Cyanoketene and Iminopropadienones

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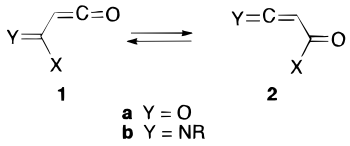
Cyanoketene (**8**) is generated in high yields on flash vacuum thermolysis (FVT) of suitably substituted Meldrum's acid derivatives (5-[(alkylamino)(methylthio or alkylamino)methylene]-2,2-dimethyl-1,3-dioxane-4,6-diones) (**3e**−**j**), and also on FVT of cyanoacetic acid derivatives **9e**,**f**,**g**,**j**,**k**,**m**. The major reaction pathway from **3** proceeds via ketenimines **6** and (alkylimino)propadienones **7**, the latter undergoing a retro-ene reaction to **8**. A minor pathway is via imidoylketenes **4e**,**h** and oxoketenimines **5e**,**h**, which undergo retro-ene reactions to **9**. All intermediates were characterized by Ar matrix FTIR and tandem mass spectrometry (collisional activation MS). Trapping of **4**, **5**, and **8** with nucleophiles is also reported. The preference of 1,3-X shifts over 1,5-H shifts in imidoylketenes **12** (X = SMe or NMe_2) is corroborated by the calculated activation barriers. Neat cyanoketene is highly reactive, reacting at or below 80 K, and this is attributed to the availability of a low-lying ketene LUMO. The IR spectrum of cyanoketene (Ar, 14 K) is dominated by two absorptions at 2163 (s; C═C═O) and 2239 (w; CN) cm^{-1} in excellent agreement with density functional (B3-LYP/6-31G*) and ab initio (QCISD/6-31G*) calculations.

Introduction

Cyanoketene (NC−CH═C═O) has been the subject of several studies,[2] but due to its presumed high reactivity, there is little direct spectroscopic information available. Its photoelectron spectrum was obtained by using thermolysis of cyanoacetyl chloride at 920 K.[3] The mass and collisional activation mass spectra, the ion molecule reactions of cyanoketene, and its relationship with the unsubstituted iminopropadienone (HC═C═C═C═O) have been investigated.[4] Recently, flow pyrolysis of cyanoacetyl chloride has also been employed to obtain the microwave spectrum of cyanoketene and several of its isotopomers.[5] However, an infrared spectrum of cyanoketene has never been reported.

The reported[2b] isolation of cyanoketene as a *not* highly reactive liquid with a boiling point of −34 °C, and the attribution of ^1H and ^{13}C NMR spectra to this compound, obtained by treatment of ethyl cyanoacetate with P_2O_5, are in disagreeement with the high reactivity of cyanoketene reported below; for example, neat cyanoketene disappears at temperatures below 80 K. Dicyanoketene is even more reactive.[2c]

During our investigations of (alkylimino)propadienones[6] (RN═C═C═C═O) and the oxoketene−oxoketene[7] (**1a** → **2a**) and imidoylketene−oxoketenimine[8] (**1b** → **2b**) rearrangements, we have discovered several facile and efficient methods of generating cyanoketene by flash vacuum thermolysis (FVT). These reactions are detailed in the present paper.



Work in collaboration with J. Chuche on the synthesis of α-cyano carbonyl compounds such as cyanoacetic acid derivatives **9** led to the realization that facile, thermal 1,3-shifts of electron rich migrating groups X (SMe or RR′NH, and later also OMe and Cl) was taking place in the postulated imidoylketene intermediates **4e**−**j**, interconverting them with **5e**−**j**.[8a] This was subsequently proven by direct IR spectroscopic monitoring of the intermediates in FVT/matrix isolation experiments, whereby these intermediates were generated from both Meldrum's acid derivatives (2,2-dimethyl-1,3-dioxane-4,6-diones (**3**)) and pyrrole-2,3-dione precursors.[8b] The high migratory aptitude of electron rich groups in the interconversion **1** → **2** has been corroborated by ab initio calculations[9] and can be understood in terms of a favorable interaction between a high-lying lone pair orbital

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of the migrating group X and the low-lying ketene LUMO; the latter lies in the same plane as X and has a high coefficient at the electrophilic central carbon atom of the ketene function. Thermodynamics will usually displace the equilibrium between **4** and **5** toward the latter, which can be isolated in several cases, particularly when X = OMe.[8d,e] However, when R = Ph, imidoylketenes **4** efficiently cyclize to quinolones, and the equilibrium is therefore displaced toward **4** at high temperatures, when quinolones can be isolated in almost quantitative yields.[8b,d,e]

Furthermore, we have demonstrated that iminopropadienones **7a** and **7b** can be isolated at temperatures below −50 and −70 °C, respectively, following FVT of Meldrum's acid precursors of type **3a**,**b** or isoxazolopyrimidinones.[6,7e] Some (*N*-arylimino)propadienones are even isolable at room temperature.[10] The fragmentation of Meldrum's acid derivatives **3** to ketenes **4** dominates with X = SMe or OMe, which are good migrators (giving **5**) but relatively poor leaving groups (giving **6** and **7**). The competing formation of **7** is observed in both of these cases at high temperatures, but it becomes the near-exclusive reaction when X is an amine function.[6a] These derivatives, therefore, are excellent precursors of iminopropadienones **7a**,**b**.

Consequently, there are two ways that the final products, cyanoacetic acid derivatives **9e**−**j**, may be formed in FVT reactions of *N*-alkyl-substituted Meldrum's acid derivatives **3e**−**j**: (i) the ketene−ketenimine route via **4** and **5** followed by retro-ene type alkene elimination to give **9**; or (ii) initial formation of iminopropadienone **7** followed by alkene elimination to give cyanoketene (**8**). As will be shown below, the latter is reactive enough to react with the nucleophile (RSH or RR′NH) in the cold trap to regenerate **9**. The present study seeks to unravel these mechanistic alternatives.

Results and Discussion

Imidoylketenes, Ketenimines, Iminopropadienones, Cyanoketene, and Retro-Ene Reactions. The Meldrum's acid derivatives **3e**−**j** all gave rise to a strong absorption at 2163 cm^{-1} together with a very weak one at 2239 cm^{-1} upon FVT with Ar matrix isolation of the products at 14 K for IR spectroscopy. As detailed below, these absorptions are due to cyanoketene (**8**) (Scheme 1). In the cases **3e** and **3h**, cyanoketene became the dominant species above *ca.* 600 °C (*cf.* Figure 1). In the cases **3f**,**g**,**i**,**j**, cyanoketene was always the major species, even under the mildest FVT conditions, starting at 300−400 °C. An example is shown in Figure 2b.Detailed IR monitoring of the products of FVT of **3e** as a function of temperature revealed several intermediates. Analogous monitoring of the reaction by mass spectrometry permitted a direct correlation between IR, mass, and collisional activation mass spectra (CAMS) (Figures 1−5). As seen in Figure 1 and Table 1, the first-formed species is a ketenimine (**5e**; 2054 cm^{-1}; *m*/*z* 157), which starts appearing already at 200 °C, at which temperature there is very little reaction taking place. As the temperature increases, a signal ascribed to the isomeric ketene **4e** (2112 cm^{-1}) becomes visible, while that due to **5e** remains stronger. This is the normal intensity ratio for interconverting imidoylketenes and oxoketenimines.[8c,d] The second intermediate detected by MS has a mass of 211 and corresponds to the transient ketenimine **6e**, formed by thermal elimination of MeSH (*m*/*z* 48; also detected). **6e** rapidly loses CO_2 and acetone to furnish the third intermediate, (isopropylimino)propadienone (**7e**; 2234, 2221 cm^{-1}; *m*/*z* 109). The cumulenic stretching vibrations of iminopropadienones in the 2200 cm^{-1} region have extremely high extinction coefficients and often appear as multiple bands due to matrix site splitting.[6a,c] We have previously calculated the structures and IR spectra of iminopropadienones **7** (R = H, Me, and Ph) at the HF- and MP2/6-31G* (MP2/3-21G for Ph) levels.[6e] New B3-LYP/6-31G* calculations confirm very strong antisym-

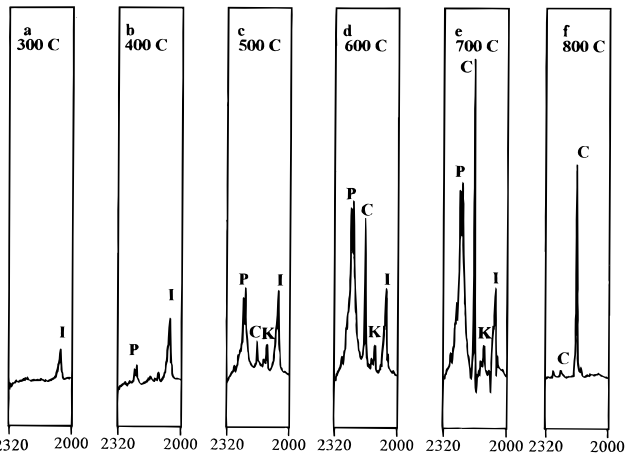
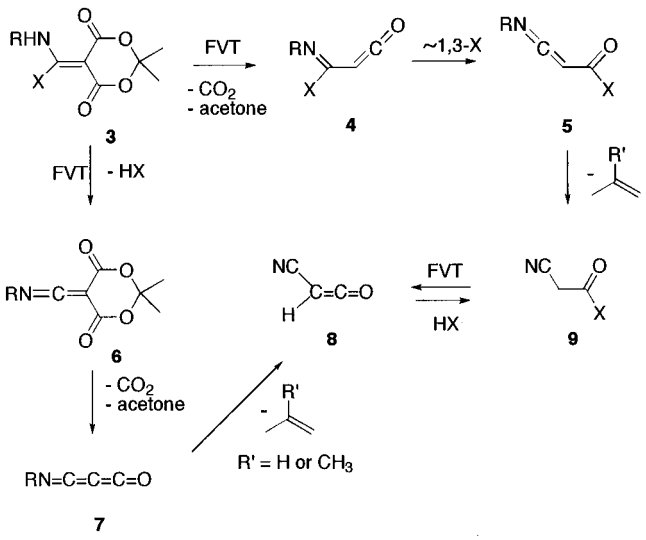


Figure 1. Partial FTIR spectra (14 K; 2000−2320 cm^{-1} range) of the products of FVT of **3e** as a function of temperature. I = oxoketenimine **5e** (2054 cm^{-1}); P = (isopropylimino)propadienone **7e** (2221, 2234 cm^{-1}); C = cyanoketene **8** (2163 (s), 2239 (w) cm^{-1}; K = imidoylketene **4e** (2112 cm^{-1}).

Scheme 1



3 - 7

a R = Ph, X = SMe
b R = Me, X = SMe
c R = Ph, X = NMe_2
d R = Me, X = NMe_2
e R = iPr, X = SMe
f R = iPr, X = NMe_2
g R = iPr, X = iPrNH
h R = tBu, X = SMe
i R = tBu, X = NMe_2
j R = tBu X = tBuNH

9

e X = SMe
f X = NMe_2
g X = iPrNH
j X = tBuNH
k X = OMe
m X =

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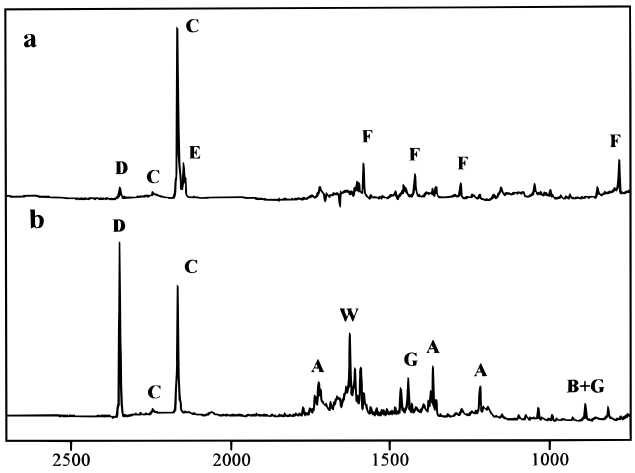
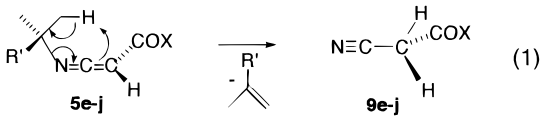


Figure 2. FTIR spectra (14 K; abscissa in wavenumbers) of cyanoketene **8** produced by (a) FVT of **9m** at 800 °C; (b) FVT of **3j** at 700 °C. A = acetone; B = *tert*-butylamine; C = cyanoketene **8** (2163, 2239 cm^{-1}); D = CO_2; E = CO, F = 3,5-dimethylpyrazole; G = 2-methylpropene; W = water.

Table 1. Relative Abundancies of Some Ions of Interest in the Mass Spectra of 3e during FVT

temp, °C	*m/z* 259 (M^+, **3e**)	211 (**6e**)	157 (**4**/**5**)	115 (**9e**)	109 (**7**)	67 (**8**)
200	100	6	65	10	4	8
300	36	54	100	5	61	33
400	3	13	76	60	100	73
600	0	0	3	3	17	100

metric absorptions of **7** (R = H, Me, iPr, *t*-Bu, Ph) in the 2200 cm^{-1} range (*ca.* 4000 km mol^{-1}) together with very weak symmetric ones in the 2100 cm^{-1} range (*ca.* 60 km mol^{-1}). Consequently, the signals seen in Figure 1 do not correspond to large amounts of **7e**. These signals disappear above 700 °C, with concomitant increased signals for propene and cyanoketene in both the IR and mass spectra. However, cyanoketene (**8**; 2163s, 2239w cm^{-1}; *m/z* 67) and propene start appearing below 500 °C, and cyanoketene is the only species remaining at 800 °C (together with CO_2, acetone, methanethiol, and propene). The formation of methyl cyanothiolacetate (**9e**; *m/z* 115) is observed by MS at 350−400 °C. In the low pressure gas phase of the mass spectrometer, this must be due to thermal elimination of propene from **5e** via a six-centered six-electron cyclic transition state of the retro-ene type[8a] (eq 1), giving **9e** directly; however, the signal (*m/z* 115)



(1)

due to **9e** never becomes strong. As shown below, compounds **9** themselves undergo thermal elimination of HX above 400−500 °C to give cyanoketene (**8**), but this process is inefficient below *ca.* 600 °C. Thus, cyanoketene always becomes the near-exclusive product when using FVT temperatures of 700−800 °C.

Chemical evidence for the assignment of ketene **4e** and ketenimine **5e** was obtained in a preparative trapping experiment with MeOH at 77 K, whereby esters **10** and **11** were isolated in 19 and 58% yields, respectively, reflecting the predominance of **5e** in the thermal equilibrium.

The *tert*-butyl analogue **3h** is more sensitive than **3e**. Decomposition with formation of cyanoketene (**8**) starts already at 200 °C. Nevertheless, all the intermediates, **5h** (2054 cm^{-1}; *m/z* 171), **7h** (2214, 2239 cm^{-1}; *m/z* 123), **6h** (*m/z* 225), and **9e** (*m/z* 115), as well as isobutene, methanethiol, CO_2, and acetone, were detectable by Ar matrix IR and/or mass spectrometry. The most impor-

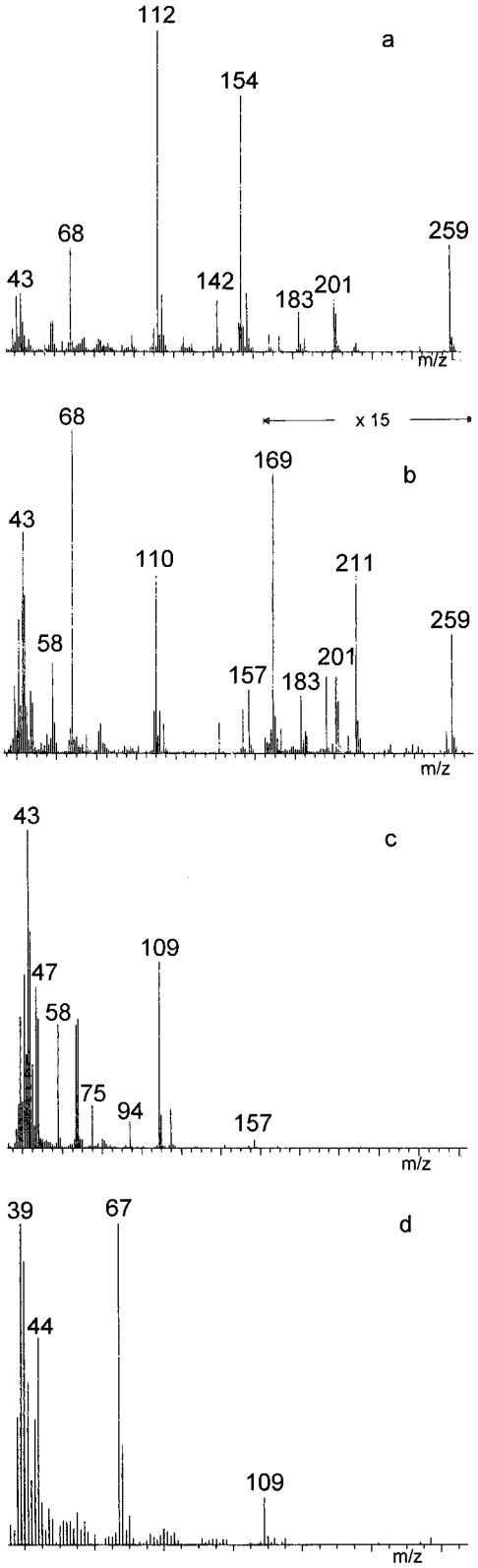


Figure 3. FVT/mass spectra of **3e** at (a) 100 °C (no thermal decomposition); (b) 250 °C (ketenimine **6e**, *m/z* 211 appears); (c) 350 °C (iminopropadienone **7e**, *m/z* 109 at optimal intensity; *m/z* 115 (**9**) and 67 (**8**) present); (d) 400 °C (*m/z* 109, 115, and 157 disappearing; *m/z* 67 (cyanoketene **8**) dominant; at 600 °C this becomes the only significant species in the spectrum).

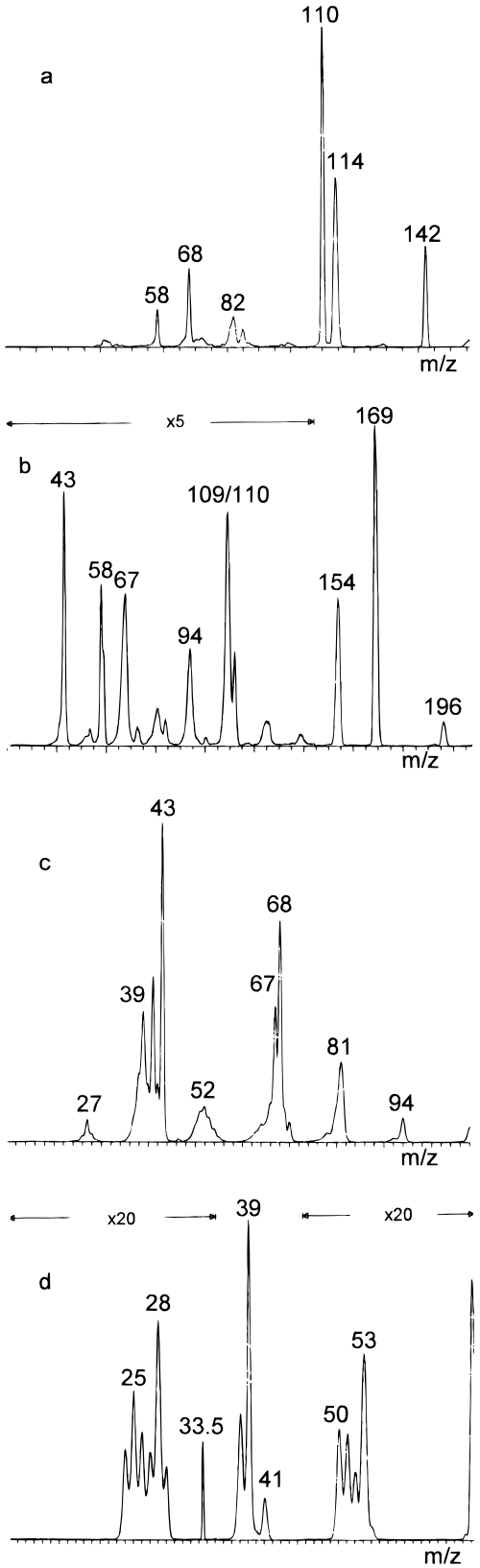
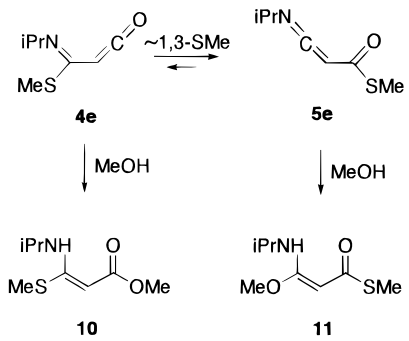
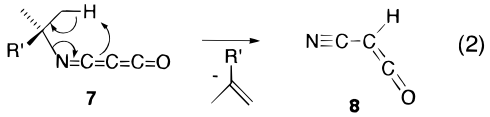


Figure 4. Collisional activation mass spectra [CA(O_2)] of isopropyl-substituted intermediates; (a) *m/z* 157 (**4e** and/or **5e**); (b) *m/z* 211 (**6e**); (c) *m/z* 109 (**7e**); (d) *m/z* 67 (**8**), generated by FVT/MS of **3e** (*cf.* Figure 3).

tant CA mass spectra are illustrated in Figure 5. The CAMS of **8** and **9** were identical with those obtained from **3e** (vide supra). In the IR spectra, cyanoketene (**8**) was the major product from **3h** already at an FVT temperature of 400 °C (*cf.* 700 °C for **3e**). From 450 °C onward, essentially only cyanoketene was formed.



The amine derivatives **3f**,**g**,**i**,**j** gave cyanoketene immediately on FVT over the whole temperature range (300−800 °C), with little evidence for the other intermediates being present according to Ar matrix IR spectroscopy. The appropriate alkene (propene or isobutene) was also immediately detected (*cf.* Figure 2b). This reaction, too, is formulated as a six-centered six-electron retro-ene type reaction (eq 2): Both of these retro-ene reactions



(eqs 1 and 2) and other, related pericyclic reactions in cumulenes are under theoretical investigation in our group. the orbital topology of the cumulene systems makes it possible to transfer the hydrogen atom and create the third bond of the CN triple bond *in the plane* of the molecules.

1,3-X versus 1,5-H Shifts in Imidoylketenes 4. It was shown previously[8a,11] that (*N*-alkylimidoyl)ketenes **12** possessing at least one α-hydrogen atom undergo 1,5-H shifts to produce enaminoacroleins **14** as final products in good yields (Scheme 2). However, no trace of such 1,5-H shift products was obtained from **4b** or **4e**, which instead underwent the 1,3-shifts of the methylthio group, giving **5** (Scheme 1). Thus, one should expect the activation barriers for the 1,3-shifts (**12** → **13**) of the most efficient migrators[9] (X = NMe_2 or SMe) to be lower than that of the 1,5-H shift (**12** → **14**). Conversely, with poor 1,3-migrators (e.g. X = Ph, H, or Me[8a]), the 1,5-H shift will dominate. These expectations are nicely supported by our theoretical calculations of ground state and transition structure energies at the MP2/6-311+G(2d,p)//MP2/6-31G* level (Table 2). The calculated 1,5-H shift barriers are similar for the three model systems considered, of the order of 100 kJ mol^{-1}. However, the barrier for the 1,3-X shift falls dramatically from the high values for H and CH_3, which are known to be poor migrators (the methyl group not migrating at all),[9] to ca. 90 kJ mol^{-1} for X = NH_2. Thus, already the 1,3 shift of the amino group will compete effectively with the 1,5-H shift. We have shown in other studies[9] that the 1,3-shift barriers of SMe and NMe_2 are lower than that of NH_2 by 20−40 kJ mol^{-1}. Therefore, only the 1,3-X shift will be observed in compounds **12** (X = SMe or NMe_2). The

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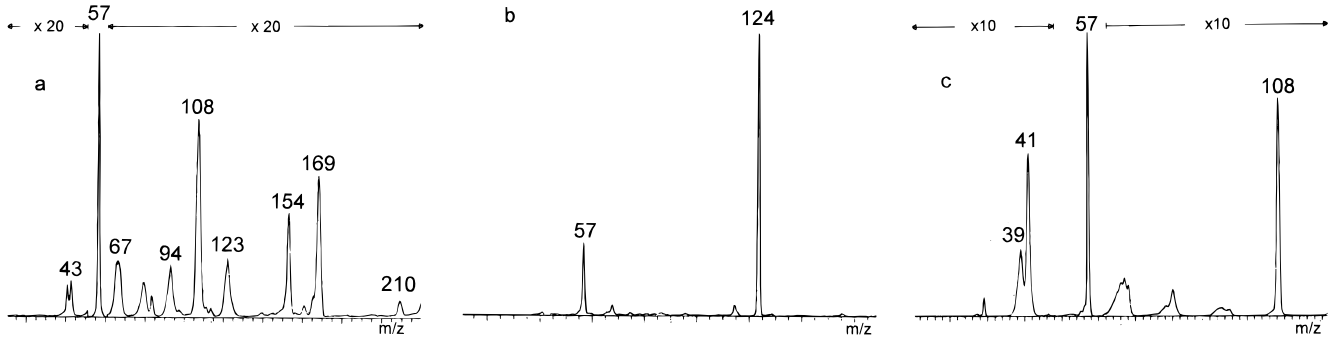


Figure 5. CA(O_2) mass spectra of *tert*-butyl-substituted intermediates; (a) *m*/*z* 225 (**6h**); (b) *m*/*z* 171 (**4h**/**5h**); (c) *m*/*z* 123 (**7h**), generated by FVT/MS of **3h**. The spectrum of *m*/*z* 67 (**8**) was identical with the one shown in Figure 4.

Scheme 2

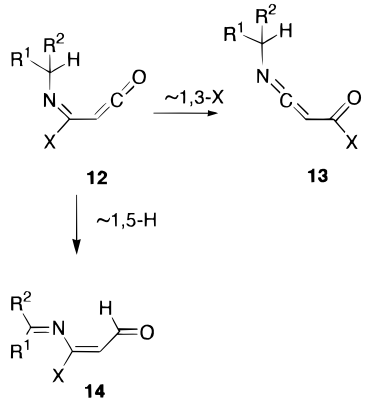


Table 2. Calculated Relative Energies (kJ mol^{-1}) for 1,3 and 1,5 Shifts in Imidoylketenes[a]

species[b]	X = H	X = CH_3	X = NH_2
s-trans $CH_3N{=}CX{-}CH{=}C{=}O$	0.0	0.0	0.0
s-cis $CH_3N{=}CX{-}CH{=}C{=}O$	0.5	4.0	−0.2
1,5-H shift transition structure	112.4	97.3	96.7
1,3-X shift transition structure	179.8	233.2	90.2
s-trans $O{=}CXCH{=}C{=}NCH_3$	22.3	6.5	−19.2
s-cis $O{=}CXCH{=}C{=}NCH_3$	25.3	7.9	−19.8
E $CH_2{=}N{-}CX{=}CHCHO$	20.1	24.2	29.5
Z $CH_2{=}NCX{=}CHCHO$	23.4	17.7	27.0

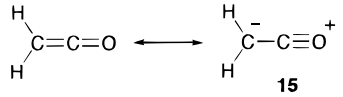
[a] Cf. Scheme 2. MP2/6-311+G(2d,p)//MP2/6-31G* values are reported. [b] Imidoylketenes and ketenimines are defined as *s-trans* or *s-cis* based on the π systems, regardless of the nature of X.

same can be expected for SH and Cl groups. The low barriers for the 1,3-shifts of these electron rich groups was rationalized in terms of a favorable interaction between a lone pair on the migrating group and the vacant central carbon p orbital of the ketene LUMO.[9]

Cyanoketene from Cyanoacetic Acid Derivatives 9. Further proof for the identity of cyanoketene was adduced by FVT of the reaction products **9e**,**f** (X = SMe or NMe_2) as well as methyl cyanoacetate (**9k**) and 1-(cyanoacetyl)-3,5-dimethylpyrazole (**9m**) (Scheme 1),[4a,12] all of which produced cyanoketene (**9e** starting at 500 °C, but reaction still incomplete at 800 °C; **9f** starting at 400 °C and reaction complete at 700 °C; **9k** starting at 550 °C; **9m** starting at 450 °C and reaction complete at 800 °C). The Ar matrix IR spectrum obtained from **9m** is shown in Figure 2a.

Infrared Spectrum and Structure of Cyanoketene. The assignment of the IR spectrum of cyanoketene (**8**) is supported by theoretical calculations, at the B3-LYP and QCISD levels in particular. HF/ and MP2/6-31G* calculations were also carried out (Table 3). Note that all three methods predict only the two observed bands with a reasonable intensity in the range 700−3000 cm^{-1}, in agreement with observations (apart from the two absorptions at 2163 and 2239 cm^{-1} described above, a weak band at 3076 cm^{-1} is always observed in the matrix IR spectra of **8**, but it is more hazardous to assign this since alkenes and other intermediates also give rise to absorptions in this region). The MP2 calculated intensities of the CCO and CN vibrations are drastically different and in disagreement with experiment. This is due to the fact that these vibrations are strongly coupled at both the HF and MP2/6-31G* levels of theory. The MP2 CCO and CN frequencies are also in poor agreement with experiment and with the other theoretical results. We have shown elsewhere that the standard scaling factor[13] of 0.9427 is not applicable to cyano compounds.[14]

The C=C=O stretching frequency of cyanoketene (ν_3; exptl in Ar: 2163; B3LYP/6-31G*: 2165 cm^{-1}) is higher than that of the parent ketene (Ar: 2142; gas: 2151; B3LYP/6-31G*: 2153 cm^{-1}), roughly midway between this and dicyanoketene[2b] (Ar: 2175 cm^{-1}). This is consistent with the expectation that resonance structure **15** of ketene is favored by the electron-withdrawing cyano group, thus leading to a higher frequency.[15]



15

Our best calculated structure of cyanoketene is shown in Figure 6. The very short C=O bond (and slightly elongated C=C bond) are again in agreement with an enhancement of resonance structure **15** as in a highly electronegatively substituted ketene.[16] For comparison, the calculated structural parameters for ketene at the

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Table 3. Calculated Vibrational Frequencies[a] (cm^{-1}) and IR Intensities[b] (km mol^{-1}) of Cyanoketene

mode	HF/6-31G*	MP2/6-31G*	B3-LYP/6-31G*	QCISD/6-31G*	assignment
A′ ν_1	3048 (26)	3088 (33)	3084 (24)	3110 (24)	CH stretch
ν_2	2322 (40)	2128 (487)	2258 (21)	2231 (20)	CN stretch
ν_3	2145 (1253)	2099 (49)	2165 (730)	2126 (699)	CCO stretch
ν_4	1364 (13)	1336 (6)	1358 (5)	1361 (5)	in phase CH wag
ν_5	1109 (0)	1094 (1)	1106 (2)	1113 (2)	out of phase CH wag
ν_6	945 (1)	937 (1)	949 (1)	947 (1)	CC stretch
ν_7	644 (8)	618 (2)	631 (3)	625 (3)	sym CCO + CCN bend
ν_8	420 (4)	390 (1)	401 (1)	389 (2)	asym CCO + CCN bend
ν_9	147 (11)	136 (7)	139 (7)	141 (8)	CCC wag
A′ ν_{10}	612 (113)	528 (73)	577 (67)	547 (77)	CH oop bend
ν_{11}	528 (1)	489 (0)	494 (2)	491 (2)	CCO oop bend
ν_{12}	400 (5)	363 (7)	391 (5)	370 (5)	CCN oop bend

[a] Scaled values.[13] [b] IR intensities are given in parentheses.

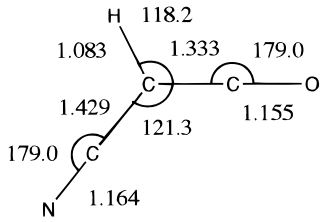

Figure 6. Optimized structure of cyanoketene (QCISD/6-311+G**). Bond lengths in angstroms and angles in degrees. The calculated rotational constants for this geometry, A, B, and C are 28.968, 2.7858, and 2.5414 GHz, respectively.

same level (QCISD/6-311+G**) are: r(C═O) = 1.165; r(C═C) = 1.321; r(C−H) = 1.080 Å, ∠HCH = 120.6°.

Reactivity of Cyanoketene. Cyanoketene is a highly reactive molecule. After preparation by FVT of e.g. **3j** at 600 °C, with isolation as a neat film at 14 K, subsequent warmup in 10 K intervals demonstrated that **8** vanishes at 80 K. In other words, it is practically impossible to isolate cyanoketene at liquid nitrogen temperature (77 K). Therefore, although all the FVT reactions manifestly produce cyanoketene, preparative thermolysis experiments with product isolation at 77 K invariable gives acetic acid derivatives **9**.[8a] Thus, even when the products of FVT (600 °C) of **3i** were isolated on a 77 K cold finger previously coated with methanol, subsequent warmup to rt gave only *N*,*N*-dimethylcyanoacetamide (**9f**; 69%); **9k** was not detected. A likely explanation is that cyanoketene reacts at 77 K with the dimethylamine with which it is cocondensed before it has time to diffuse through this medium to the methanol surface. We have demonstrated elsewhere that other ketenes react with amines (pyridine) at temperatures between 15 and 40 K via zwitterionic ("ketene−pyridine ylide") intermediates.[17]

Tidwell et al.[18] have shown that the stabilization energy of cyanoketene is similar to that of alkylketenes (e.g. methylketene), but the cyano group is less stabilizing as a π acceptor than is formyl (by about 4 kcal mol^{-1}). Our calculations (Table 4) demonstrate that, as expected, the cyano group lowers both the HOMO and the LUMO energies of ketene, in particularly the latter, making the ketene more electrophilic. The cyano group is more effective than the formyl group in this respect, and the two cyano groups in dicyanoketene have a very pronounced effect. A methyl group increases the HOMO energy and lowers the LUMO by a much smaller amount than do the formyl or cyano groups. The in-plane LUMO plays an important role in governing the reactivity of ketenes, in particular cycloaddition reactions[19] and, as shown above, 1,3-X shifts.[9] Hence, the high reactivity of cyanoketenes[2c] may be attributed to the availability of a low-lying ketene LUMO.

Table 4. Calculated HOMO and LUMO Energies (eV) of Some Ketenes (HF/6-311+G)**

species	HOMO	LUMO
ketene	−10.07	1.80
methylketene	−9.50	1.66
formylketene	−10.72	1.44
cyanoketene **8**	−10.67	1.20
dicyanoketene	−11.24	0.71

Conclusion

Cyanoketene (**8**) is formed efficiently by flash vacuum thermolysis of Meldrum's acid derivatives **3**. The amine derivatives **3f**,**g**,**i**,**j** give cyanoketene particularly cleanly, without any other intermediates being detectable in significant quantites. The methylthio derivatives **3e**,**h** fragment by two routes: (i) elimination of acetone and CO_2 starting at *ca.* 300 °C leads to imidoylketenes **4** which undergo a facile 1,3-shift of the methylthio group to give oxoketenimines **5**, detected by both matrix IR and mass spectrometry. At higher temperatures, retro-ene type alkene elimination from **5** gives cyanoacetic acid derivatives **9**, which eliminate methanethiol to produce cyanoketene (**8**). (ii) The major route is HX elimination from the starting material **3**, which creates a transient Meldrum's acid-ketenimine **6**, detectable by mass spectrometry. Facile elimination of CO_2 and acetone from **6** furnishes the iminopropadienones **7**, detectable by MS and IR (giving strong absorptions in the 2200 cm^{-1} region). However, above 300 °C, the iminopropadienones undergo a facile retro-ene type alkene elimination to give cyanoketene (**8**). Thus, in all cases, cyanoketene becomes the exclusive ultimate product.

The 1,3-shifts of methylthio (and amino) groups converting imidoylketenes **4**(**12**) to oxoketenimines **5**(**13**) compete efficiently with 1,5-H shifts to give enaminoacroleins **14** (Scheme 2).

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The cyanoacetic acid derivatives **9** (X = OMe, SMe, NMe_2, and 3,5-dimethylpyrazol-1-yl) can also be used as cyanoketene precursors, cleanly on FVT at 600−800 °C. Since the Meldrum's acid derivatives **3** generally produce cyanoketene at lower temperatures than do the acetic acid derivatives **9**, the route via (alkylimino)propadienones **7** is the major one in all cases. This is in agreement with the fact that mehyl- (**7b**), phenyl- (**7a**), and other (arylimino)propadienones (**7**)[10] can be isolated from FVT of the corresponding Meldrum's acid derivatives **3**.

The IR spectrum of cyanoketene is well reproduced by DFT and ab initio calculations, and the high reactivity of cyanoketene is attributed to the availability of a very low energy LUMO.

Experimental Section

Computational Methods. Ab initio[20] and density functional[21] calculations were carried out using the GAUSSIAN 92/DFT series of programs.[22] The equilibrium structure, charge distribution, dipole moment, ionization potential and thermochemistry (not reported here), and the vibrational spectrum of cyanoketene were examined with the Hartree−Fock (HF), MP2,[20] QCISD,[23] and B3−LYP[24] methods using the 6-31G* and 6-311+G** basis sets.[20]

Materials. 3e−h and **3j** were prepared as previously reported.[8a]

5-[(*tert*-Butylamino)(dimethylamino)methylene]-2-dimethyl-1,3-dioxane-4,6-dione (3i). To 5-[bis(methylthio)-methylene]-2,2-dimethyl-1,3-dioxane-4,6-dione[8a,25] (2.48 g; 10 mmol) in 30 mL of THF was added *tert*-butylamine (0.73 g; 10 mmol), and the mixture was allowed to stir overnight. To the stirring solution was added dimethylamine solution (4 g; 10 mmol, as a 10% w/v solution in ethanol), mercuric oxide (2.16 g; 10 mmol), and mercuric chloride (2.71 g; 10 mmol), the mixture was stirred for a further 2 days and filtered, and the filtrate was evaporated. The resulting solid was recrystallized from THF to yield colorless crystals (0.41 g, 15%), mp 174−176 °C; 1H NMR ($CDCl_3$) δ 1.43 (s, 9 H), 1.72 (s, 6 H), 3.16 (s, 6 H), 6.36 (s 1 H); ^{13}C NMR ($CDCl_3$) δ 26.9, 30.2, 40.5, 56.7, 71.8, 163.5, 165.0; IR ($CHCl_3$) δ 1653, 1635 cm^{-1}; MS *m/z* 270.1580 (M^+, 18%), 213 (11), 212 (11), 167 (60), 153 (11), 112 (100). Anal. Calcd for $C_{13}H_{21}N_2O_4$: C, 57.75; H, 8.21; N, 10.37. Found: C, 57.97; H, 8.41; N, 10.38.

***N*-(Cyanoacetyl)-3,5-dimethylpyrazole (9m).** To a stirred suspension of 3,5-dimethylpyrazole (1.94 g, 20 mmol) and dicyclohexylcarbodiimide (4.17 g, 20 mmol) was added cyanoacetic acid (1.38 g, 20 mmol) at 0 °C. The mixture was then stirred at room temperature overnight. The resulting suspension was filtered and the solid washed several times with dry acetone. Evaporation of the filtrate gave an orange gum, which was distilled (40 °C, 3.5×10^{-4} mbar) to give an orange oil, 34 mg (69%); 1H NMR ($CDCl_3$) δ 2.25 (s, 3 H), 2.60 (s, 3 H), 4.91 (s, 2 H), 6.05 (s, 1 H); IR (CHCl3) ν 1735, 1654, 1602 cm^{-1}. Anal. Calcd for $C_8H_9N_3O$: C, 59.25; H, 4.97; N, 25.91. Found: C, 59.24; H, 5.05; N, 25.82.

Apparatus and Procedure for FVT/Matrix Isolation and Mass Spectromety. The apparatus for FVT/matrix isolation[26] was as previously reported. Samples were deposited with Ar on BaF_2 disks at 14 K for FTIR spectroscopy. The preparative FVT apparatus[26] employed a 25 × 1.8 (i.d.) cm quartz tube in an electrically heated oven. The system was continuously pumped at better than 10^{-4} mbar. The six-sector mass spectrometer (*EBEEBE* configuration) and the FVT/MS unit have been described elsewhere.[28] Collisional activation (CA) mass spectra were obtained using oxygen (80% transmittance). The resulting spectra are referred to as $CA(O_2)$ spectra.

Matrix IR and mass spectra of known compounds were recorded for comparison with FVT products. Acetone[29] was monitored by Ar matrix IR spectroscopy at 3018, 1721, 1361, 1217, 1092 cm^{-1}; CO_2 at 2344, 2340 cm^{-1}; CO at 2141 cm^{-1}; MeSH[30] at 2941, 2547, 1446, 1436, 1327, 1072, 962 cm^{-1}; propene[31] at 3091, 2983, 1453, 998 cm^{-1}; 2-methylpropene[31] at 2984, 2942, 1463, 1444 cm^{-1}; MeOH[29] at 3666, 3005, 2848, 1474, 1466, 1333, 1076, 1034 cm^{-1}; dimethylamine at 3193, 2973, 2832, 1482, 1479, 1159, 1148, 1025, 861 cm^{-1}; isopropylamine at 1383, 1346, and 794 cm^{-1}; *tert*-butylamine at 1388, 1249, 1219, and 889 cm^{-1}; 3,5-dimethylpyrazole at 3500, 2997, 2926, 1812, 1582, 1419, 1354, 1273, 996, 780 cm^{-1}; and *N,N*-dimethylcyanoacetamide at 3023, 2943, 2261, 1697, 1672, 1506, 1458, 1401, 1260, 1139, 1065, 980, 936 cm^{-1}.

Cyanoketene (8). (a) From Meldrum's Acid Precursors 3e−j. A sample of the precursor (*ca.* 10 mg) was sublimed at 80 °C in the FVT apparatus using the desired oven temperature. The FVT product was matrix isolated with Ar at 10^{-4} mbar over a 20 min period and examined by FTIR spectroscopy. Cyanoketene was observed at 2239 (w), 2163 (s) cm^{-1}, as discussed in the text and shown in Figures 1 and 2b.

(b) From *N,N*-Dimethylcyanoacetamide (9f). A 10 mg sample was sublimed at 40 °C and FVT/matrix isolation was carried out as above. Cyanoketene was observed at 2239 (w), 2163 (s) cm^{-1}, commencing at an FVT temperature of 400 °C; the reaction was complete at 700 °C.

(c) From Methyl Cyanoacetate (9k). Methyl cyanoacetate (20 mg) was cooled in an ice/salt bath, evacuated, and subjected to FVT by allowing the sample to warm to room temperature over a 20 min period. Ar matrix isolated cyanoketene was observed at 2239 (w), 2163 (s) cm^{-1}, commencing at 550 °C. The conversion was complete at 850 °C.

(d) From 1-(Cyanoacetyl)-3,5-dimethylpyrazole (9m). The precursor (10 mg) was sublimed at ca 50 °C and FVT/matrix isolation was performed as above. Cyanoketene was observed together with dimethylpyrazole starting at *ca.* 450 °C. The conversion was complete at 800 °C (Figure 2a).

Preparative FVT of 5-[(Isopropylamino)(methylthio)-methylene]-2,2-dimethyl-1,3-dioxane-4,6-dione (3e). A sample (440 mg, 1.9 mmol) was gently sublimed at ca. 80 °C and subjected to FVT at 600 °C/1.5×10^{-3} mbar in the course of 3 h, using a dry ice/acetone (−78 °C) cooled U-tube as a cold trap. Upon completion of the thermolysis, methanol (2 mL) was injected onto the pyrolysate. The apparatus was flushed with nitrogen and the U-tube allowed to warm to room temperature. The methanol solution was collected and the solvent removed by rotary evaporation. The resulting yellow oil was filtered through a plug of silica gel (*ca.* 1 cm^3) and purified by column chromatography (silica gel; ether/hexane). The following products were isolated:

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Methyl 3-Methoxy-3-(isopropylamino)prop-2-enethiolate (11). $R_f = 0.80$, 186 mg (58%), yellow oil; ^{1}H NMR ($CDCl_3$) δ 1.73 (d, 6 H), 2.26 (s, 3 H), 3.57 (s, 3 H), 3.76 (sept, 1 H), 4.33 (s, 1 H), 8.76 (br s, 1 H); ^{13}C NMR ($CDCl_3$) δ 14.2; 23.4; 45.5; 50.0; 76.1; 165.2; 169.6; IR ($CHCl_3$) ν 2957, 1693, 1439, 1399, 1273, 1012 cm^{-1}; MS *m*/*z* 189 (M^+, 67%), 174 (54), 158 (36), 142 (44), 100 (100), 84 (54), 68 (35); HRMS: calcd for $C_8H_{15}NO_2S$ *m*/*z* 189.0822; found 189.0822. Anal. Calcd for $C_8H_{15}NO_2S$; C, 50.77; H, 7.99; N, 7.40. Found: C, 50.62; H, 8.06; N, 7.57.

Methyl 3-(Isopropylamino)-3-(methylthio)prop-2-enoate (10). $R_f = 0.60$, 61 mg (19%), yellow oil; ^{1}H NMR ($CDCl_3$) δ 1.39 (d, 6 H), 2.23 (s, 3 H), 3.39 (s, 3 H), 3.65 (s, 1 H), 8.75 (br s, 1 H); IR ($CHCl_3$) ν 2960 (CH), 1694 (CO), 1444, 1340, 1001 cm^{-1}; MS *m*/*z* 189 (M^+, 32%), 174 (16), 158 (100), 142 (65), 124 (64), 82 (51), 68 (91); HRMS: calcd for $C_8H_{15}NO_2S$ *m*/*z* 189.0822; found 189.0822. Anal. Calcd for $C_8H_{15}NO_2S$: C, 50.77; H, 7.99; N, 7.40. Found: C, 50.71; H, 7.86; N, 7.36.

Preparative FVT of 5-[(*tert*-Butylamino)(methylthio)-methylene]-2,2-dimethyl-1,3-dioxane-4,6-dione (3h). A sample (120 mg, 0.48 mmol) was sublimed at *ca.* 80 °C through the FVT tube at 600 °C/1.5 × 10^{-3} mbar in the course of 2 h. The products were collected in a liquid nitrogen (−196 °C) cooled U-tube which had been previously coated with methanol (2 mL). Upon completion of the pyrolysis, additional methanol (2 mL) was injected onto the pyrolysate. The apparatus was flushed with nitrogen and the U-tube allowed to warm to room temperature. The methanol solution was collected and the solvent removed in vacuo. The resulting yellow oil was filtered through a plug of silica gel (*ca.* 1 cm^3), purified by column chromatography (silica gel; ethyl acetate/hexane), and shown to be identical with the previously described *N*,*N*-dimethylcyanoacetamide,[8a] 34 mg (69%).

Acknowledgment. The Brisbane laboratory thanks the Australian Research Council for financial support and for a Fellowship for M.W.W. The Mons laboratory thanks the Fonds National de la Recherche Scientifique for its contribution toward the acquisition of the VG (Micromass) Autospec 6F tandem mass spectrometer.

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