Aryliminopropadienone−*C*-Amidoketenimine−Amidinoketene−2-Aminoquinolone Cascades and the Ynamine−Isocyanate Reaction

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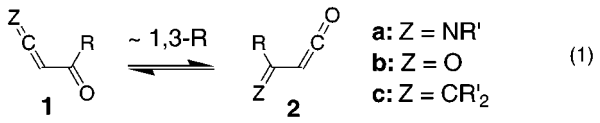
Received December 18, 1998

Imidoylketenes **11** and oxoketenimines **12** are generated by flash vacuum thermolysis of Meldrum's acid derivatives **9**, pyrrolediones **17** and **18**, and triazole **19** and are observed by IR spectroscopy. Ketenimine-3-carboxylic acid esters **12a** are isolable at room temperature. Ketenes **11** and ketenimines **12** undergo rapid interconversion in the gas phase, and the ketenes cyclize to 4-quinolones **13**. When using an amine leaving group in Meldrum's acid derivatives **9c**, the major reaction products are aryliminopropadienones, ArN=C=C=C=O (**15**). The latter react with 1 equiv of nucleophile to produce ketenimines **12** and with 2 equiv to afford malonic acid imide derivatives **16**. *N*-Arylketenimine-*C*-carboxamides **12c** cyclize to quinolones **13c** via the transient amidinoketenes **11c** at temperatures of 25−40 °C. This implies rapid interconversion of ketenes and ketenimines by a 1,3-shift of the dimethylamino group, even at room temperature. This interconversion explains previously poorly understood outcomes of the ynamine−isocyanate reaction. The solvent dependence of the tautomerism of 4-quinolones/4-quinolinols is discussed. Rotational barriers of NMe_2 groups in amidoketenimines **12c** and malonioc amides and amidines **16** (**24**) are reported.

Introduction

It was demonstrated in earlier work that oxoketenimines (**1a**) and imidoylketenes (**2a**) undergo facile thermal 1,3-shifts of electron donating substituents (R).[1−4] Analogous rearrangements of oxoketenes (**1b**)[5,6]



(1)

and vinylketenes (**1c**)[7] are also known. The 1,3-shifts take place in the *s-trans* isomers shown, but the *s-cis* rotamers are usually of lower energy.[6,7b,8] According to recent ab initio calculations on the oxoketenes **1b**,[6,8] the migratory aptitudes of the groups R follow the order NMe_2 > SMe > SH > Cl > NH_2 > OMe > OH > F > H > Ph ≫ Me (G2(MP2,SVP) calculations). The activation barrier for the 1,3-Cl shift in the oxoketenes **1b** and **2b** (R = Cl) was determined by dynamic ^{13}C NMR spectroscopy in solution as 10 kcal mol^{-1}, and this reaction is rapid at −30 °C.[6] The calculated barrier for the corresponding 1,3-NMe_2 shift in **1b**/**2b** is ca. 6−8 kcal mol^{-1}. Higher barriers for analogous shifts are expected in imidoylketenes, and thus a value of ca. 25 kcal mol^{-1} is found for **1a**/**2a**. These are among the lowest computed activation barriers for these types of reaction. Therefore, it is very desirable to examine systems **1**/**2** with R = NMe_2 experimentally. For **1c**/**2c** (R = NMe_2), see reference 7. The amidoketenes (**1b**, R = NMe_2) are not stable at room temperature; in fact, no example of the characterization of an amidoketene has been reported. Amidoketenimines (**1a**, R = NMe_2) are observable molecules but until now were only generated in a few cases, by flash vacuum thermolysis (FVT) of 4-carboxamidotriazoles **3**.[9]

There are three ways that oxoketenimines/imidoylketenes **1a**/**2a** can be generated in FVT reactions: from triazoles **3**,[1,4e,9] pyrrolediones **4**,[2,3,4a,4b] and Meldrum's acid derivatives (5-methylene-1,3-dioxane-4,6-diones)[1,3,4c] **5**. The *N*-arylimidoylketenes **2a** cyclize very easily to quinolones **7**.[1,3,9] In the case of the Meldrum's acid precursors **5**, a competing fragmentation can lead to the new cumulenes, iminopropadienones, **6**.[10,11] The ease of this process increases on changing the leaving group from MeO or MeS to NMe_2 in the Meldrum's acid derivative

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(8) For calculations on the 1,3-shifts in α-oxoketenes, see also: (a) Wong, M. W.; Wentrup, C. *J. Org. Chem.* **1994**, *59*, 5279. (b) Koch, R.; Wong, M. W.; Wentrup, C. *J. Org. Chem.* **1996**, *61*, 6809.
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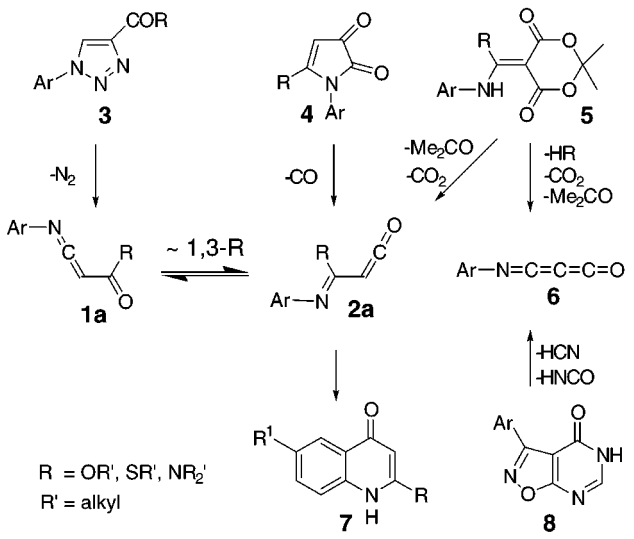
10.1021/jo982471y CCC: $18.00 © 1999 American Chemical Society
Published on Web 04/29/1999



5, so much so that in the latter case, iminopropadienone formation becomes almost the only reaction. Another type of precursor, the isoxazolopyrimidinone **8**, leads directly to **6** on FVT.[10,11] The iminopropadienones **6** can be isolated in good yields at 77 K, using either **5** or **8** as precursor. Aryliminopropadienones usually undergo chemical reactions at temperatures of −100 to −50 °C; only in special cases are they isolable at room temperature.[12]

Here, we report full details of the synthesis of aryliminopropadienones **6** (**15**), as well as their conversion to amidoketenimines **1a** (**12**) in solution at low temperature. This is followed by facile rearrangement to 2-amino-4-quinolones[13] at or near room temperature, thereby indicating a rapid equilibration of amidoketenimines **1a** (**12**) with amidinoketenes **2a** (**11**). The results have implications also for the mechanism of the reaction between ynamines and isocyanates.

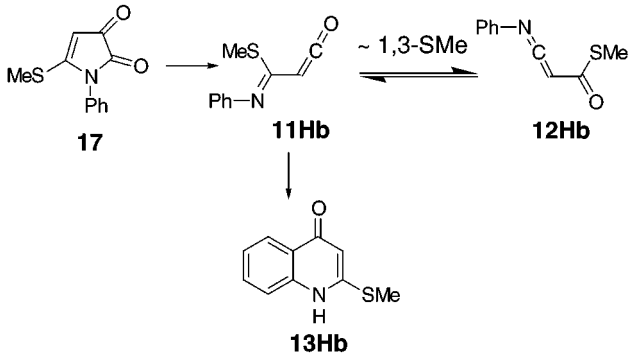
Results and Discussion

1. FVT Experiments. We will describe the differently substituted starting materials and products in Scheme 1 as the **H** series (R^1 = H), the **M** series (R^1 = Me), and the **X** series (R^1 = methoxy). To investigate the primary reaction products from the FVT of the Meldrum's acid precursors **9**, the products were isolated either neat at 77 K or in Ar matrix at 14 K for IR spectroscopy.

In the **9H** series, the familiar ketene and ketenimine **11Ha** and **12Ha** were formed (2135 and 2050 cm^{-1}, respectively, at 77 K) starting at ca. 200 °C, and both of these intermediates were replaced by PhNCCCO (**15H**) above 500 °C.[1] Compound **15H** can be trapped with added MeOH on the coldfinger to yield **16Ha** in 30−67% yield.[1] The ketenimine **12Ha** has been isolated and characterized,[1,2] and FVT of this compound did *not* produce **15H**.

Using the SMe leaving group in the **9Hb** series, weak signals due to a ketene and a ketenimine, assigned to **11Hb** and **12Hb**, were observed on FVT at 260 °C (Figure 1a). The ketenimine peak increased in intensity at 300−400 °C, but already at 400 °C phenyliminopropadienone **15H** (2222, 2140 cm^{-1}) started to form. This was virtually the only observable product at 600 °C, apart from CO_2, acetone, MeSH, and quinolone **13Hb**, all of which were identified by comparison with authentic materials. A representative series of spectra of the ketene region is shown in Figure 1. An Ar matrix IR spectrum of **15H** was identical with that published previously.[11b] Quinolone **13Hb** was obtained in 70% yield by preparative FVT of **9Hb**. It has been obtained previously as the product of thermolysis of **9Hb** in diphenyl ether at 240 °C.[14] Generally, the MeS derivatives of **9** give very good yields of quinolones but poor yields of ArNCCCO (**15**); route a in Scheme 1 dominates.

The same ketene and ketenimine **11Hb** and **12Hb** were also obtained on FVT of the pyrroledione **17** and observed by IR spectroscopy.[3] Importantly, there was no



corresponding formation of iminopropadienone **15H** in this case, either at 400 °C or at higher temperatures. Above 600 °C, there was simply disappearance of both **11Hb** and **12Hb** and virtually quantitative formation of quinolone **13Hb** instead (90%). *Therefore, **11** and **12** cannot be the source of iminopropadienones **15*** from Meldrum's acid derivatives **9**. Instead, **15** must be formed via initial elimination of HX to yield a transient ketenimine **14**, which undergoes a cycloreversion to **15**, CO_2, and acetone (route b, Scheme 1). The transients **14** are often formed in quantities too small for reliable identification by IR spectroscopy, but they have been detected unambiguously by on-line mass spectrometry (a thermally produced *m*/*z* 245 at 350 °C in the case of **14H**).[10,15]

Thus, Meldrum's acid derivatives **9Ha,b** yield iminopropadienone **15H** and quinolones **13Ha,b** as the ultimate products, formed via two different pathways, routes a and b in Scheme 1. The pyrroledione **17** gives *only* quinolone **13Hb** because of the dynamic equilibrium between ketene and ketenimine (**11Hb/12Hb**), with all of the ketene cyclizing to the quinolone. Similarly, 5-methoxypyrroledione (**4**, R = OMe) affords **13Ha**.[2]

Quite a different situation occurs when a dimethylamino group is used as the leaving group in the Meldrum's acid precursor **9Hc**. At first sight, there is little or no quinolone formation, but as we shall see, this depends on how the experiment is carried out. Only minor amounts of ketene and ketenimine **11Hc** and **12Hc** are formed in this case, and therefore also only

(12) Moloney, D. W. J. Ph.D. Thesis, The University of Queensland, 1997. Moloney, D. W. J.; Wentrup, C. To be submitted for publication.

(13) The term 4-quinolone as used in this paper includes the 4-hydroxyquinoline tautomers. Only one tautomer is observed by NMR in each case, but different tautomers predominate in different solvents. This subject is expounded in Section 5. For early literature, see: Elguero, J.; Marzin, C.; Katritzky, A. R.; Linda, P. *The Tautomerism of Heterocycles*; Academic: New York, 1976; p 87 and references therein.

(14) Ye, F.-C.; Chen, B.-C.; Huang, X. *Synthesis* **1989**, 317.

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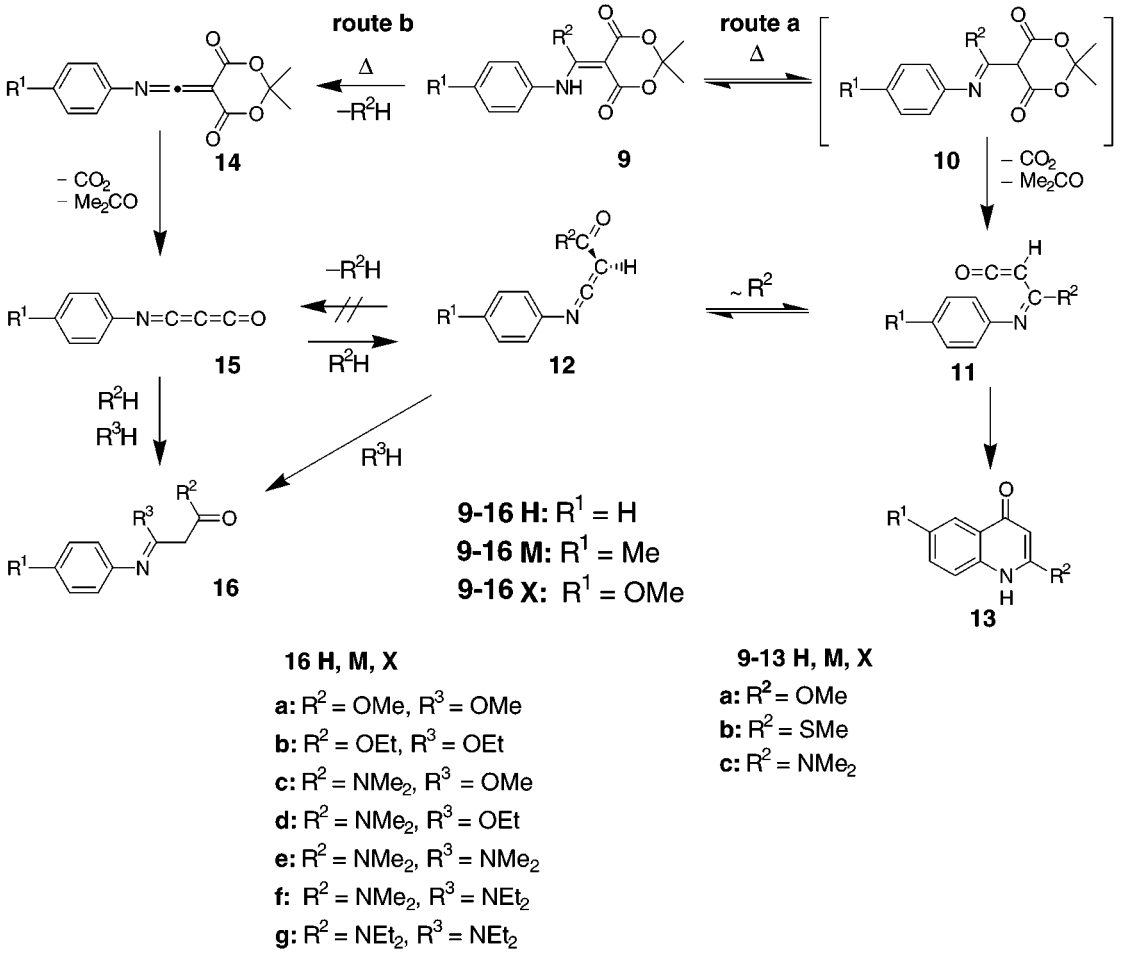
Scheme 1



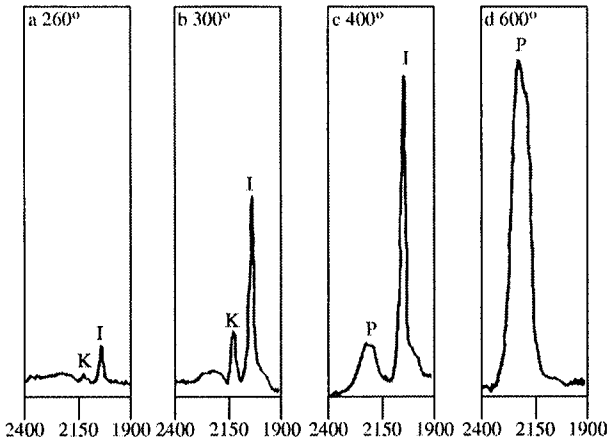


Figure 1. Partial FTIR spectra (1900−2400 cm^{-1} range) of the products (77 K) of FVT of **9Hb** at 260−600 °C (a−d). K = ketene **11Hb** (2121, 2106 (sh) cm^{-1}). I = ketenimine **12Hb** (2040 cm^{-1}). P = phenyliminopropadienone **15H** (2222 (vs), 2140 (sh) cm^{-1}).

little 2-dimethylaminoquinolone **13Hc** is produced. Instead, there is immediate formation of phenyliminopropadienone **15H**, dimethylamine, CO_2, and acetone, as observed in the IR spectra at 77 K and at 14 K. The ketenimine **12Hc** was observable only at FVT temperatures of 310−360 °C (2035−2051 vw cm^{-1} in Ar matrix, 15 K; 2033/2042 vw cm^{-1} neat, 77 K). The position and shape of this complex peak was the same as observed previously for the ketenimine formed from the triazole **3** (R = NMe_2, Ar = Ph).[9] A very weak absorption at 2137 cm^{-1} may be due to formation of a trace of the ketene **11Hc**. As we have concluded before,[9] this ketene was not identifiable with any degree of certainty from the triazole route as a result of the facts that the ketenimine is the primary product in that case, a high temperature (500 °C) was required, and the cyclization to quinolone **13Hc** is very facile. In the case of the Meldrum's acid aminal **9Hc**, a strong signal due to PhNCCCO (**15H**) appeared already at 360 °C, and the putative ketene and ketenimine signals disappeared completely above 360 °C (Ar matrix) or at 500 °C (neat isolation at 77 K). The conversion of the starting material (**9Hc**) is only complete at ca. 600 °C. On preparative FVT of **9Hc** at 600 °C, PhNCCCO (**15H**) is isolated on a 77 K coldfinger, where it can be trapped with alcohols to give malonic ester imides **16c,d**, with added dimethylamine to give **16e**, and with added diethylamine to give **16f** and **16g** in total yields up to 84%. This trapping reaction is described more fully in Section 2. The quinolone **13Hc** is very involatile and also very insoluble in solvents other than DMSO or DMF, and therefore this compound is never present on the coldfinger or in the solutions of this material for NMR spectroscopy. However, **13Hc** deposited in yields of 15−20% in the air-cooled part of the apparatus before the coldfinger, immediately outside the oven in the 600 °C preparative FVT experiment. This compound must be formed by cyclization of ketene **11Hc** in the gas phase and therefore represents the fraction of the reaction taking place via path a (Scheme 1). Therefore, the reason

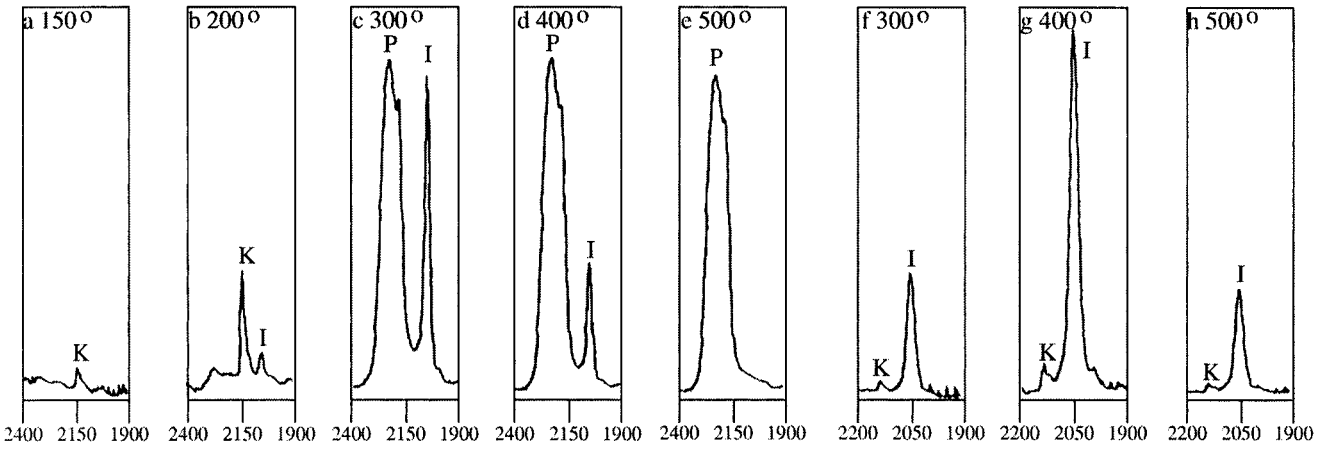


Figure 2. Partial FTIR spectra (1900−2400 cm^{-1} range) of the products (77 K) of FVT of **9Ma** at 150−500 °C (a−e) and of triazole **19** at 300−500 °C (f−h). K = ketene **11Ma** (2136, 2119 (sh) cm^{-1}). I = ketenimine **12Ma** (2046 cm^{-1}). P = 4-methylphenyliminopropadienone **15M** (2221, 2182 (sh) cm^{-1}).

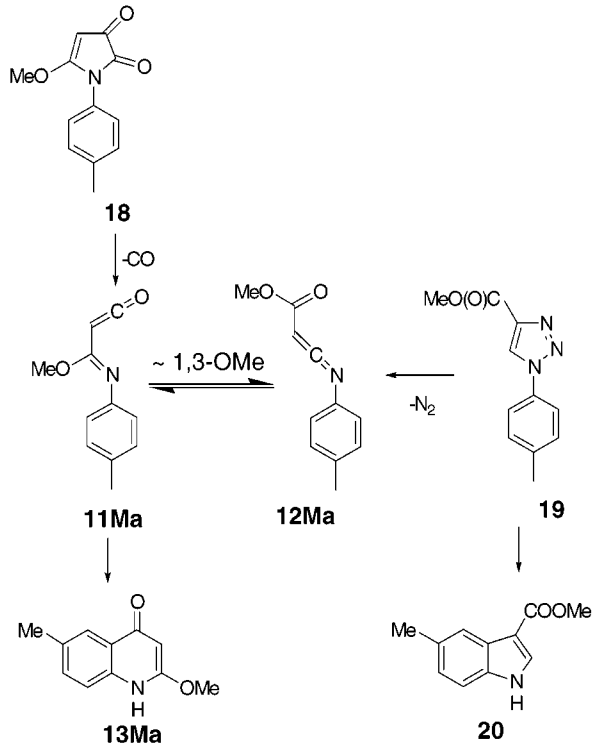
that the intermediates **11c**/**12c** cannot be observed above ca. 360 °C (where very little reaction has taken place) is not that they are not formed but that **11c** cyclizes very easily to **13c**.

The methyl (**M**) series, using the *p*-tolylaminomethylene−Meldrum's acid precursors **9M**, gave results analogous to those reported for the **H** series above. The ketene **11Ma** was already detectable at a FVT temperature as low as 150 °C (Figure 2a), and the ketenimine **12Ma** appeared from at least 200 °C (Figure 2b)). The signal for iminopropadienone, 4-MePhNCCCO (**15M**) became strong already at 300 °C, and this was the only cumulene signal remaining at 500 °C (Figure 2c−e). Preparative FVT of **9Ma** at 500 °C with subsequent trapping of **15M** with MeOH on the coldfinger gave a 38% yield of malonic ester imide **16Ma** and a 55% yield of quinolone **13Ma**. The ketenimine **12Ma** was isolable in 34% yield from FVT at 300 °C. FVT of the isolated and distilled ketenimine **12Ma** at 400 °C gave a small amount of ketene **11Ma**, together with mostly unchanged **12Ma**, as observed by IR spectroscopy, and a little quinolone **13Ma**. Importantly, the FVT of **12Ma** did *not* give any iminopopadienone, **15M**.

The same ketene and ketenimine, **11Ma** and **12Ma**, *but not the iminopropadienone 4-MePhNCCCO (**15M**)*, were also obtained on FVT of the pyrroledione **18** and the triazole **19** (Figure 2f−h), whereby the latter also gave some indole **20** (9−17%). The formation of indoles has been described elsewhere.[1] Compounds **11Ma** and **12Ma** had the same spectral characteristics as described above. The ketenimine **12Ma** was isolable in 24% yield from the triazole and in 32% yield from the pyrroledione (using FVT at 500 °C). Quinolone **13Ma** was isolated in 74% yield from the triazole and in up to 84% yield from the pyrroledione (using FVT at 600 °C).

The methylthio-substituted Meldrum's acid precursor **9Mb** was investigated cursorily. The ketenimine **12Mb** was observed at 2048 cm^{-1} (Ar, 12 K), and 4-MePhNCCCO (**15M**) had an IR spectrum identical to that described above.

The dimethylamino analogue **9Mc** afforded strong IR signals due to 4-MePhNCCCO (**15M**) already at a FVT temperature of 300 °C. An Ar matrix IR spectrum is shown in the Supporting Information. A ketenimine was hardly detectable in this case (a very weak and diffuse peak was present at 2050 cm^{-1} (neat) in the 300 °C



experiment). As we shall see in Section 3, the ketenimine **12Mc** can be synthesized from **15M** by addition of dimethylamine.

In the methoxy (**X**) series, the elimination of CO_2 and acetone from **9Xa** started at ca. 300 °C, and both a ketenimine **12Xa** (2047 neat, 2050 Ar cm^{-1}) and a ketene (2138 (vw) neat, 2142 (vw) Ar cm^{-1}), presumably **11Xa**, were observable at 77 K. At 400 °C, a much stronger signal due to the ketenimine **12Xa**, together with a very weak signal due to the ketene, and new bands in the 2200 cm^{-1} region were observed (Figure 3a). The latter are ascribed to 4-MeOPhNCCCO (**15X**), and these became very strong at 500 °C and higher temperatures (Figure 3b,c). In an Ar matrix, this signal appeared as a characteristic, complex band with maxima at 2252 (s), 2246 (vs), 2239 (s), 2235 (s), and 2137 (w) cm^{-1} (spectrum shown in the Supporting Information). Bands due to CO_2 and acetone were also recorded. The ketene **11** and ketenimine **12** were absent above 600 °C as a result of

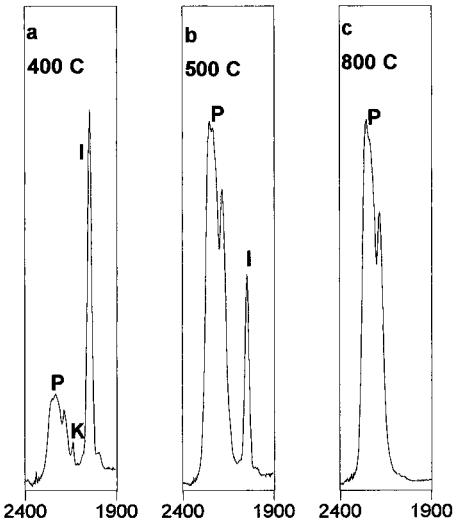


Figure 3. Partial FTIR spectra (1900−2400 cm^{-1} range) of the products (77 K) of FVT of **9Xa** at 400−800 °C (a−c). K = ketene **11Xa** (2138 cm^{-1}). I = ketenimine **12Xa** (2047 cm^{-1}). P = 4-methoxyphenyliminopropadienone **15X** (2257, 2237 (sh), 2184 cm^{-1}).

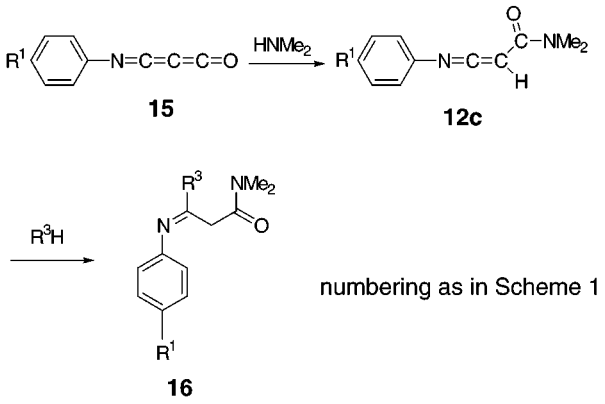
the formation of the involatile quinolone **13Xa**, which was isolated in 34% yield from a preparative FVT experiment and in 24% yield from refluxing diphenyl ether (vide infra). Trapping of **15X** with methanol on the coldfinger afforded the malonic ester imide **16Xa** in 47% yield.

An analogous FVT experiment with **9Xb** (500 °C/14 K Ar) produced the same IR spectrum of 4-MeOPhNCCCO (**15X**) as reported above.

Similar FVT of **9Xc** was studied between 300 and 800 °C. At 300 °C, the IR spectrum showed extremely weak bands at 2039, 2049, and 2127 cm^{-1} possibly due to **12Xc** and/or **14X** and **11Xc**, but already at this temperature, weak bands ascribed to 4-MeOPhNCCCO (**15X**) were present. At FVT temperatures of 400 °C and above, this was the only cumulene observed, the other ketenimine absorptions having completely disappeared. The IR spectrum of **15X** in an Ar matrix displayed the characteristic multiplet structure described above. Trapping of **15X** with added dimethylamine on the coldfinger afforded the malonic amidoamidine derivative **16Xe** in 67% yield. Because of its involatility, no quinolone was present on the coldfinger, but a ca. 20% yield of quinolone **13Xc** condensed in the air-cooled part of the apparatus immediately after the exit of the pyrolysis oven. Thus, the 67% yield of **16Xe** represents the yield of 4-MeOPhNCCCO (**15X**) arriving on the coldfinger, and the 20% yield of quinolone **13Xc** represents the cyclization of ketene **11Xc** in the gas phase.

Thus, in general, *with $HNMe_2$ as the leaving group, route b in Scheme 1 dominates the reaction*. The iminopropadienones ArNCCCO (**15**) are obtained essentially pure on the liquid N_2 cooled coldfinger. This is found in the **H**, **M**, and **X** series.

2. Formation of Ketenimines and Malonic Acid Derivatives. When the Meldrum's acid derivatives **9c** having amine leaving groups are used in FVT experiments, we know from direct IR spectroscopic observation at either 77 K or in Ar matrixes that the products arriving on the cold targets are iminopropadienones, ArNCCCO (**15**), together with $HNMe_2$. Subsequent warmup caused formation of ketenimines **12c** ($R^2 = NMe_2$).



For example, when **15X**, generated by FVT of **9Xc** at 600 °C, was slowly warmed from −196 °C, reaction with the cocondensed dimethylamine took place at ca. −70 °C with irreversible formation of ketenimine **12Xc**, which persisted on further warmup till 0 °C (Figure 4). This ketenimine was also observed by IR and NMR spectroscopy in solution by injecting CD_2Cl_2 on the 77 K coldfinger containing **15X** and allowing the material to thaw and flow into a precooled NMR tube at −80 to −70 °C. The ^1H NMR spectrum at −70 °C displayed characteristic signals due to ketenimine **12Xc** at δ 2.93, 2.98, 3.75, and 5.05 ppm, corresponding to the two NMe signals due to slow rotation of the NMe_2 group, the OMe group, and the C=CH function, respectively.[16] On slow warming of this solution to room temperature, coalescence of the two methyl signals of the NMe_2 group took place at −10 °C, from which the free energy of activation for rotation about the amide C−N bond is calculated[17] as $\Delta G^{\ddagger} = 13.6$ kcal/mol.

The IR spectrum of the cold CD_2Cl_2 solution revealed a strong band at 2036 cm^{-1} (also present in CH_2Cl_2 solution), ascribed to ketenimine **12Xc** and persisting till room temperature.

Similar reactions of iminopropadienones **15H** and **15M** afforded ketenimines **12Hc** and **12Mc**. According to IR spectroscopy, **12Mc** started forming at −90 °C (2030 cm^{-1}, neat). FVT of **9Hc** at 500 °C gave a very strong band due to PhNCCCO (**15H**, 2222 cm^{-1}), together with a very weak one due to ketenimine **12Hc** (2042, 2033 cm^{-1}, neat, 77 K). On warming this mixture to −100 °C, the band due to PhNCCCO started to decrease, and that due to ketenimine **12Hc** increased strongly as a result of reaction with dimethylamine.

The ^1H and ^{13}C NMR spectra of **12Hc** are reported in the Experimental Section and shown in the Supporting Information. From the coalescence of the methyl signals of the dimethylamino group in **12Hc** at −10 °C, $\Delta G^{\ddagger} = 13.0$ kcal/mol was calculated. Dimethylamides normally have rotational barriers of ca. 16−20 kcal mol^{-1} as a result of the partial double bond character of the C−N bond in the zwitterionic resonance structure.[17,18] The low value for the keteniminecarboxamide **12Hc** and the mesityl analogue **23** described below can be attributed

(16) NMR data for ketenimines: see ref 1, and the Supporting Information to ref 1 and to this paper, and (a) Firl, J.; Runge, W.; Hartmann, W.; Utikal, H.-P. *Chem. Lett.* **1975**, 51. (b) Eberl, K.; Roberts, J. D. *Org. Magn. Reson.* **1981**, *17*, 180.

(17) Free energy of activation calculations according to, e.g., Bovey, F. A. *Nuclear Magnetic Resonance Spectroscopy*; Academic Press: San Diego, 1988. The estimated error is 1 kcal/mol.

(18) Kessler, H. *Angew. Chem., Int. Ed. Engl.* **1970**, *9*, 219.

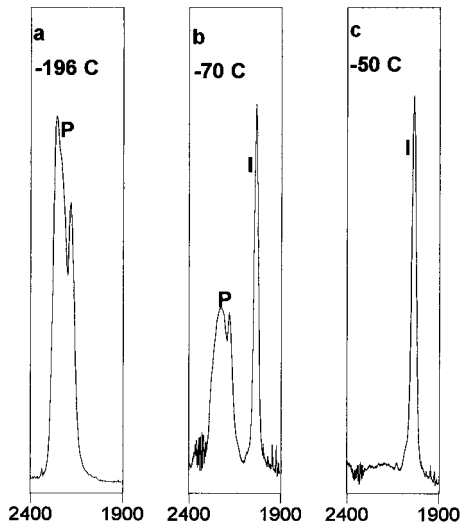
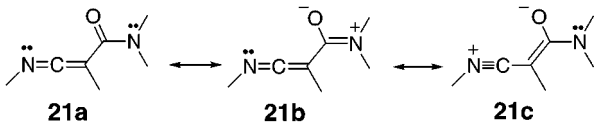


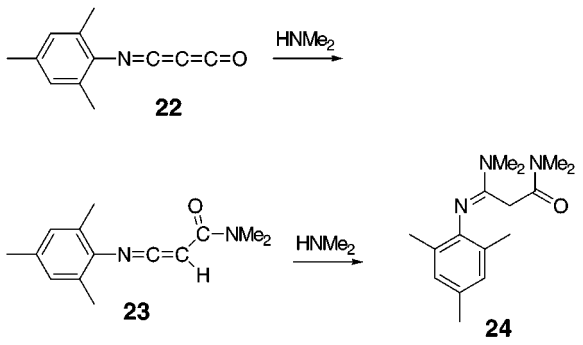
Figure 4. Partial FTIR spectra (1900−2400 cm^{-1} range) of the products of FVT of **9Xc** at 600 °C, recorded at −196 °C (a) and after warmup to −70 °C (b) and −50 °C (c). I = ketenimine **12Xc** (2034 cm^{-1}). P = 4-methoxyphenyliminopropadienone **15X** (2257 cm^{-1}).

to a contribution from the resonance structure **21c**,[19]



which reduces the C−N double bond character expressed in structure **21b**. Such an effect is not present in allenecarboxamides,[7b,20] which normally exhibit two distinct resonances for the two *N*-alkyl groups at room temperature, thus suggesting normal rotational barriers.

The synthesis and chemistry of the mesityl-NCCCO compound **22** is described in other work.[12] This derivative reacts in the same manner to give a ketenimine **23**. The



closeness of the two NMe signals causes a low coalescence temperature of −25 °C, but the free energy of activation is similar to the above: $\Delta G^{\ddagger} = 13.2$ kcal mol^{-1}.

The amidoketenimines **12c** ($R^2 = NMe_2$) are not usually isolable as pure compounds. Their further fate at room temperature in the absence of nucleophiles, viz., quinolone formation, is described in Section 3. The corresponding esters **12a** (R^2 = OMe) are much more stable, usually distillable liquids.[1,2]

Ketenimines **12** and **23** react with nucleophiles at or below room temperature to afford malonic ester imides **16** (**24**). For example, addition of excess dimethylamine to a solution of **12Xc** gives **16e** quantitatively. Addition of ethanol in $CHCl_3$ affords **16d** quantitatively. To prepare compounds **16**, the easiest would seem to be injection of the nucleophile R^3H on the cold (77 K) thermolysate from **9** (Scheme 1). Thus, injection of MeOH on the thermolysate from **9a** affords **16a**. The thermolysate from **9c** affords **16e** with $HNMe_2$. Whenever $HNMe_2$ is used as the leaving group, subsequent injection of methanol will, however, afford **16c**, and ethanol will give **16d**. In other words, the cocondensed dimethylamine reacts first, at the ketene terminus of the iminopropadienone **15**, to produce amidoketenimine **12c**. That **16** is formed via **15** (route b, Scheme 1) and not directly from **12** (route a, Scheme 1) under such conditions is shown by the fact that one can remove part of the cocondensed $HNMe_2$ from the pyrolysates by intermittant warming of the coldfinger to ca. −80 °C while pumping in high vacuum. Subsequent addition of a second nucleophile (e.g., MeOH) then provides a mixture of products, e.g., **16c** due to reaction with residual $HNMe_2$ and then MeOH and **16a** due to reaction with MeOH only. If an excess of diethylamine is cocondensed with the pyrolysate, $HNEt_2$ can compete with $HNMe_2$, and the product with two diethylamino groups, **16g**, will dominate. Added amine also competes efficiently with cocondensed methanol. Thus, the pyrolysate from **9Xa** reacts with $HNMe_2$ to give **16Xe**.

The malonic acid derivatives **16** and **24** exist only in the tautomeric forms shown according to NMR spectroscopy. In the ^1H NMR spectra of the amidoamidines **16e−g**, the amidine function appears at lowest field, and the two methyl or alkyl groups are equivalent at room temperature as a result of rapid rotation. The higher field amide function appears as two nonequivalent methyl groups as a result of slow rotation. For example, the spectrum of **16Xe** exhibits two singlets at δ 2.68 (3H) and 2.84 (3H) (OC−NMe_2) and a singlet at δ 3.09 (6H) (N=C−NMe_2). We have measured the high and low coalescence temperatures and derived[17] the rotational barriers for some of these amidoamidines and find that they are in the order of 11−13 kcal mol^{-1} for the amidines and ca. 18 kcal/mol for the amides (e.g., for **24**, 11.0 and 18.3 kcal mol^{-1}, respectively). The lower barriers for the amidine functions are to be expected because of the lower electronegativity of N compared to O, which will reduce the C−N double bond character. These barriers are diagnostically valuable as a means of secure assignment of structures to compounds of the type **16** and hence asserting the sequence and positions of addition of the nucleophiles.

The formation of malonic imide derivatives of type **16** from ketenimines is thermally reversible in some cases when the leaving group is an amine. Thus, FVT or GC−MS (injector temp 200 °C) of **16Xe** afforded quinolone **13Xc**. Work to be published on other substances indicates that $HNMe_2$ is eliminated from the amido group, generating the imidoylketene, which then cyclizes to the quinolone.

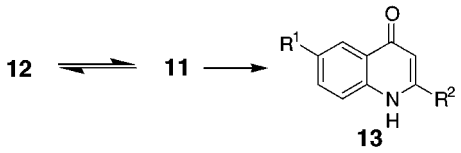
$$\mathbf{16Xe} \rightarrow \mathbf{11Xc} + \mathbf{HNMe_2} \rightarrow \mathbf{13Xc} + \mathbf{HNMe_2}$$

(19) For the importance of resonance structure **21c**, see ref 16b and Jochims, J. C.; Lambrecht, J.; Burkert, U.; Zsolnai, L.; Huttner, G. *Tetrahedron* **1984**, *40*, 839. Wolf, R.; Stadtmüller, S.; Wong, M. W.; Barbieux-Flammang, M.; Flammang, R.; Wentrup, C. *Chem. Eur. J.* **1996**, *2*, 1318.

(20) Himbert, G. *Justus Liebigs Ann. Chem.* **1979**, 829.

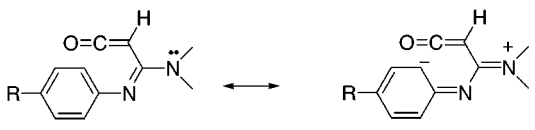
The other compounds **16** described in this paper were stable under GC−MS conditions.

3. Rearrangement of Ketenimines to Quinolones. The amidoketenimines **12c** and **23** are observable by NMR in solution at room temperature as described above. However, the signals of **12Hc** disappeared in the course of 24 h at room temperature in $CDCl_3$ or CD_2Cl_2 solution, and at the same time, quinolone **13Hc** precipitated from the solution, from which it was isolated in 20% yield based on the Meldrum's acid precursor, **9Hc**. The yield was improved to 25% by refluxing the methylene chloride solution for 1 h. The ketenimine **12Xc** disappeared from the NMR spectrum in 3 days at room temperature, mainly polymerizing and giving only a trace of quinolone, but at 40 °C the quinolone **13Xc** was formed in 15% yield and at 83 °C in 20% yield (38% yield of the material arriving on the coldfinger). We know from the low-temperature IR and NMR studies that no quinolone was present in these solutions initially. They must therefore have formed by rearrangement of the ketenimines or molecules derived therefrom. The structures of the quinolones are without doubt, being identical with the materials obtained from two other routes (the triazole route[9] and the ynamine−isocyanate route; see Section 5). Imidoylketenes **11** cyclize very readily to quinolones at or near room temperature.[9,21] Therefore, our results strongly support the hypothesis of an equilibrium between amidoketenimine **12** and imidoylketene **11**, taking place via a 1,3-shift of the NMe_2 group. This equilibrium is fast at room temperature:

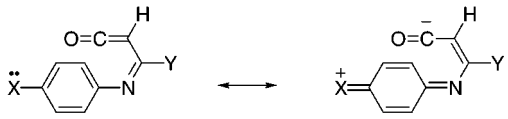


The ketene **11** is not observed in the equilibrium by NMR or IR spectroscopy at room temperature because the ketenimine is more stable by ca. 5 kcal/mol according to calculations.[22] As described above, this ketene *is* observed by low temperature IR spectroscopy, following population in high-temperature FVT reactions, especially when the NMe_2 group is replaced by OMe (**11a**), in which case the cyclization to quinolones becomes slower.

The alkoxyimidoylketenes/oxoketenimines **11a**/**12a** do not undergo such facile cyclization to quinolones. The ketenimines are isolable at room temperature, and quinolones are formed only on heating to 100 °C or by FVT at 200 °C. The dimethylamino group in amidinoketenes helps make the aromatic ring more electron rich, thus accelerating cyclization:[9]

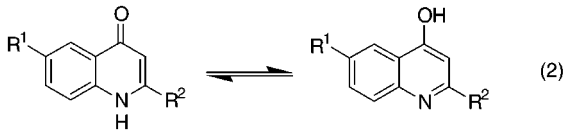


However, a donor group X on the aromatic ring makes the ketene less electrophilic, thus decelerating cyclization:



This can explain why **12Hc** rearranges to quinolone at room temperature, whereas **12Xc** requires ca. 40 °C.

4. Preparation of Quinolones in Solution and Assignment of Structure. Several quinolones in the **13H** and **13X** series were prepared in yields of 24−76% by refluxing the Meldrum's acid derivatives **9** in diphenyl ether. The yields obtained on preparative FVT of **9** at 600−700 °C are often as good. The formation of quinolones **13Ha** and **13Hb** in refluxing diphenyl ether solution was reported previously.[1,14] The ^1H NMR spectra of 3-unsubstituted quinolones display characteristic signals for H(C-3) at ca. δ 6 ppm, and these are particularly broad in DMSO-d_6 solution. The ^{13}C NMR signal for C-3 appears in the region of δ 90−105 ppm. The sequence of the ^1H NMR signals for H(C-5) and H(C-8) is reversed when going from DMSO-d_6 to $CDCl_3$ (or more conveniently, for better solubility $CDCl_3/CD_3OD$ mixed solvent). This solvent change also causes C-8 to move to higher field. In DMSO-d_6, C-2 usually appears at lower field than C-4 (when the 2-substituent is MeO, MeS, or NMe_2). The signals due to the quaternary carbons C-2 and C-8a are often very weak and broad as a result of the neighboring nitrogen quadrupole moment. In DMSO-d_6 solution in particular, the appearance of the spectra (chemical shifts and broadness of both proton and carbon signals) is highly dependent on the amount of water present; the tautomeric mixture undoubtedly depends on solvent polarity, water content, and other factors. In DMSO-d_6 solution, all of the signals due to quaternary carbons and also often that of C-8 are particularly weak and broad; it can help to heat the sample to 80 °C. The ensemble of data strongly indicates that there is a preponderance of the 4-hydroxyquinoline tautomer in DMSO solution and of the 1*H*-quinoline-4-one tautomer in $CDCl_3/CD_3OD$ (eq 2).



This is supported by comparisons with unpublished data for *N*-alkyl-4-quinolones and *O*-alkyl-4-quinolinols in our laboratory and with calculated values (increment method). The NMR assignments made here were based on $^1H-^1H$ coupling constants, DEPT, and 2D experiments. Examples of the latter are presented in the Supporting Information.

Also of importance is the fact that H/D exchange[9] takes place in these quinolones at H(C-3) in protic solvents, e.g., in the case of **13Xa** in the course of several days at room temperature in $CDCl_3/CD_3OD$ solution, thus indicating that the less favorable and not directly observed 3*H* tautomer also participates.

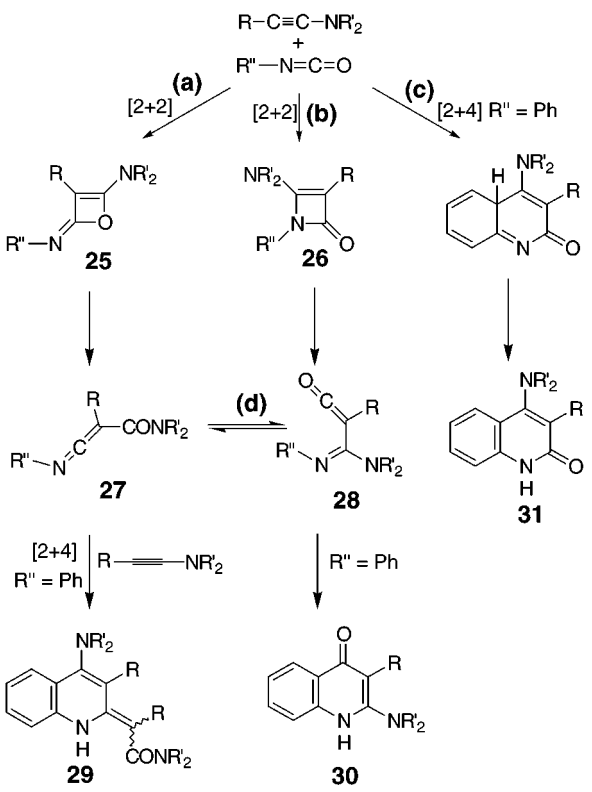
Not surprisingly, the IR spectra of the quinolones/quinolinols can vary widely depending on the method of sample preparation. In some but not all cases, a carbonyl group appears around 1640 cm^{-1} in the solid state (KBr) spectra.

5. The Ynamine−Isocyanate Route to Quinolones. The results described in Section 3 made us conclude that

(21) Bouvy, A.; Janousek, Z.; Viehe, H. G.; Arietta, J. M. *Bull. Soc. Chim. Belg.* **1985**, *94*, 869.

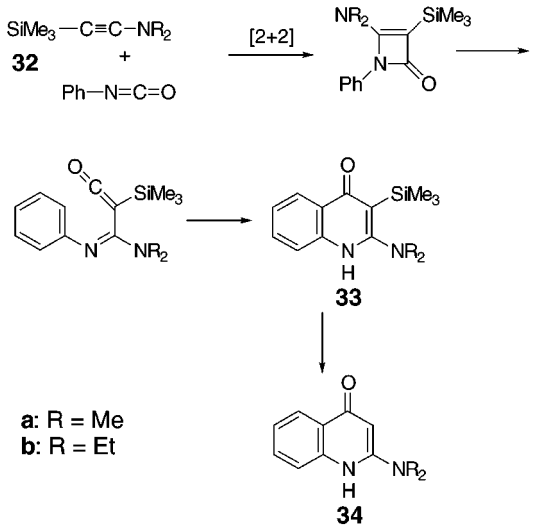
(22) Finnerty, J.; Wong, M. W.; Wentrup, C. To be submitted for publication.

Scheme 2



the ketenimine−ketene interconversion between **12c** and **11c** is fast at room temperature. The formation of quinolones under these conditions then requires that the cyclization of ketenes **11c** also be rapid at room temperature. There are several reports of quinolone formation from putative imidoylketenes at elevated temperatures (typically 100−200 °C).[23] More importantly, ynamines react with isocyanates at or near room temperature to furnish ketenimines, 4-quinolones, and/or other products.[21,24] There is much speculation about the mechanism of this reaction in the literature, and it is usually assumed that the ynamine can undergo [2+2] cycloaddition to either the C=O (route a) or the C=N bond (route b) of the isocyanates, leading to putative oxete **25** and azetinone **26** intermediates (Scheme 2). The third possibility is a [2+4] cycloaddition of the ynamine to aryl isocyanates utilizing one of the benzenoid C=C double bonds (route c).[25] Perplexingly, alkyl isocyanates appeared to react by route a only, giving ketenimines **27**.[26] In light of our results reported in this paper, we reinterpret all of these ynamine−isocyanate reactions in terms the rapid equilibrium between ketenimine **27** and ketene **28** (route d) regardless of whether path a or path b is followed. When ketene **28** possesses an unhindered *N*-aryl group, it cyclizes to the quinolone **30** at or near room temperature. If no such unhindered aryl group is available, the more stable ketenimine **27** is isolable or undergoes further reaction to **29**.

It was desirable to provide independent verification that ketenes akin to **11** (**28**) would actually cyclize to quinolones **13** (**30**) at room temperature. We chose the silyl-substituted ynamines **32** of the type recently described by Himbert[27] to demonstrate this. Thus, reaction of *N*,*N*-dimethyl-*N*-(trimethylsilylethynyl)amine (**32a**) with phenyl isocyanate in either benzene or acetonitrile solution *at room temperature* afforded quinolone **34a** (= **13Hc**) in ca. 25% yield. The yield is typical for this type



of reaction.[21,23−25] The analogous diethylamino compound **32b** afforded 2-diethylamino-4-quinolone (**34b**).The trimethylsilyl derivative **33b** was detectable by GC−MS of the crude reaction mixture, but the trimethylsilyl group was lost on chromatographic purification.

Conclusion

Meldrum's acid derivatives **9** can undergo fragmentation by two different paths, routes a and b in Scheme 1. Route b is an almost exclusive route when the leaving group is an amine substituent ($R^2 = NMe_2$). This leads via the transient ketenimine **14** to clean formation of aryliminopropadienones, ArN=C=C=C=O (**15**), isolable at 77 K and in some cases observable till room temperature. Compounds **15** react with 2 equiv of nucleophiles to afford malonic acid imide derivatives **16** and with 1 equiv to afford ketenimines **12** cleanly.

Route a (Scheme 1) leads to the interconverting imidoylketenes and oxoketenimines **11** and **12**, the former cyclizing to quinolones **13**. This is the dominant route when the leaving group in **9** is MeO or MeS.

The *C*-alkoxycarbonylketenimines **12** ($R^2 = OR$) are isolable and distillable; they isomerize to ketenes **11** and quinolones **13** on heating (ca. 200 °C in the gas phase). The *C*-carboxamidoketenimines **12** ($R^2 = NR_2$) are stable in solution at room temperature for short periods of time but cyclize to quinolones **13** via amidinoketenes **11** at or near room temperature, thus implying low activation barriers for both the interconversion between **11** and **12** and for the cyclization of **11** to **13**.

(23) Potts, K. T.; Ehlinger, R.; Nichols, W. M. *J. Org. Chem.* **1975**, *40*, 2596. Kappe, T.; Zadeh, K. *Synthesis* **1975**, 247. Moderhack, D.; Stolz, K. *Chem.-Z.* **1987**, *12*, 372. Mass, H.; Bensimon, C.; Alper, H. *J. Org. Chem.* **1998**, *63*, 17.

(24) (a) Kuehne, M. E.; Linde, H. *J. Org. Chem.* **1972**, *37*, 1846. (b) Ficini, J.; Krief, A. *Tetrahedron Lett.* **1968**, 947 (see correction of structures in ref 24c). (c) Kuehne, M. E.; Sheehan, P. J. *J. Org. Chem.* **1968**, *33*, 4406 (regarding the ynamine−ketene reactions also reported here, see the reassignment of the alleged oxete structures **10** in this paper as allenes in ref 20).

(25) Ficini, J. *Tetrahedron* **1976**, 1449.

(26) (a) Piper, J. U.; Allard, M.; Faye, M.; Hamel, L.; Chow, V. *J. Org. Chem.* **1977**, *26*, 4261. (b) Ficini, J.; Pouliquen, J. *Tetrahedron Lett.* **1972**, 1139.

(27) Himbert, G.; Nasshan, H.; Gerulat, O. *Synthesis* **1997**, 293.

Iminopropadienones **15** are not formed from the ketenes/ketenimines **11** or **12**, or at most in only trace amounts. Triazoles **3** (**19**) and pyrroledione **4** (**17**, **18**) afford the interconverting ketene/ketenimines **11**/**12** and not, to any significant extent, iminopropadienones **15**. In the FVT of triazoles **3** (R = NMe_2) at high temperatures, we did observe weak bands in the IR spectra corresponding to PhNCCCO (**15H**).[9] Because ArNCCCO compounds are extremely strong absorbers, these bands correspond to only trace amounts of material.

The [2+2] cycloaddition reaction between ynamines and isocyanates is reinterpreted: the products are derived from the rapidly interconverting amidinoketene and amidoketenimine (**28**−**27**).

The assigned structures of ketenimines and malonic imides are strongly supported by measured rotational barriers of dimethylamino groups. In ketenimines **12** (R = NMe_2) and **23** they are ca. 13 kcal mol^{-1}. In the malonic imides **16** (**24**) they are of the order of 18 kcal mol^{-1} for the amides and 11−13 kcal mol^{-1} for the amidines.

Experimental Section

The pyrolysis apparatus and general equipment were as previously reported for Ar matrix (12 K),[28] neat film (77 K)[29] deposition, and preparative scale work (77 K isolation).[30] NMR spectra are at 200 MHz for ^1H and 50.3 MHz for ^{13}C unless otherwise indicated. Mass spectra were obtained by 70 eV electron ionization. GC−MS employed a BP-5 capillary column (30 m × 0.25 mm; He carrier at 20 psi head pressure; injector 200 °C; detector 280 °C; column temperature 100−125 °C, programmed at 16 °C/min). Column chromatography was performed on silica gel (200−400 mesh unless otherwise stated). Melting points are uncorrected. Compounds **9Ha**−**c**,[1,11b] **9Mb**,[14] **17**,[3] and **18**[2] were prepared according to reported procedures.

5-[(4-Methylphenylamino)(methoxy)methylene]-2,2-dimethyl-1,3-dioxane-4,6-dione (9Ma). To a solution of 5-[(4-methylphenylamino)(methylthio)methylene]-2,2-dimethyl-1,3-dioxane-4,6-dione (**9Mb**) (0.154 g; 0.5 mmol) in methanol (5 mL) was added HgO (yellow; 0.109 g; 0.5 mmol) and $HgCl_2$ (0.135 g; 0.5 mmol) [In this type of reaction, we find that a mixture of HgO and $HgCl_2$ sometimes gives better yields than either of these compounds alone[1]]. The mixture was refluxed for 20 min and filtered, and the filtrate was evaporated. H_2O (10 mL) was added to the residue to assist precipitation of the product, which was recrystallized from THF/hexane: yield 0.11 g (78%); mp 174−175 °C; ^1H NMR ($CDCl_3$) δ 1.74 (s, 6H), 2.34 (s, 3H), 4.11 (s, 3H), 7.18 (s, 4H); ^{13}C NMR ($CDCl_3$) δ 21.0, 26.2, 62.6, 75.2, 103.4, 123.2, 129.8, 132.3, 137.0, 164.2, 171.2; IR (KBr) 1720, 1660 cm^{-1}. Anal. Calcd for $C_{15}H_{17}NO_5$: C, 61.83; H, 5.89; N, 4.81. Found: C, 61.71; H, 5.85; N, 4.75.

5-[(Dimethylamino)(4-methylphenylamino)methylene]-2,2-dimethyl-1,3-dioxane-4,6-dione (9Mc). To **9Ma** (307 mg; 1.0 mmol) in 15 mL THF was added 2 mL of a solution of dimethylamine in water (40% w/v), followed by HgO (216 mg; 1.0 mmol). The mixture was stirred overnight and filtered. The filtrate was evaporated in a vacuum, and the resulting solid was recrystallized from THF to yield colorless needles: 250 mg (79%); mp 232 °C; IR (KBr) 1640, 1611, 1587 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.70 (s, 6H), 2.32 (s, 3H), 2.87 (s, 6H), 6.93 (d, 2H), 7.17 (d, 2H), 9.28 (br s, 1H, exchanging with D_2O); ^{13}C NMR ($CDCl_3$) δ 20.9, 26.3, 41.8, 76.0, 102.2, 123.0, 130.1, 136.0, 136.2, 163.6, 164.5. Anal. Calcd for $C_{16}H_{20}N_2O_4$: C, 63.14; H, 6.62; N, 9.20. Found: C, 62.99; H, 6.50; N, 9.21.

5-[(4-Methoxyphenylamino)(methylthio)methylene]-2,2-dimethyl-1,3-dioxane-4,6-dione (9Xb) was prepared according to the literature:[14] yield 71%; mp 147−148 °C (lit.[14] 146−147 °C); ^{13}C NMR ($CDCl_3$) δ 18.7, 26.2, 55.4, 85.3, 102.9, 114.4, 126.6, 129.6, 159.0, 163.8, 178.2.

5-[Methoxy(4-methoxyphenylamino)methylene]-2,2-dimethyl-1,3-dioxane-4,6-dione (9Xa) was prepared as **9Ma** in 67% yield; mp 162−164 °C; IR (KBr) 1714, 1663, 1621, 1576 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.77 (s, 6H), 3.83 (s, 3H), 4.13 (s, 3H), 6.92 (d, 2H, J = 6.8 Hz), 7.26 (d, 2H, J = 6.8 Hz), 11.8 (bs, 1H, N−H); ^{13}C NMR ($CDCl_3$) δ 26.1, 55.4, 62.5, 75.4, 102.9, 114.4, 124.7, 127.7, 158.3, 164.1, 171.1. Anal. Calcd for $C_{15}H_{17}NO_6$: C, 58.63; H, 5.58; N, 4.56. Found: C, 58.51; H, 5.60; N, 4.51.

5-[(Dimethylamino)(4-methoxyphenylamino)methylene]-2,2-dimethyl-1,3-dioxane-4,6-dione 9Xc was prepared as **9Mc** (48 h reaction; 81% yield): mp 191−193 °C; IR (KBr) 1688, 1636, 1608, 1585 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.53 (s, 6H), 2.92 (s, 6H), 3.73 (s, 3H), 6.89 (d, J = 9 Hz, 2H), 7.08 (d, J = 8.9 Hz, 2H), 9.23 (bs, 1H); ^{13}C NMR ($CDCl_3$) δ 26.1, 41.1, 55.3, 73.9, 102.1, 114.2, 125.0, 131.6, 157.6, 163.5, 163.9. Anal. Calcd for $C_{16}H_{20}N_2O_5$: C, 59.97; H, 6.30; N, 8.75. Found: C, 60.12; H, 6.24; N, 8.72.

Methyl 1-(4-Methylphenyl)-1*H*-1,2,3-triazole-4-carboxylate (19) was prepared from methyl propiolate (1.68 g; 0.02 mol) and *p*-tolyl azide (2.66 g; 0.02 mol) in ethanol (150 mL) at reflux for 22 h. The solvent was removed by rotary evaporation, and the resulting solid was recrystallized from ethanol/diethyl ether to produce white crystals: yield 3.0 g (70%); mp 159−160 °C; ^1H NMR ($CDCl_3$) δ 2.41 (s, 3H), 3.97 (s, 3H), 7.29−7.62 (m, 4H), 8.45 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 18.9, 52.3, 96.0, 125.5, 130.4, 139.8, 141.0, 161.1; IR (KBr) 1713, 1543 cm^{-1}. Anal. Calcd for $C_{11}H_{11}N_3O_2$: C, 60.82; H, 5.10; N, 19.34. Found: C, 60.79; H, 5.14; N, 19.28.

Preparation of 2-Substituted 4-Quinolones 13 in Diphenyl Ether. Compounds **13Hc**, **13Xa**, **13Xb**, and **13Xc** were obtained by refluxing **9** in Ph_2O/N_2 for 20−30 min.[1,14]

2-Dimethylamino-4-quinolone (13Hc). White crystals (70%); mp 290 °C, identified by rigorous comparison of IR, ^1H and ^{13}C NMR, and mass spectra with those of the previously characterized material.[9]

2,6-Dimethoxy-4-quinolone (13Xa). Yellow crystals (24%); IR (KBr) 3266, 3082, 1654, 1620, 1589 cm^{-1}; ^1H NMR (DMSO-d_6, 400 MHz) δ 3.83 (s, 3H, OMe), 3.94 (s, 3H, OMe), 6.26 (br s, 1H, H(C-3)), 7.33 (dd, J = 3 and 9 Hz, 1H, H(C-7)), 7.39 (d, J = 3 Hz, 1H, H(C-5)), 7.60 (d, J = 9 Hz, 1H, H(C-8)), 11.3 (br s, 1H); ^1H NMR ($CDCl_3/CD_3OD$ 1:1, 200 MHz) δ 3.89 (s, 3H, OCH_3), 3.97 (s, 3H, OCH_3), 5.89 (s, 1H, H(C-3), slowly exchanging with D), 7.21 (dd, J = 3 and 9 Hz, 1H, H(C-7)), 7.37 (d, J = 9 Hz, 1H, H(C-8)), 7.59 (d, J = 3 Hz, 1H, H(C-5)); note that the chemical shifts of H(C-5) and H(C-8) are interchanged in these two solvents; the assignments are based on the observed coupling constants and a HSQC 2D $^{13}C-^1H$ correlation spectra (Supporting Information); ^{13}C NMR ($CDCl_3/CD_3OD$ 1:1) δ 55.8 (MeO), 56.3 (MeO), 89.2 (C-3), 104.7 (d, C-5), 119.7 (d, C-8, broad), 123.3 (d, C-7), 123.8 (s, C-4a), 133.9 (s, C-8a, weak, broad), 156.5 (s), 161.8 (s), 179 (s, weak, broad); the assignments are based on the HSQC 2D carbon−proton correlation and a DEPT spectrum; the broad signals are ascribed to vicinity of the ^{14}N quadrupole moment; MS m/z 205.0729, calcd for $C_{11}H_{11}NO_3$ 205.0733.

6-Methoxy-2-methylthio-4-quinolone (13Xb).[14] Yellow solid, (49%); mp 230−232 °C (dec) (lit.[14] 229−230 °C); IR (KBr) 3189, 1612, 1576, 1537, 1500 cm^{-1}; ^1H NMR (DMSO-d_6, 400 MHz) δ 2.56 (s, 3H, SMe), 3.82 (s, 3H, OMe), 6.20 (br s, 1H, H(C-3)), 7.24 (dd, J = 3 and 9 Hz, 1H, H(C-7)), 7.43 (d, $J \approx 3$ Hz, 1H, H(C-5)), 7.56 (d, $J \approx 9$ Hz, 1H, H(C-8), 11.84 (br s, 1H); ^1H NMR ($CDCl_3/CD_3OD$ 1:1, 400 MHz) δ 2.60 (s, 3H, SMe), 3.90 (s, 3H, OMe), 6.25 (s, 1H, H(C-3)), 7.23 (dd, J = 3 and 9 Hz, 1H, H(C-7)), 7.44 (d, J = 9 Hz, 1H, H(C-8)), 7.60 (d, J = 3 Hz, 1H, H(C-5)); ^{13}C NMR ($CDCl_3/CD_3OD$ 1:1, 100 MHz) δ 14.7 (SCH_3), 55.8 (OCH_3), 104.4 (C5), 104.8 (C3), 119.5 (d, C-8), 123.7 (d, C-7), 125.2 (s), 136.2 (s), 154.0 (s), 156.9 (s), 176.9 (s). A DEPT spectrum confirmed the assignments. The sequence of C-7 and C-8 is reversed in DMSO-d_6 solution: δ

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(29) Briehl, H.; Lukosch, A.; Wentrup, C. *J. Org. Chem.* **1984**, *49*, 2772.
(30) Wentrup, C.; Blanch, R.; Briehl, H.; Gross, G. *J. Am. Chem. Soc.* **1988**, *110*, 1874.

121.8 (C-7), 122.5 (C-8, weak, broad). HSQC $^1H-^{13}C$ 2D correlation spectra (for both $CDCl_3/CD_3OD$ and DMSO-d_6 solutions) are shown in the Supporting Information. MS *m/z* 221.0510, calcd for $C_{11}H_{11}NO_2S$ 221.0505. Anal. Calcd for $C_{11}H_{11}NO_2S$: C, 59.71; H, 4.98; N, 6.34. Found: C, 59.78; H, 5.11; N, 6.33.

2-(*N*,*N*-dimethylamino)-6-methoxy-4-quinolone (13Xc). Light brown solid (76%), identical with previously characterized material.[9]

Analytical FVT of 9Hb. This compound was subjected to FVT over the temperature range 200−600 °C (sublimation temperature 100−130 °C) with IR spectroscopic analysis of the products at 77 K. At 200 °C, only the unchanged starting material was obtained. At 260 °C, a ketenimine (**12Hb**; 2040 w cm^{-1}) and a ketene (**11Hb**; 2121, 2106 w cm^{-1}) were observed. At 300 °C, peaks due to phenyliminopropadienone (**15H**) appeared at 2222 vs, 2140 w sh cm^{-1}. At 600 °C, both **11Hb** and **12Hb** had disappeared from the spectrum, and **15H** had become the main absorber, together with 2-methylthio-4-quinolone (**13Hb**), which was isolated and identified by comparison with the compound described in the following entry.

2-Methylthio-4-quinolone (13Hb). Compound **9Hb** (100 mg) was subjected to preparative FVT at 600 °C, giving 46 mg (70%) of **13Hb**, which condensed in the air-cooled part of the apparatus. **13Hb**: mp 225−226 °C (lit.[3] 225−226 °C; lit.[14] 220−222 °C); IR (KBr) 3442, 1632, 1580 cm^{-1}; ^1H NMR (DMSO-d_6) δ 2.50 (s, 3H), 6.20 (br s, 1H), 7.30 (t, 1H), 7.55 (m, 2H), 8.00 (d, 1H), 11.9 (br s, 1H); ^1H NMR ($CDCl_3/CD_3OD$ 1:1, 100 MHz) δ 2.55 (s, 3H), 6.24 (s, 1H, H(C-3)), 7.34 (apparent t, $J = 7.6$ Hz, 1H, H(C-6)), 7.48 (apparent d, $J = 8$ Hz, 1H, H(C-8)), 7.63 (complex t, apparent $J = 7.2$ Hz, 1H, H(C-7)), 8.20 (d, $J = 8$ Hz, 1H, H(C-5)); ^{13}C NMR (DMSO-d_6, 80 °C) δ 13.3, 104.3, 119.9, 122.6, 122.7, 123.7, 130.6, 142.8, 154.3, 171.0; ^{13}C NMR ($CDCl_3/CD_3OD$ 1:1, 100 MHz) δ 14.6 (SCH_3), 105.4 (s, C-3), 118 (d, C-8), 124.5 (d, C-6), 124.6 (s), 125.7 (d, C-5), 132.9 (d, C-7), 141.6 (s), 155.9 (s), 178.3 (s). A DEPT spectrum confirmed the quarternary carbon assignments. A HSQC 2D $^1H-^{13}C$ correlation is shown in the Supporting Information. **13Hb** is also obtained in ∼100% yield by FVT of **17**.[3]

Phenyliminopropadienone (15H). FVT of **9Ha**, **9Hb**, and **9Hc** (ca.10 mg portions) with Ar matrix isolation of the products were carried out as previously described.[1,11b] IR of **15H** (Ar, 15 K) 2247 vs, 2141 w, 1633 m, 1620 m, 1490 m, 1284 w, 1210 w, 754 w cm^{-1}. Other signals: acetone, 3012 w, 1768 w, 1721 m, 1361 m, 1217 m, 1094 m cm^{-1}; CO_2, 2344 vs, 2340 vs cm^{-1}; dimethylamine (using **9Hc** as the precursor), 3193 w, 2973 w, 2832 w, 1482 w, 1479 w, 1159 w, 1184 w, 1025 w, 861 w cm^{-1}.

***N*-Phenylketenimine-2-(*N*,*N*-dimethylcarboxamide) (12Hc) and Its Conversion to Quinolone 13Hc.** Compound **9Hc** (80 mg; 0.27 mmol) was subjected to preparative FVT at 700 °C/1.3×10^{-3} mbar (3 h), and the products were collected at 77 K on a coldfinger coated with $CDCl_3$. The system was then brought to atmospheric pressure with N_2. The coldfinger was allowed to warm, causing the resulting solution to flow into an NMR tube fitted below the coldfinger and cooled at −196 °C. The NMR tube was flame sealed, and spectra were recorded at temperatures between −50 and 27 °C. ^1H NMR ($CDCl_3$, −50 °C) δ 3.004 (s, 3H), 3.026 (s, 3H), 5.1 (s, 1H), 7.38 (m, 5H) (acetone was present at 2.26 (s, 6H)); ^{13}C NMR ($CDCl_3$, −50 °C) δ 35.3, 37.6, 53.8, 124.4, 128.3, 129.4, 136.9, 166.9, 179.6 (acetone was present at 31.2 and 208.6 ppm). The two CH_3 signals at ca. 3 ppm in the ^1H NMR spectrum coalesced to a singlet at 263 K (500 MHz, $\Delta\nu = 10.85$ Hz). After 24 h at room temperature, all signals, except for that due to acetone, had disappeared and quinolone **13Hc** had crystallized from the solution (20−25% yield for the two steps based on **9Hc**; at least 32% based on **12Hc**.) When analogous $CDCl_3$ (or $CHCl_3$) solutions were examined by IR spectroscopy at room temperature, immediately after warming from −196 °C, a strong ketenimine absorption ascribed to **12Hc** was observed at 2046 cm^{-1}. In an analogous experiment with isolation of the neat FVT product on a BaF_2 or KBr target at 77 K, phenyliminopropadienone (**15H**) was observed as a very strong peak at 2222, 2140 (sh) cm^{-1}. A very weak peak due to ketenimine **12Hc** was detectable at 2042, 2033 cm^{-1}. On slow warmup of this material to −100 °C, the signals due to **15H** started to decrease, and those due to ketenimine **12Hc** started growing at 2042/2033 cm^{-1} (neat film).

Preparation of 16Hd by Trapping of Ketenimine 12Hc. Meldrum's acid derivative **9Hc** (85 mg; 0.29 mmol) was subjected to preparative FVT at 600 °C with isolation of the products in a U-tube at 77 K. The system was then brought to atmospheric pressure with N_2, and the U-tube was warmed to room temperature. [As shown above, ketenimine **12Hc** would now be present.] The content of the U-tube was immediately dissolved in a solution of 2% EtOH in $CHCl_3$ (50 mL), the solution was refluxed, and the solvent was then removed by rotary evaporation. The resulting yellow oil (53 mg; 77% based on **9Hc**) was shown by ^1H NMR to be a mixture of **16Hd** and **16He** (1:0.35), which was easily separated into the pure constituents by chromatography through a short column, first eluting **16Hd** with $CHCl_3$, and then **16He** with $CHCl_3$/MeOH (10:1) (cf. spectra below). From the air- cooled part of the apparatus, between the oven and the U-tube, was isolated a 15−20% yield of quinolone **13Hc**, identical in all respects with the previously characterized material.[9]

Preparation of Compounds 16Ha,c,f,g by Trapping of Phenyliminopropadienone 15H. 15H was generated by FVT of **9Hc** (ca. 100 mg) at 600 °C. The products were isolated on a coldfinger previously coated with the added nucleophile (MeOH or $HNEt_2$; ca. 2 mL) and kept at either ca. −190 or −80 °C. The coldfinger was then allowed to warm to room temperature, and the products were separated by column chromatography on SiO_2 (70−230 mesh), eluting with Et_2O.

Methyl 3-Methoxy-3-(phenylimino)propanoate (16Ha). Obtained with added MeOH. Yield 43% when using a coldfinger at −80 °C; 0% at −190 °C. Yellow oil, identical with the previously described material.[1]

3-Methoxy-3-(phenylimino)-*N*,*N*-dimethylpropanamide (16Hc). Obtained with added MeOH. Yield 25% at −80 °C; 73% at −190 °C. Yellow oil; IR (CCl_4) 1682, 1662, 1597, 1490 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 2.83 (s, 3H), 2.92 (s, 3H), 3.25 (s, 2H), 3.86 (s, 3H), 6.85 (m, 2H), 7.04 (m, 1H), 7.28 (m, 2H); ^{13}C NMR ($CDCl_3$, 100.5 MHz) δ 35.6 (t), 37.5 (q), 53.8 (q), 121. 2 (d), 123.3 (d), 129.0 (d), 148.3 (s), 158.3 (s), 167.2 (s); MS *m/z* 220.1215 (calcd for $C_{12}H_{16}N_2O_2$ 220.1212) (33%), 176 (24), 148 (13), 134 (10), 128 (16), 118 (20), 93 (59), 91 (16), 77 (18), 72 (100).

3-Diethylamino-3-(phenylimino)-*N*,*N*-dimethylpropanamide (16Hf). Obtained with added $HNEt_2$. Yield 30% at −80 °C; 61% at −190 °C. Yellow oil; IR 1661, 1611, 1591 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.21 (t, $J = 7$ Hz, 6H), 2.61 (s, 3H), 2.88 (s, 3H), 3.28 (s, 2H), 3.43 (q, $J = 7$ Hz, 4H), 6.72 (m, 2H), 6.91 (m, 1H), 7.20 (m, 2H); ^{13}C NMR ($CDCl_3$, 100.5 MHz) δ 13.44 (q), 33.1 (t), 35.6 (q), 37.1 (q), 42.1 (t), 121.4 (d), 122.4 (s), 128.7 (d), 152.1 (s), 152.9 (s); MS *m/z* 261.1842 (calcd for $C_{15}H_{23}N_3O$ 261.1841) (28%), 189 (24), 120 (12), 77 (16), 72 (100).

3-Diethylamino-3-(phenylimino)-*N*,*N*-diethylpropanamide (16Hg). Obtained with added $HNEt_2$. Yield 54% at −80 °C. Yellow oil; IR (CCl_4) 1654, 1612, 1591 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 0.81 (t, $J = 7$ Hz, 3H), 1.09 (t, $J = 7$ Hz, 3H), 1.21 (t, $J = 7$ Hz, 6H), 2.90 (q, $J = 7$ Hz, 2H), 3.25 (s, 2H), 3.31 (q, $J = 7$ Hz, 2H), 3.43 (q, $J = 7$ Hz, 4H), 6.73 (m, 2H), 6.89 (m, 1H), 7.17 (m, 2H); ^{13}C NMR ($CDCl_3$, 100.5 MHz) δ 12.8 (q), 13.7 (q), 33.4 (t), 40.6 (t), 42.0 (t), 42.1 (t), 121.4 (d), 122.4 (d), 128.7 (d), 152.1 (s), 167.0 (s); MS *m/z* 289.2155 (calcd for $C_{17}H_{27}N_3O$ 289.2154) (63%), 260 (16), 217 (49), 120 (29), 100 (100).

Trapping of 15H with Ethanol and Dimethylamine. Meldrum's acid derivative **9Hc** (200 mg; 0.68 mmol) was pyrolyzed at 700 °C in the course of 3 h, using a U-tube cooled in MeOH/liquid N_2 (−96 °C) to trap the products. Upon completion of the pyrolysis, ethanol (4 mL) was injected onto the cold product (−96 °C), and the U-tube was purged with N_2 gas and warmed to room temperature. The resulting solution was filtered through a plug of silica gel (ca. 1 × 1

cm), excess solvent was evaporated, and the products were separated by preparative gas chromatography on an OV-101 column (isothermal, 130 °C) to give **16Hb**, **16Hd**, and **16He**.

Ethyl 3-Ethoxy-3-(phenylimino)propanoate (16Hb). Yellow oil, R_t 15 min, 34 mg (21%); IR ($CHCl_3$) 1735, 1674, 1579 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.17 (t, 3H), 1.27 (t, 3H), 3.12 (s, 2H), 4.07 (q, 2H), 4.22 (q, 2H), 6.73 (m, 2H), 6.97 (m, 1H), 7.21 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 14.0, 36.5, 61.2, 62.2, 121.0, 123.3, 129.0, 148.1, 156.5, 167.9; MS *m/z* 235.1236 (calcd for $C_{13}H_{17}NO_3$ 235.1236) (60%), 207 (40), 190 (27), 120 (46), 104 (55), 93 (100), 77 (45). Anal. Calcd for $C_{13}H_{17}NO_3$: C, 66.36; H, 7.28; N, 5.95. Found: C, 66.39, H, 7.12; N, 6.10.

3-Ethoxy-3-(phenylimino)-*N*,*N*-dimethylpropanamide (16Hd). Yellow oil, R_t 37 min, 66 mg (40%); IR ($CHCl_3$) 1647, 1597, 1489 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.35 (t, 3H), 2.83 (s, 3H), 2.91 (s, 3H), 3.23 (s, 2H), 4.30 (q, 2H), 6.83 (m, 2H), 7.03 (m, 1H), 7.26 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 14.1, 35.5, 35.7, 37.5, 62.1, 121.1, 123.1, 129.0, 148.3, 157.6, 167.2; MS *m/z* 234.1370 (calcd for $C_{13}H_{18}N_2O_2$ 234.1370) (22%), 120 (22), 93 (52), 87 (55), 77 (35), 72 (100). Anal. Calcd for $C_{13}H_{18}N_2O_2$: C, 66.64; H, 7.47; N, 11.96. Found: C, 66.56; H, 7.76; N, 11.77.

3-Dimethylamino-3-(phenylimino)-*N*,*N*-dimethylpropanamide (16He). Yellow oil, R_t 49 min, 31 mg (19%); IR ($CHCl_3$) 1652, 1615, 1591, 1481 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.64 (s, 3H), 2.87 (s, 3H), 3.03 (s, 6H), 3.30 (s, 2H), 6.72 (m, 2H), 6.91 (m, 1H), 7.18 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 33.5, 35.7, 37.2, 38.4, 122.0, 123.1, 129.0, 151.1, 155.0, 167.6; MS *m/z* 233.1530 (calcd for $C_{13}H_{19}N_3O$ 233.1530) (26%), 189 (22), 77 (40), 72 (100). Anal. Calcd for $C_{13}H_{19}N_3O$: C, 66.92; H, 8.21; N, 18.01. Found: C, 66.84; H, 8.15; N, 17.85.

4-Methylphenyliminopropadienone (15M). FVT of 9Mb and 9Mc. These precursors were both subjected to FVT at 700 °C with Ar matrix isolation of the products on a BaF_2 disk. IR of **15M** (Ar, 15 K) 2944 w, 2794 w, 2248 vs, 2142 w, 1634 w, 1429 w, 1354 w, 728 w cm^{-1}. Other peaks: acetone, CO_2, and dimethylamine, as reported for **15H** above; methanethiol, 2948 m, 2603 w, 1445 m, 800 w cm^{-1}. When **9Mb** was used as the precursor, a weak band ascribed to a ketenimine was observed at 2048 cm^{-1} for FVT temperatures of 300−500 °C; it had disappeared at 600 °C. When **9Mc** was used as the precursor, **15M** was formed immediately, at 300 °C, with no other intermediates reliably detectable. When **9Mc** was the precursor and **15M** was isolated together with Me_2NH at 77 K, subsequent warmup to −90 °C caused slow reaction of the two products with formation of ketenimine **12Mc** (2030 cm^{-1}, neat). When the cocondensed Me_2NH was partially removed by evaporation, **15M** remained observable up to 0 °C.

Analytical FVT of Triazole 19. The compound was sublimed at ca. 85 °C and pyrolyzed over the temperature range 200−700 °C/3 × 10^{-5} mbar with isolation of the products at 77 K (neat) for IR spectroscopy. At a FVT temperature of 200 °C, only the unchanged starting material was observed (3140, 1717, 1548, 1520, 1269, 1153, 1039 cm^{-1}). At temperatures of 300−500 °C, the oxoketenimine **12Ma** was observed (2046, 1712, 1697, 1442, 1241, 1153 cm^{-1}) together with the imidoylketene **11Ma** (2136 (w), 2119 (w sh) cm^{-1}). At 500 °C, the intensities of these two bands decreased but remained in approximately the same ratio. Also at 500 °C, new peaks emerged corresponding to quinolone **13Ma** (1643, 1610 cm^{-1}). At 600 °C, the latter was the only species still observed. The quinolone was also isolated from the cryostat and identified by GC−MS and ^1H NMR. The absence of quinolone **13Ma** from the IR spectrum at FVT temperatures below 500 °C is due merely to its involatility.

Analytical FVT of 9Ma. Compound **9Ma** was sublimed at ca. 95 °C/1.5 × 10^{-5} mbar. No reaction was observable using FVT temperatures below 150 °C. From 150 to 400 °C, the IR spectra (neat film, 77 K) revealed the imidoylketene (2135, 2119 (sh) cm^{-1}); from ca. 200 to 400 °C, the oxoketenimine appeared (2046 cm^{-1}); and from ca. 300 °C, 4-methylphenyliminopropadienone was present (**15M**; 2221 (vs) and 2182 (sh, w) cm^{-1}, 77 K, neat). At 400 °C, the peak due to the oxoketenimine decreased, and those due to **15M** increased in intensity. The imidoylketene was now no longer detectable in the spectrum, being absent or obscured by **15M**. By 500 °C, only peaks due to **15M** and quinolone **13Ma** remained.

Methyl *N*-(4-Methylphenyl)ketenimine-2-carboxylate (12Ma) and 2-Methoxy-6-methylquinoline-4-one (13Ma). Compound **9Ma** (68 mg) was subjected to preparative FVT at 300 °C. The product was collected in a 77 K U-tube, dissolved in CCl_4, and purified by Kugelrohr distillation (60 °C/7 × 10^{-5} mbar) to give a clear oil, identified as **12Ma** (15 mg; 34%): IR (CCl_4) 2046, 1718, 1437, 1240, 1152 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.35 (s, 3H), 3.70 (s, 3H), 4.55 (s, 1H), 7.18 (s, 4H); ^{13}C NMR ($CDCl_3$) δ 21.2, 51.7, 52.1, 124.6, 130.3, 139.59, 139.61, 168.8, 175.6; MS *m/z* 189.0793, calcd for $C_{11}H_{11}NO_2$ 189.0789. Chromatography of the remaining material on SiO_2, eluting with ether/hexane, afforded quinolone **13Ma** (10 mg; 23%): mp 292−294 °C; IR (KBr) 3369, 1634, 1591 cm^{-1}; ^1H NMR (DMSO-d_6) δ 2.36 (s, 3H), 3.49 (s, 3H), 5.83 (s, 1H), 7.33−7.67 (m, 3H), 11.25 (s, 1H); ^{13}C NMR (DMSO-d_6) δ 20.7, 58.8, 98.4, 114.9, 116.3, 123.2, 130.6, 138.5, 162.9, 189.9; MS *m/z* 189.0790, calcd for $C_{11}H_{11}NO_2$ 189.0789. Anal. Calcd for $C_{11}H_{11}NO_2$: C, 69.81; H, 5.86; N, 7.41. Found: C, 70.01; H, 6.16; N, 7.20.

Methyl 3-Methoxy-3-(4-methylphenylimino)propanoate (16Ma) and Quinolone 13Ma. FVT of **9Ma** was carried out at 500 °C. MeOH was then injected onto the coldfinger, the mixture was allowed to thaw, and the resulting solution was condensed and distilled (80 °C/5.5 × 10^{-5} mbar) to give a yellow oil, identified as **16Ma** (18 mg; 38%: IR (CCl_4) 1750, 1680 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.28 (s, 3H), 3.21 (s, 2H), 3.67 (s, 3H), 3.82 (s, 3H), 6.65−7.09 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 20.7, 35.9, 52.3, 53.7, 120.8, 128.6, 145.3, 156.8, 168.3; MS *m/z* 221.1054, calcd for $C_{12}H_{15}NO_3$ 221.1052. Anal. Calcd for $C_{12}H_{15}NO_3$: C, 65.13; H, 6.84; N, 6.33. Found: C, 64.98; H, 6.72; N, 6.12. An involatile solid depositing in the air-cooled part of the apparatus was identified as quinolone **13Ma** (22 mg; 55%) by NMR.

Trapping of Ketenimine 12Ma. Compound **16Ma** was obtained in 83% yield by stirring the distilled ketenimine **12Ma** (17 mg) with excess MeOH at room temperature for 16 h.

Isomerization of Ketenimine 12Ma. The freshly distilled ketenimine was subjected to FVT at 400 °C, and the neat pyrolysate was isolated at 77 K on KBr: IR (77 K) 2046, 1711, 1699, 1441, 1242 cm^{-1} due to **12Ma**. A new, weak band at 2136 cm^{-1} is ascribed to ketene **11Ma**. A white solid depositing in the air-cooled part of the apparatus was identified as quinolone **13Ma**.

Preparative FVT of Triazole 19. (a) **19** (80 mg) was thermolyzed at 500 °C (sublimation temperature 95 °C) for 2 h. Kugelrohr distillation of the product mixture afforded ketenimine **12Ma** (17 mg; 24%), identified by IR, ^1H and ^{13}C NMR, and MS. The residue from the distillation was separated into two compounds by column chromatography (hexane/$CHCl_3$ 60:40). The first was identified as **methyl 5-methylindole-3-carboxylate** (**20**): 12 mg (17%); R_f = 0.31; mp 160−161 °C; IR (KBr) 3236, 1667, 1529 cm^{-1};^1H NMR ($CDCl_3$) δ 2.47 (s, 3H), 3.91 (s, 3H), 7.05−7.97 (m, 3H), 7.85 (d, 1H), 8.53 (br s, 1H); ^{13}C NMR ($CDCl_3$) δ 21.6, 51.0, 108.3, 111.1, 121.1, 124.8, 126.0, 131.0, 134.3, 165.7; MS *m/z* 189.0790, calcd for $C_{11}H_{11}NO_2$ 189.0789. Anal. Calcd for $C_{11}H_{11}NO_2$: C, 69.81; H,. 5.86: N, 7.41. Found: C, 69.66; H, 5.70; N, 7.42. The second compound was identified as quinolone **13Ma** (28 mg; 40%; R_f = 0.10; mp 292−294 °C). (b) Analogous FVT of triazole **19** (65 mg) at 600 °C afforded indole **20** (5 mg; 9%) and quinolone **13Ma** (41 mg; 74%).

4-Methoxyphenyliminopropadienone (15X). Compounds **9Xa**, **9Xb**, and **9Xc** were each subjected to FVT at 700 °C with isolation of the products in Ar matrix on a BaF_2 disk. IR of **15X** (Ar, 15 K) 2252 (s), 2246 (vs), 2239 (s), 2137 (w) cm^{-1}. Other peaks: acetone, CO_2, methanethiol, and dimethylamine, as described above.

Preparative FVT of 9Xa. (a) (150 mg) was performed at 700 °C and the intermediates on the 77 K coldfinger were trapped with MeOH. The resulting material was washed with $CHCl_3$−MeOH (1:1) and separated by column chromatography to afford **16Xa** (54 mg; 47%) and **13Xa** (34 mg; 34%). Spectral data for **16Xa**: ^1H NMR ($CDCl_3$, 400 MHz) δ 3.17 (s, 2H), 3.63 (s, 3H), 3.71 (s, 3H), 3.76 (s, 3H), 6.75 (m, 4H); ^{13}C NMR

($CDCl_3$) δ 35.9, 52.4, 53.8, 55.4, 114.4, 121.9, 141.1, 150.5, 155.9, 168.4. MS *m*/*z* 237.0999, calcd for $C_{12}H_{15}NO_4$ 237.1001.

Preparative FVT of 9Xc. 3-Dimethylamino-3-(4-methoxyphenylimino)-*N*,*N*-dimethylpropanamide (16Xe). Compound **9Xc** (100 mg) was sublimed at 130−140 °C (3×10^{-5} mbar) and thermolyzed through the oven at 700 °C onto a 77 K coldfinger. The system pressure was then equalized with N_2, and excess dimethylamine in ether was injected onto the coldfinger. After warming to room temperature, the oily residue was passed through a short column. Elution with $CHCl_3$ afforded **16Xe** (55 mg; 67%): ^{1}H NMR ($CDCl_3$) δ 2.68 (s, 3H), 2.84 (s, 3H), 3.09 (s, 6H), 3.42 (s, 2H), 3.70 (s, 3H), 6.74 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 34.2, 35.5, 37.3, 39.4, 55.4, 114.2, 124.8, 139.2, 156.4, 157.6, 166.6; MS *m*/*z* 263.1613, calcd for $C_{14}H_{21}N_3O_2$ 263.1628.

3-Methoxy-3-(4-methoxyphenylimino)-*N*,*N*-dimethylpropanamide (16Xc). Compound **9Xc** (100 mg) was thermolyzed as above, and the products were collected in a U-tube at 77 K. During sublimation, the U-tube temperature was periodically raised to remove $NHMe_2$. It was not possible to eliminate the amine completely. After 2 h of thermolysis, MeOH was injected onto the U-tube. After the U-tube had warmed to room temperature under N_2, column chromatography ($CHCl_3$) of the oily residue afforded **16Xc** as a yellow oil (40 mg; 51%): ^{1}H NMR ($CDCl_3$) δ 2.83 (s, 3H), 2.90 (s, 3H), 3.23 (s, 2H), 3.74 (s, 3H), 3.80 (s, 3H), 6.78 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 35.4, 35.5, 37.5, 53.7, 55.4, 114.2, 122.2, 141.4, 155.8, 158.5, 167.2; MS *m*/*z* 250.1313, calcd for $C_{13}H_{18}N_2O_3$ 250.1312.

***N*-(4-Methoxyphenyl)ketenimine-*C*-(*N*,*N*-dimethylcarboxamide) (12Xc).** After similar FVT of **9Xc** as above, CD_2Cl_2 was condensed on the 77 K coldfinger. On thawing, the resulting solution flowed into a precooled NMR tube at −80 °C. The NMR tube was flame sealed under N_2. Spectral data for **12Xc**: ^{1}H NMR (CD_2Cl_2, −70 °C) δ 2.93 (s, 3H, NMe), 2.98 (s, 3H, NMe), 3.75 (s, 3H), 5.05 (s, 1H), 6.85 (d, 2H), 7.23 (d, 2H). The two NMe singlets coalesced on warming to −10 °C (400 MHz, $\Delta\nu$ = 20 Hz). IR (CD_2Cl_2 or CH_2Cl_2, rt) 2036 (s) cm^{-1}.

Conversion of Ketenimine 12Xc to Quinolone 13Xc. (a) Ketenimine **12Xc** was prepared in CD_2Cl_2 solution as in the previous entry. Warming to room temperature resulted mainly in polymerization of the ketenimine in the course of 3 d. Only traces of quinolone were formed under these conditions. (b) Warming a CD_2Cl_2 solution to 40 °C and maintaining it at this temperature for 15 h resulted in a 15% isolated yield of quinolone **13Xc**. (c) Refluxing an analogous sample in 1,2-dichloroethane at 83 °C for 24 h resulted in an improved yield of quinolone **13Xc** (20% based on the starting material **9Xc**; 38% based on the material arriving on the coldfinger).

FVT of 16Xa,c,e. Analytical and preparative FVT of **16Xa,c,e** at 600 °C and above did not give detectable ketenimine **12X**, which would not have survived this temperature. Instead, there was formation of quinolone **13Xc** from **16Xe** in the sublimation tube itself, as confirmed by TLC and ^{1}H NMR. **13Xc** was also formed from **16Xe** on GC−MS (injector temp 200 °C). In contrast, **16Xa** and **16Xc** were stable and did not form the corresponding quinolones **13Xa,c** under these conditions.

***N*-Mesitylketenimine-2-(*N*,*N*-dimethylcarboxamide) (23) and 3-Dimethylamino-3-[(2,4,6-trimethylphenyl)-imino]-*N*,*N*-dimethylpropanamide (24).** *N*-Mesitylaminopropadienone (**22**)[12] (30 mg; 0.16 mmol) was treated with 1 equiv of $HNMe_2$ (7.3 mg) in $CDCl_3$ or CD_2Cl_2 (0.5 mL) in an NMR tube at −60 °C. No significant reaction was observed until −40°, when signals ascribed to ketenimine **23** appeared at δ 2.24 (s, 6H), 2.33 (s, 3H), 2.96 (s, 3H), 2.97 (s, 3H), 4.58 (s, 1H), 6.75 (s, 2H) ($CDCl_3$, 500 MHz). The two singlets at 2.96 and 2.97 ppm ($\Delta\nu$ = 5 Hz) coalesced on warming to 248 K. This NMR spectrum is similar to that reported for methyl 1-mesitylketenimine-3-carboxylate.[31] By using IR spectral monitoring, the formation of a ketenimine absorbing at 2088 cm^{-1} (neat) became noticeable from −70 °C onward. Treatment of the NMR solution with excess $HNMe_2$ at either −40 °C or room temperature gave amidoamidine **24**: ^{1}H NMR (CD_2Cl_2, 400 MHz) δ 1.96 (s, 6H mesityl), 2.21 (s, 3H, mesityl), 2.53 (s, 3H, amide-NMe_2), 2.79 (s, 3H, amide-NMe_2), 3.01 (s, 6H, amidine-NMe_2), 3.13 (s, 2H, CH_2), 6.75 (s, 2H,). The assignment was confirmed by a DEPT spectrum and by the coalescence experiments described below. Addition of the shift reagent Eu(fod)$_3$ caused shifting but no splitting of any of the singlets. The 6-proton amidine NMe_2 signal at 3.01 ppm decoalesced on cooling the CD_2Cl_2 solution to 227 K (400 MHz, $\Delta\nu$ = 49.8 Hz). The two 3-proton amide NMe signals coalesced on heating the solution in CD_2ClCD_2Cl to 383 K (400 MHz, $\Delta\nu$ = 134.6 Hz).

Quinolones from the Ynamine−Isocyanate Reaction. (a) 2-Dimethylamino-4-quinolone (34a = 13Hc). *N*,*N*-Dimethyl-*N*-(trimethylsilylethynyl)amine (**32a**) was prepared from dimethylamine in the manner described for the diethyl analogue:[27] ^{1}H NMR ($CDCl_3$) δ 0.25 (s, 9H), 2.86 (s, 6H); ^{13}C NMR ($CDCl_3$) δ 0.99, 42.9, 65.4, 111.0. Equimolar amounts of this compound (100 mg; 0.70 mmol) and phenyl isocyanate (84 mg) were stirred in benzene or MeCN solution at room temperature under N_2 for 3 d. Preparative TLC, eluting with 10% MeOH/$CHCl_3$ afforded 30 mg (23%) of **13Hc**.

(b) 2-Diethylamino-4-quinolone (34b). *N*,*N*-Diethyl-*N*-(trimethylsilylethynyl)amine (**32b**) was prepared according to the literature:[27] ^{1}H NMR ($CDCl_3$) δ 0.1 (s, 9H), 1.53 (t, 6H), 2.90 (q, 4H); ^{13}C NMR ($CDCl_3$) δ 0.98, 12.7, 47.7, 64.2, 108.6; IR 2142 cm^{-1}. A 100 mg (0.59 mmol) portion of this compound was stirred with 70 mg (0.59 mmol) of PhNCO in 10 mL of either benzene or MeCN at room temperature for 24 h. GC−MS of the crude product indicated the presence of **33b** (*m*/*z* 288) and **34b** (*m*/*z* 216). Workup as in (a) afforded **34b** (20 mg (16%) from benzene or 30 mg (26%) from MeCN): ^{1}H NMR (DMSO-d_6) δ 1.16 (t, 6H), 3.50 (q, 4H), 5.70 (br s, 1H, typical of H(C-3)), 7.01 (t, J = 15 Hz, 1H), 7.43 (t, J = 15 Hz, 1H), 7.53 (d, J = 8 Hz, 1H), 7.90 (d, J = 8 Hz, 1H); IR (KBr) 3263, 1637, 1596 cm^{-1}. Anal. Calcd for $C_{13}H_6N_2O$: C, 72.22; H, 7.40; N, 12.96. Found: C, 72.11; H, 7.57; N, 12.62.

Acknowledgment. This research was supported by the Australian Research Council. We also thank the Deutsche Forschungsgemeinschaft for a postdoctoral fellowship for T.M..

Supporting Information Available: Partial FTIR spectra of the products of FVT of **17** and **18**; FTIR spectra of **12Ma** and its FVT product at 400 °C, showing ketene formation; Ar matrix FTIR spectra of **15M** and **15X**; ^{1}H NMR spectra of **12Ma**, **12Hc** (223 and 300 K), **12Xc** (203 K), **16Hc**, **16Xa, 16Xe**, and **24**. ^{13}C NMR spectra of **12Ma**, **12Hc, 16Hc**, **16Xe** (DEPT), and **24** (DEPT). HSQC 2D ^{1}H−^{13}C NMR correlations for **13Hb**, **13Xa**, and **13Xb**. This material is available free of charge via the Internet at http://pubs.acs.org.

JO982471Y

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