Acyl Azides

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Experimental and Theoretical Studies on the Synthesis, Spectroscopic Data, and Reactions of Formyl Azide**

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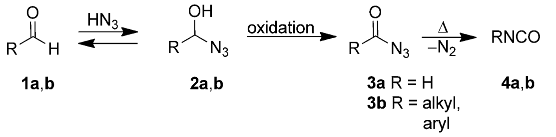
Dedicated to Professor Adalbert Maercker on the occasion of his 80th birthday

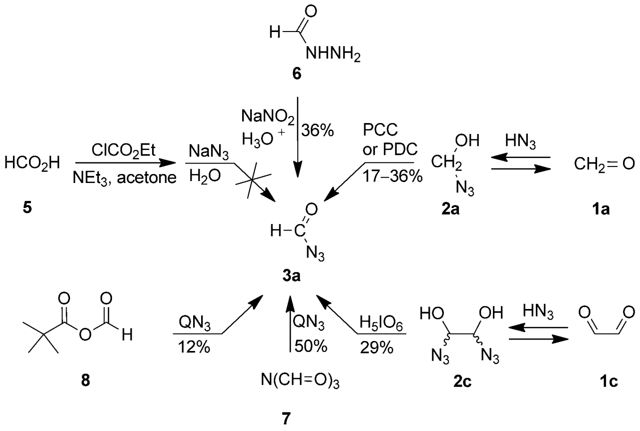
Acyl azides **3b** and their Curtius rearrangement to produce isocyanates **4b** have been well-known for more than hundred years (Scheme 1).[1] These azides are also of great importance in modern organic synthesis.[2] The parent compound **3a** was investigated in about a dozen theoretically studies dealing with its structure, spectroscopic data, and various reactions.[3] To the best of our knowledge, however, spectroscopic proof or any other indication for the existence of formyl azide (**3a**) is still missing. There may be two reasons why **3a** has not been generated experimentally. Quantum chemical calculations predicted activation energies for the process **3a**→**4a** that were significantly lower than those of the Curtius rearrangement reactions of acetyl or benzoyl azide (differences of 3.4–4.9 and 6.5–10.5 kcal mol^{-1}, respectively).[3e–j] Thus, **3a** should be highly unstable at ambient or even lower temperature. Furthermore, formyl chloride cannot be utilized as a convenient precursor of **3a** because this acyl chloride is a short-lived species, which excludes its simple synthesis and ease of handling.[4]



Scheme 1. Curtius rearrangement of acyl azides **3**, which can be prepared from aldehydes **1** via α-azido alcohols **2**.

Recently, we discovered that nearly all types of aldehydes **1** establish an equilibrium with α-azido alcohols **2** when treated with hydrazoic acid. The products **2b** can be oxidized under very mild conditions to afford acyl azides **3b**.[5] Herein, we show for the first time that the title compound **3a** can be prepared by oxidation of azidomethanol (**2a**) and by several other methods. The spectroscopic data and some reactions of **3a** are now investigated, with strong support from high-quality quantum chemical calculations.

Our attempts to generate **3a** from formic acid (**5**) by using the Weinstock route[6] were unsuccessful (Scheme 2). This classical method possibly failed because of insufficient stability or inferior reactivity of the intermediate anhydride[7] or because of the presence of an aqueous solution, which excluded low temperatures. However, nitrosation of formylhydrazine (**6**) at −10 °C led to formyl azide (**3a**) in moderate yield (36 %). Oxidation of azidomethanol (**2a**),[5] prepared from **1a** and hydrazoic acid, was successfully performed at −35 °C in the presence of pyridinium chlorochromate (PCC) or pyridinium dichromate (PDC) to furnish **3a** in yields of 36 and 17 %, respectively.[8] Moreover, cleavage of the diol **2c**,[5] which is accessible from glyoxal (**1c**) and hydrazoic acid, by treatment with periodic acid at −35 °C gave **3a** in 29 % yield.[8] Formylation of azide salts can also lead to **3a** if carried



Scheme 2. Syntheses of formyl azide (**3a**).

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out at low temperature (−30 to −15 °C) with a highly soluble azide source such as QN_3[9] (hexadecyltributylphosphonium azide). Reagent **7** was found to be superior to **8**[10] in producing **3a** in good yield. Solutions of pure **3a** could be conveniently obtained in 50 % yield when such reaction mixtures were recondensed at −50 to −15 °C and 10^{-6} bar.[11] ^{15}N-Labeled formyl azide ([$^{15}N_3$]-**3a**) was also synthesized by using $Q^{15}N_3$[9,12] and **7**.

We characterized **3a** by its UV, IR (Figure 1, Table 2), ^{1}H NMR, ^{13}C NMR, and ^{15}N NMR spectra (Table 1). The ^{15}N NMR spectrum of [$^{15}N_3$]-**3a** indicated that N_γ resonated at lower field than N_β, which is typical for electron-poor azides.[13] Furthermore, we observed a remarkable $^{2}J(^{15}N,^{1}H)$ coupling constant of 30.7 Hz in both the ^{1}H NMR and ^{15}N NMR spectra.[14]

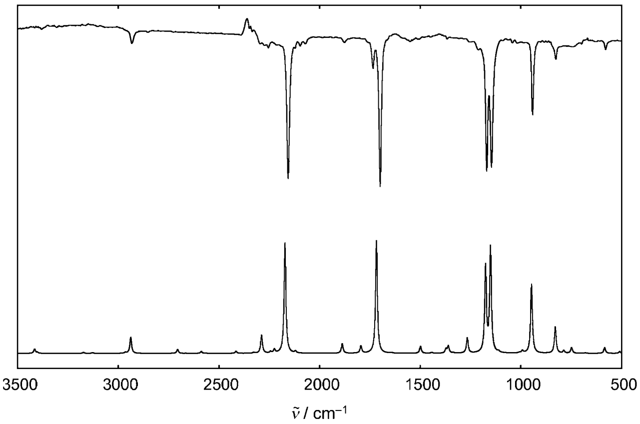


Figure 1. Top: IR spectrum of formyl azide (**3a**) in CCl_4; bottom: calculated spectrum.

Table 1: Selected spectroscopic data of formyl azide (**3a**) and [$^{15}N_3$]-**3a**.[a]

3a	UV (MeCN):	$\lambda_{max} = 233$ nm
	^{1}H NMR:	$\delta = 8.10$ (br s)
	^{13}C NMR:	$\delta = 167.34$ (d, $^{1}J_{CH} = 223$ Hz)
[$^{15}N_3$]-**3a**	^{1}H NMR:	$\delta = 8.10$ (dd, br $^{2}J_{HN} = 30.7$ Hz, $^{3}J_{HN} = 7.3$ Hz)
	^{13}C NMR:	$\delta = 167.34$ (dd, $^{1}J_{CN} = 11.5$ Hz, $^{2}J_{CN} = 7.3$ Hz)
	^{15}N NMR:	$\delta = -241.8$ (ddd, $^{2}J_{NH} = 30.7$ Hz, $^{1}J_{\text{N}\alpha\text{Nß}} = 17.5$ Hz, $^{2}J_{NN} = 1.6$ Hz, N_α), -144.8 (ddd, $^{1}J_{\text{NßN}\alpha} = 17.5$ Hz, $^{3}J_{NH} = 7.3$ Hz, $^{1}J_{\text{NßN}\gamma} = 6.0$ Hz, $\text{N}_{\text{ß}}$), -132.7 (dt, br, $^{1}J_{\text{N}\gamma\text{Nß}} = 6.0$ Hz, $^{2}J_{NN} \approx {}^{4}J_{NH} = 1.6$ Hz, N_γ)

[a] ^{1}H, ^{13}C, and ^{15}N NMR spectra were recorded in $CDCl_3$ at −20 °C and 400, 100.6, and 40.5 MHz, respectively. The UV spectrum was measured at room temperature.

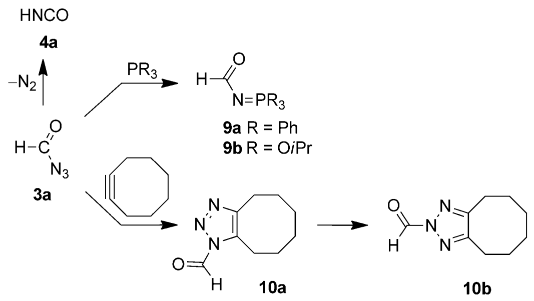
The experimental IR spectrum of formyl azide (**3a**; upper spectrum in Figure 1) indicates two strong bands at 1146 and 1169 cm^{-1}. These bands cannot be explained on the basis of the harmonic frequencies obtained from the B3LYP/6-311++G** calculations of Badawi[3d] (Table 2). Our high-level CCSD(T)-F12a[15–17] investigationsalso do not explain these nearly degenerate bands. In both of the calculated spectra, only the fundamental frequency of ν8 close to 1146 or 1169 cm^{-1} is found. Since all the other fundamental frequencies are too far away from these two signals, there must be a strong coupling between two or several modes. Therefore, we calculated the potential energy surface at the CCSD(T)-F12a/cc-pVTZ-F12 level by making use of a multimode expansion up to the third order.[17] Vibrational configuration interaction (VCI) calculations were subsequently performed, which yielded a multitude of vibrational overtones and combination bands. As a result, we found a strong coupling of ν8 with the first overtone of ν4. This Fermi resonance results in the intensities of both bands being quite similar, which is in nice agreement with the experimental spectrum. A comparison of the calculated vibrational frequencies with the experimental ones led to mean absolute deviations of 55 cm^{-1} for the scaled B3LYP harmonic frequencies and 8 cm^{-1} for the anharmonic CCSD(T)-F12a results. The remaining differences between the experimental and the theoretical data most likely arise from truncations within the calculations, as well as from the fact that the experimental spectrum was determined in solution rather than the gas phase. Thus, we conclude that our new calculations are in excellent agreement with the experimental spectrum and explain all the qualitative aspects of the vibrational spectrum of **3a** (Figure 1).

Table 2: Experimental and computed fundamental frequencies (cm^{-1}) of formyl azide (**3a**) at the CCSD(T)-F12a and B3LYP level of theory.[a]

Basis mode	Symmetry	Expt. spectrum in CCl_4 at RT	CCSD(T)-F12a cc-pVTZ-F12 surface	B3LYP 6-311++G** scaled harm. (0.989)
ν12	A′	2932 (w)	2938	3023
ν11	A′	2156 (s, N_3)	2172	2252
ν10	A′	1699 (s)	1717	1744
ν9	A′	–	1361	1386
2ν4	A′	1169 (s)	1175	–
ν8	A′	1146 (s)	1151	1241
ν7	A′	–	993	1008
ν6	A′	942 (m)	947	945
ν5	A′	827 (w)	829	826
ν4	A″	–	584	583
ν3	A′	–	491	497
ν2	A″	–	252	256
ν1	A′	–	171	173

[a] The harmonic B3LYP frequencies were taken from Ref. [3d].

Even at 0 °C, solutions of **3a** liberated dinitrogen to form isocyanic acid (**4a**)[18] by Curtius rearrangement (Scheme 3). We investigated this process kinetically with the help of ^{1}H NMR spectroscopy by analyzing solutions of **3a** in $CDCl_3$ between 0 and 25 °C. This study led to $E_a = (20.3 \pm 1.1)$ kcal mol^{-1}, $\ln A = 27.0 \pm 2.0$, $\Delta H^{\neq} = (19.7 \pm 1.1)$ kcal mol^{-1}, $\Delta S^{\neq} = (-6.86 \pm 2.96)$ cal $mol^{-1} K^{-1}$, and $\Delta G^{\neq}_{285.5} = (21.7 \pm 1.4)$ kcal mol^{-1}.[19] When the decay of **3a** was analyzed at 21 °C in CD_3CN as the solvent instead of the less-polar $CDCl_3$, the *k* value increased only slightly by a factor of 1.07, whereas the same reaction in the nonpolar solvent [D_{12}]cyclohexane resulted in a significantly lower (factor of 0.55) *k* value. On the other hand, the Curtius rearrangement of **3a** in $CDCl_3$ at 25 °C was much faster (factor of 106) compared with the analogous reaction of acetyl azide[20,21] under the same



Scheme 3. Reactions of formyl azide (**3a**).

conditions. Our experimental results correspond well with high-level quantum chemical calculations (see below).

The geometries of the *syn* and *anti* conformers of **3a**, and the corresponding transition states were optimized at the DFT level by using the B3LYP functional[22–24] and the def2-QZVPP basis set including the dispersion correction of Grimme[25] (Figure 2). The effect of the solvent on the activation energy was estimated by the COSMO[26] model using $\varepsilon = 4.81$. The computation of the electronic energy was performed with the CCSD(F12)(T)[24] method at the B3LYP[22] geometry using the cc-pVTZ-F12 basis set. The calculated $\Delta G^{\neq}_{285.5}$ value of 21.7 kcal mol^{-1} fits very well with the experimental value. An increase in the ε value from 4.81 to ∞ resulted—in complete agreement with the experimental observations—in a lowering of the $\Delta G^{\neq}$ value. Considering the calculated enthalpy $\Delta H^{\neq} = 22.8$ kcal mol^{-1} and entropy $\Delta S^{\neq} = 3.8$ cal mol^{-1} K^{-1}, we find that the numbers deviate slightly from the experimental ones, possibly because of the B3LYP geometry. The error in the single-point approximation was evaluated for **3a** to be -0.35 kcal mol^{-1}, thus indicating that the perfect agreement of the $\Delta G^{\neq}$ value is based on a fortuitous error cancellation. However, this agreement is good enough to conclude that the Curtius rearrangement is a one-step mechanism via TS1 and not a two-step mechanism via the nitrene, since the energy of TS3 is 6.5 kcal mol^{-1} higher than the energy of TS1 (Figure 2). This result does not change, even with the errors mentioned above.

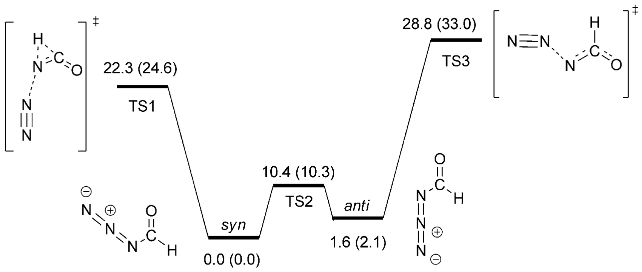


Figure 2. Relative CCSD(F12)(T) energies (kcal mol^{-1}) including a correction for solvation effects and zero-point energy of **3a** conformers and their transition states for interconversion and Curtius rearrangements. Values in brackets correspond to B3LYP/def2-QZVPP.

Intermolecular reactions of formyl azide (**3a**) can only be successful if they are able to compete with the rapid Curtius rearrangement. A Staudinger reaction of **3a** with triphenylphosphine or triisopropyl phosphite resulted in the quantitative formation of the phosphazenes **9a** and **9b**, respectively. These products could possibly have applications in aza-Wittig reactions.[27] Treatment of **3a** with cyclooctyne[28] initially gave the cycloadduct **10a**. At room temperature, however, this 1*H*-1,2,3-triazole slowly rearranged to the 2*H*-triazole **10b** (40% yield based on the precursor **7**).

Since the products **10a** and **10b** are significantly larger than the species in the Curtius rearrangement, we optimized the geometries at the RI-BP86/TZVP[29] level of theory and performed single-point calculations with B3LYP-d/def2-QZVPP using COSMO ($\varepsilon = 4.81$). The 1,3-dipolar cycloaddition of **3a** and cyclooctyne can take place by either a *syn* (8.2 kcal mol^{-1}) or an *anti* (6.0 kcal mol^{-1}) pathway. Both barriers are significantly smaller than the barrier of the Curtius rearrangement, and the cycloaddition is possible. The lowest barrier for the conversion of **10a** into **10b** is relatively high at 34.7 kcal mol^{-1}, which explains the relatively slow rearrangement (Figure 3). Further possible transition states have similar energy.[19] The reaction energies starting from the *syn* and *anti* product of **10a** are -8.5 and -3.2 kcal mol^{-1}, respectively.

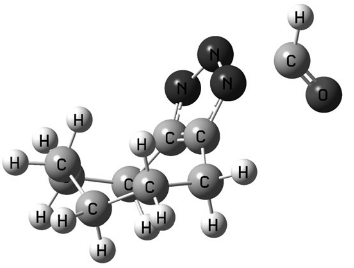


Figure 3. Transition state of lowest energy for the rearrangement of **10a** to **10b**.

In summary, we have presented four different methods to prepare formyl azide (**3a**). Two of these utilized the unusual starting compounds **2a** and **2c**, another route proceeded from the special salt QN_3 and formylation reagents **7** or **8**, while the last method made use of the nitrosation of a hydrazide, which is the oldest procedure to synthesize acyl azides.[11a] Furthermore, we were able to assign all the strong IR signals of **3a** with the help of high-level quantum chemical calculations. Although **3a** undergoes a rapid Curtius rearrangement through a concerted mechanism, it can also be applied to other reactions. Currently, we are investigating whether the irradiation of **3a** can lead to formylnitrene. This short-lived species has already been studied intensively by theoretical methods.[30]

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Keywords: acyl azides · formylation · oxidation · quantum chemistry · rearrangement

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