme 1). However, the HOMO of an aryl group can still interact favorably with the cumulene LUMO. The 1,3-migations of alkyl groups have even higher barriers and are not usually observed.[5,45,47]

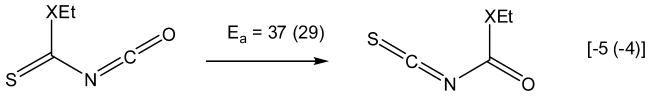
Note that Schemes 3, 12 and 14 pertain to the same energy surface. Thus, the complete set of interconversions can be described as RCO−SCN ⇌ RCO−NCS ⇌ RCS−NCO ⇌ RCS−OCN as illustrated in Scheme 15. Here, the acyl isothiocyanates R−CO−NCS are the most stable (Scheme 14). As a simple rule of thumb, carbonyl derivatives are usually the most stable because of the great thermodynamic stability of the C═O group.

The analogous 1,3-shifts of the ethoxy and ethylthio groups in the thioacyl isocyanates have activation barriers of 37 and 29 kcal/mol, respectively, in accord with the migratory aptitudes determined previously for these 1,3-shifts (Scheme 16, Table 2).[5] The two reactions are exothermic by 5 and 4 kcal/mol, respectively. Given the small exothermicities/endothermicities, thioacyl isocyanates and acyl isothiocyanates can be expected to interconvert at elevated temperatures.

Scheme 15. Interconversion of Acyl Thiocyanates, Acyl Isothiocyanates, Thioacyl Isocyanates and Thioacyl Cyanates



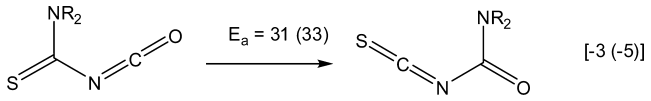
Scheme 16. 1,3-Shifts of (Ethoxy)thiocarbonyl Isocyanate (X = O) and (Ethylthio)thioacyl Isocyanate (X = S, Values in Parentheses)[a]



[a]Calculated activation barriers and reaction energies [in brackets] are in kcal/mol.

The 1,3-migrations of NMe_2 and NPh_2 groups interconverting thioamides to carbamoyl isothiocyanates have activation barriers of 31 and 33 kcal/mol, respectively, and the reactions are exothermic by 3−5 kcal/mol (Scheme 17, Table 2, Figure 5). Thus, interconversion is possible at elevated temperatures. The 1,3-shifts of the dimethylamino and methyl(phenyl)amino groups in MeRN−CS−NCS is degenerate (cf. Scheme 18). The calculated activation barrier for the dimethylamino group shift is 34 kcal/mol, i.e. the same as for Me_2N−CO−NCS, while the methyl(phenyl)amino migration requires 35 kcal/mol.

Scheme 17. 1,3-Shifts Converting Thiocarbamoyl Isocyanates to *N,N*-Dimethylcarbamoyl Isothiocyanate (R = Me) and *N,N*-Diphenylcarbamoyl Isothiocyanate (R = Ph, Values in Parentheses)[a]



[a]Calculated Activation Barriers and Reaction Energies [in Brackets] are in kcal/mol.

It is noteworthy that quite commonly the 1,3-shifts in cumulenes with migrating amino substituents take place in a

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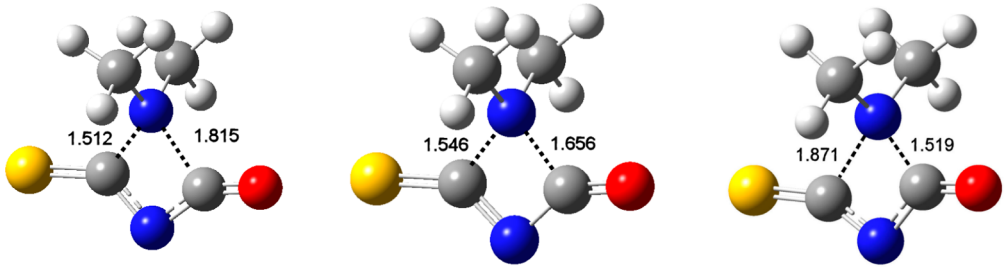
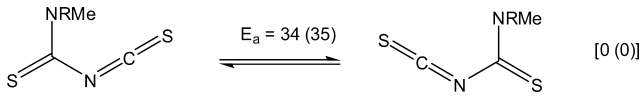


Figure 5. Transition states and intermediate (center) for the 1,3-dimethylamino group migration in *N,N*-dimethylcarbamoyl isothiocyanates/dimethylthiocarbamoyl isocyanates (cf. Scheme 17).

Scheme 18. Degenerate 1,3-Shifts in *N,N*-Dimethylthiocarbamoyl Isothiocyanate and *N*-Methyl-*N*-phenylthiocarbamoyl Isothiocyanate[a]

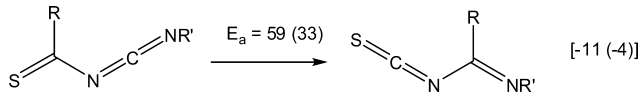


[a]Calculated activation barriers and reaction energies [in brackets] are in kcal/mol.

nonconcerted manner, that is, a high-lying intermediate structure exists between two transition states.[6,44a,45b,46b] This can also be found in the case of the two *N,N*-dimethylamino group reactions in Schemes 17 and 18 (but not for the phenylamino group migration!) (Figure 5): First, a new bond is formed between the NMe_2 group and the central isocyanate carbon atom, leading to an intermediate with two elongated C–N bonds, which is stabilized by only 0.2 to 3 kcal/mol. The second step, the breaking of the original C–NMe_2 bond, requires the highest energy and thus determines the barrier reported.

The interconversion of acyl carbodiimides and imidoyl isothiocyanates is also possible in principle (Scheme 19).

Scheme 19. 1,3-Shifts Converting Thiocarbonyl Carbodiimides to *N*-Methyl-imidoyl Isothiocyanates (R = Ph, R′ = Me) and *N,N*-Dimethylaminocarbimidoyl Isothiocyanates (R = NMe_2, R′ = H, Values in Parentheses)[a]



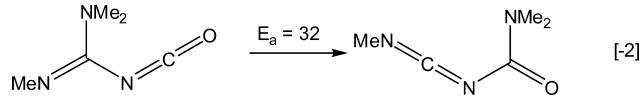
[a]Calculated activation barriers and reaction energies [in brackets] are in kcal/mol.

Both types of compound are known, but their rearrangements have not been investigated.[42,48] In accordance with other, similar 1,3-rearrangements, the calculated barrier involving a migrating Ph groups very high (59 kcal/mol from the carbodiimide side), while the dimethylamino substituent migrates more readily (E_a = 33 kcal/mol). Thus, it should be possible to observe rearrangements of the thiocarbamoyl carbodiimides. These compounds are crystalline solids, which invariable decompose at their melting points,[48] but the decomposition products have not been investigated.

The phenyl group migration in the *N*-aminocarbodiimide Ph–CS–N=C=N–NH_2 also requires a high energy (54 kcal/mol; Table 2). As mentioned above, 1,3-migration of aryl groups have much higher activation barriers than those of R-groups carrying lone pairs.[5]

Goerdeler and Raddatz[49] have described the isolation of carbamoyl carbodiimides Me_2N–CO–N=C=NR (R = tert-butyl; cyclohexyl) as products of reactions designed to yield guanyl isothiocyanates (Scheme 20). Thus, it appears that the

Scheme 20. 1,3-Shifts of NMe_2 Groups Converting Guanyl Isocyanates to Carbamoyl Carbodiimides[a]

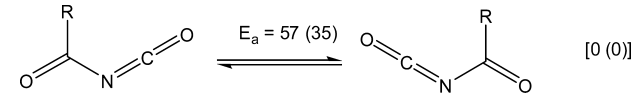


[a]Calculated activation barrier and reaction energy [in brackets] are in kcal/mol.

equilibrium lies on the side of the carbodiimides. We calculate a mildly exothermic reaction with an activation barrier of 32 kcal/mol (Scheme 20). Accordingly, a more detailed experimental investigation of this equilibrium should be possible.

The degenerate reactions of Ph–CO–NCO and EtO–CO–NCO (Scheme 21) have activation barriers comparable to

Scheme 21. 1,3-Shifts of Benzoyl Isocyanate (R = Ph) and Ethoxycarbonyl Isocyanate (R = EtO, Values in Parentheses)[a]



[a]Calculated activation barriers and reaction energies [in brackets] are in kcal/mol.

those found for the isothiocyanates: the phenyl and ethoxy group migrations require 57 and 35 kcal/mol, respectively (cf. Ph–CO–NCS: 55 kcal/mol; EtO–CO–NCS: 32 kcal/mol). These 1,3-shifts are summarized in Table 2.

CONCLUSION AND OUTLOOK

Acyl and aroyl thiocyanates RCO–SCN are mostly highly unstable compounds, which have only been isolated at room temperature in a few cases. The calculated activation barriers for their rearrangement to the corresponding isothiocyanates RCO–NCS are 30–31 kcal/mol, thus indicating that, although very unstable, they should nevertheless be isolable, at least at low temperatures. Higher barriers in the 40 kcal/mol range are calculated for the rearrangements of alkoxycarbonyl-, (alkylthio)carbonyl- and carbamoyl thiocyanates to isothiocyanates in accord with the experimental observation that many of these compounds are isolable and sometimes distillable. In contrast, all thioacyl thiocyanate derivatives are rather unstable

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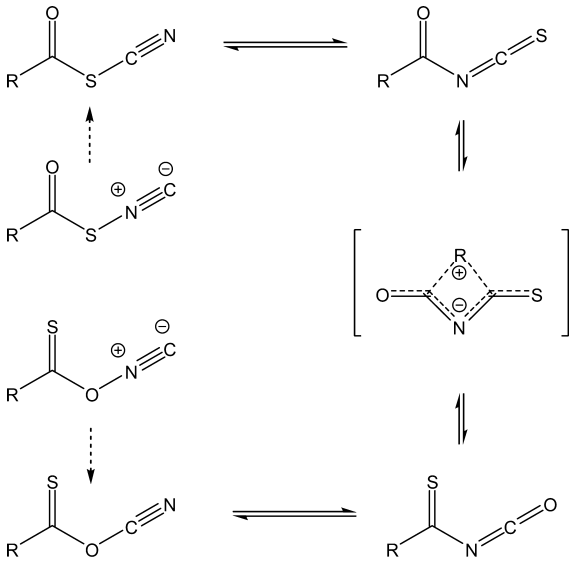
compounds with barriers in the range of 20−30 kcal/mol for rearrangement to the corresponding isothiocyanates.

Acyl-, aroyl-, and carbamoyl cyanates R−CO−OCN are unknown, but our calculations indicate barriers of 28−39 kcal/mol for rearrangement to the isocyanates RCO−NCO. Accordingly, several such cyanates may be expected to be stable and isolable at ordinary temperatures, especially the alkoxycarbonyl and carbamoyl derivatives.

All the acyl isocyanates and isothiocyanates formed in these reactions can undergo a second series of 1,3-shifts of the groups attached to the acyl (thioacyl, imidoyl) groups. This causes interconversion between acyl isothiocyanates and thioacyl isocyanates and between imidoyl isothiocyanates and thioacyl carbodiimides. The corresponding 1,3-shifts in acyl isocyanates and in thioacyl isothiocyanates are degenerate (Scheme 1).

A combination of the (thio)cyanate−iso(thio)cyanate rearrangement with the acyl isothiocyanate−thioacyl isocyanate rearrangement leads to the overall reaction scheme RCX−YCN ⇌ RCX−NCY ⇌ RCY−NCX ⇌ RCY−XCN (X and Y = O, S, NR′) as exemplified in Schemes 15 and 22 (X = O and Y = S).

Scheme 22. Interconversion of Acyl Thiocyanates with Acyl Isothiocyanates, Thioacyl Isocyanates, Thioacyl Cyanates, and Potentially Acyl Thiofulminates and Thioacyl Fulminates



It is worthwhile to note that the first type of rearrangement ((thio)cyanate to iso(thio)cyanate) involves the 1,3-migration of an essentially linear (thio)cyanate anion assisted by the carbonyl LUMO in the acyl cation moiety (Figures 1−4). In contrast, the second step, the 1,3-shift of the R-groups interconverting acyl(thio)cyanates and (thio)acyl isocyanates and related compounds, involves a four-membered cyclic, zwitterionic transition state (Figure 5), and these reactions are facilitated by migrating groups possessing lone pairs that can interact with the LUMO of the (thio)cyanate function to which migration takes place.

Further rearrangements and interconversion of isomers can be envisaged, for example, those involving the hitherto unknown acyl thiofulminates R−CO−SNC and thioacyl fulminates R−CS−ONC (Scheme 22). In addition, new interconversions of imidoyl (guanyl) carbodiimides and ketenimines by 1,3-shifts of the R-groups can be expected: R−C(═NR′)−X═C═Y ⇌ R−C(═Y)−X═C═NR′ (X = N or CR′; Y = NR or CR'_2; R = R′O, R′S, $R_2'N$). Similarly, sulfines, sulfinylamines and sulfurdiimides may undergo analogous interconversions with carbodiimides and ketenimines with experimentally accessible activation barriers: R−C(═NR′)−X═S═Y ⇌ R−S(═Y)−X═C═NR′ (X = N or CR′; Y = NR or CR'_2; R = R′O, R′S, $R_2'N$). Some of these reactions will be the subject of further investigation.

■ ASSOCIATED CONTENT

Supporting Information

Tables of B3LYP/6-311+G(d,p) calculated absolute energies and Cartesian coordinates for all calculated ground and transition states and imaginary frequencies of 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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