N-Mesityl-*C*-acylketenimines: 1,5-Sigmatropic Shifts and Electrocyclization to Quinolines

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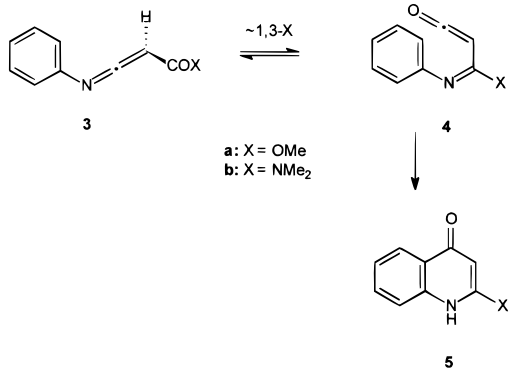
Flash vacuum thermolysis (FVT) of triazoles **6a**−**c** generates α-oxoketenimines **10**, the ester **10a** being isolable. FVT of pyrroledione **8** generates the isomeric imidoylketene **9a**. Ketenes **9** and ketenimines **10** undergo thermal interconversion by 1,3-shifts of methoxy and dimethylamino groups under mild FVT conditions (ca. 350−400 °C). Both **9** and **10** are directly observable by IR spectroscopy at either 77 K or on Ar matrix isolation at 12 K. On FVT at temperatures above ca. 400 °C, the ketenimines **10** undergo a 1,5-H shift to *o*-quinoid imines **12/13**, followed by electrocyclization to dihydroquinolines **14** (unobserved) and **15** (observed by NMR). The latter are easily oxidized to alkylquinoline-3-carboxylates or quinoline-3-carboxamides **16** by atmospheric oxygen. Ab initio calculations on model compounds **18**−**23** predict an energy barrier of ca. 38 kcal mol^{-1} (161 kJ mol^{-1}) for the 1,5-H shift in *N*-(*o*-methylphenyl)ketenimines via the transition state **TS19** followed by an electrocyclization barrier to dihydroquinoline **23a** via **TS22a** of ca. 16 kcal mol^{-1}.

Introduction

It was demonstrated in previous work that imidoylketenes **1** and oxoketenimines **2** undergo an extraordinarily facile 1,3-shift of the methoxy group at temperatures as low as 200 °C under flash vacuum thermolysis (FVT) conditions. These temperatures do not reflect the energy barriers for the interconversions **1** ⇄ **2**, but are the mildest conditions possible for the generation of **1** and **2** from their precursors (1,2,3-triazoles, pyrrole-2,3-diones, and Meldrum's acid derivatives).[2] The calculated activation barriers for 1,3-shifts of electron rich groups possessing lone pairs (e.g., **1**, X = R′O, R'_2N, and Cl) are very low in the oxoketenes, oxoketenimines, and imidoylketenes.[3] For example, the 1,3-Cl shift in chlorocarbonylketenes (PhC(O)C(Cl)═C═O) takes place at −30 °C in solution.[3c] The *C*-alkoxycarbonylketenimines 2 (X = OR′) are in some cases isolable at room temperature, being susceptible to nucleophilic attack by water or methanol at the electrophilic central carbon atom of the cumulene moiety. The imidoylketenes **1** are not isolable. The *N*-arylimidoylketenes (**4**, X = OMe or NMe_2) undergo a very facile cyclization to quinoline-4-ones (**5**).[2]

In an attempt to hinder the cyclization to a quinolin-4-one, we have studied *C*-alkoxycarbonyl- and *C*-carboxamidoketenimines **10** carrying *N*-mesityl and *N*-(2,6-dimethylphenyl) groups, generated by FVT of triazole and pyrroledione precursors **6** and **8** (Scheme 1). The outcome is another cyclization reaction, involving an aromatic *o*-methyl group and leading to quinolines **16** as the major products.



Results

1. FVT Experiments. FVT of the 1,2,3-triazole **6a** was carried out with product isolation on a BaF_2 disk at 77 K for observation by IR spectroscopy. At a FVT temperature of 400 °C, weak signals ascribed to *N*-mesityl-3-carbomethoxyketenimine **10a** and imidoylketene **9a** were observed (Figure 1a; Scheme 1). The identity of the ketenimine **10a** was established by isolation (see Experimental Section). At 500 °C, a strong signal due to the oxoketenimine **10a** together with a weak signal due to the ketene **9a** was observed (Figure 1b). As the temperature increased to 600 °C, both intermediates **9a** and **10a** decreased in absolute intensity (Figure 1c), and further decrease occurred at higher FVT temperatures. Neither **9a** nor **10a** was observable after FVT at 800 °C. Upon warming the deposition disk to room temperature, the imidoylketene **9a** disappeared at −10 °C, whereas the oxoketenimine **10a** remained observable and isolable

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(2) (a) Fulloon, B. E.; Wentrup, C. *J. Org. Chem.* **1996**, *61*, 1363. (b) Fulloon, B. E.; El-Nabi, H. A. A.; Kollenz, G.; Wentrup, C. *Tetrahedron Lett.* **1995**, *36*, 6547.(c) Clarke, D.; Mares, R. W.; McNab, H. *J. Chem. Soc., Chem. Commun.* **1993**, 1020. (d) Clarke, D.; Mares, R. W.; McNab, H. *J. Chem. Soc., Perkin Trans. 1* **1997**, 1799. (e) Synthesis of **3b** and **5b**: Rao, V. V. R.; Wentrup, C. *J. Chem. Soc., Perkin Trans 1* **1998**, in press.

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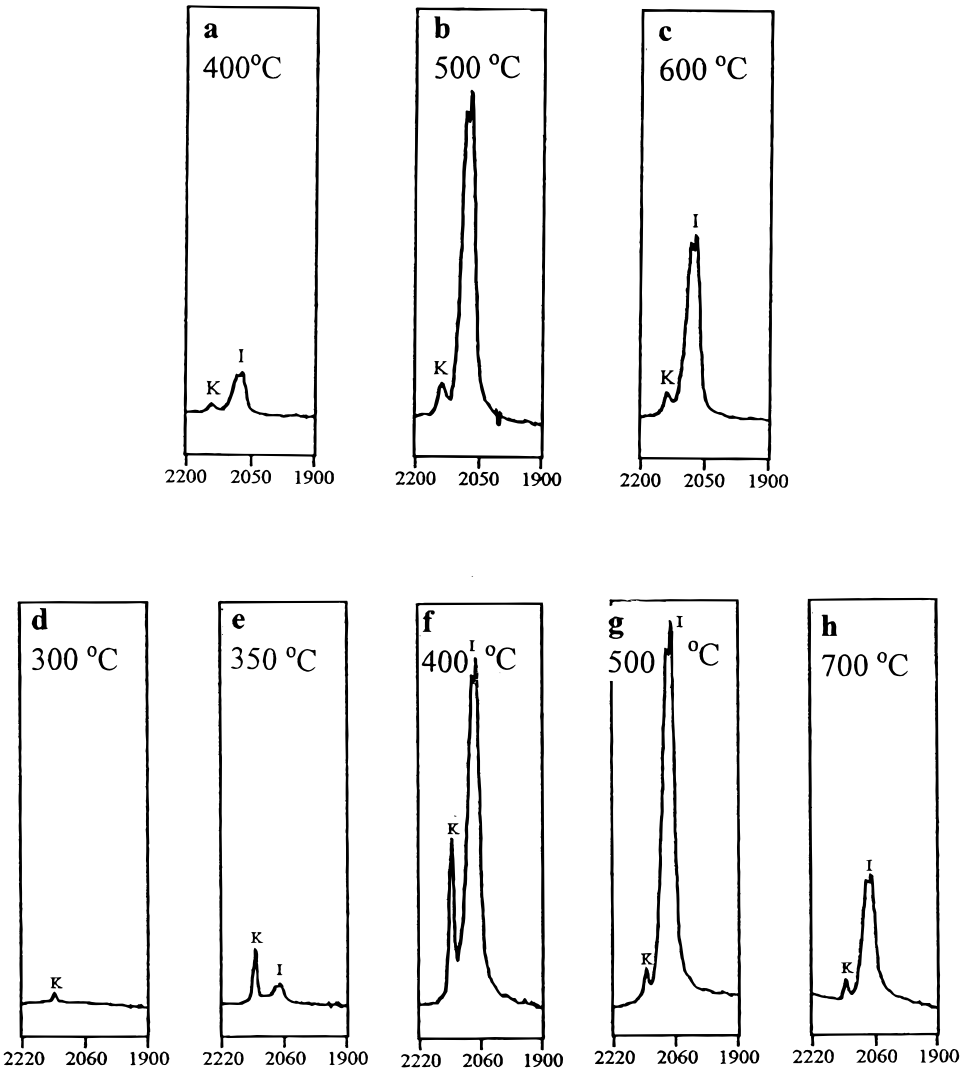
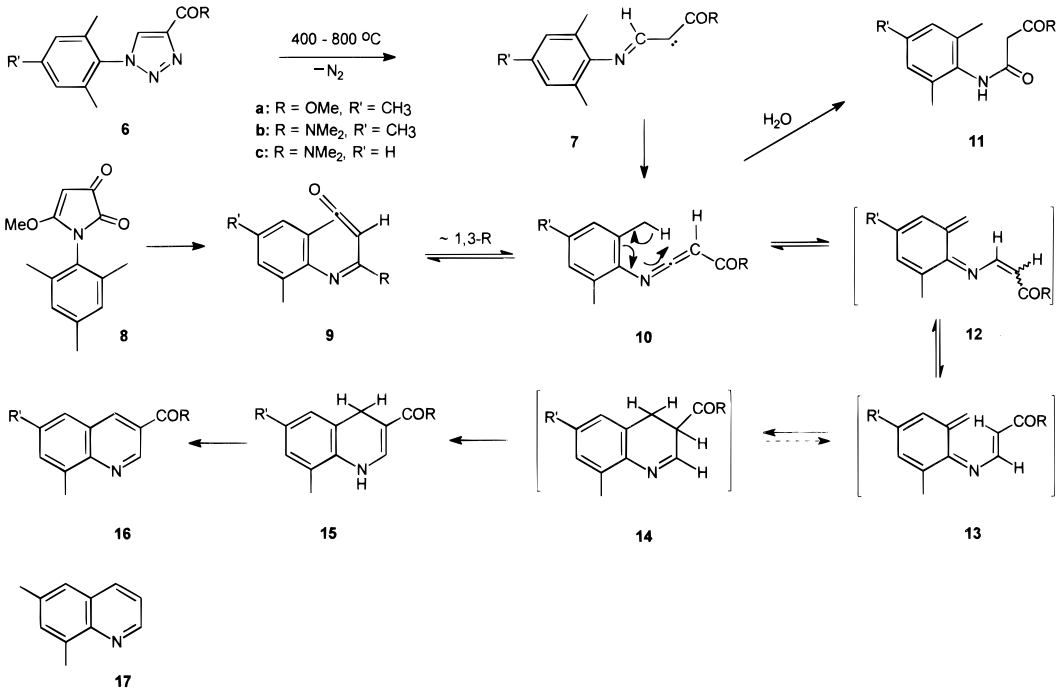


Figure 1. Partial IR spectra (77 K; 1900−2200 cm^{-1} range; absorbance 0.04−0.33) of the products of FVT (a−c) of triazole **6a** at 400−600 °C and (d−h) of pyrroledione **8** at 300−700 °C. K = ketene **9a** (2135 cm^{-1}). I = oxoketenimine **10a** (2081, 2069 cm^{-1}).

Scheme 1



at room temperature. FVT above 700 °C resulted in the appearance of a new species absorbing at 1721 cm^{-1} and assigned as quinoline **16a**, which was subsequently isolated. Quinoline **16a** actually started appearing already at ca. 400 °C but condensed in the cooler parts of the apparatus before reaching the BaF_2 disk under these conditions.

Preparative FVT of **6a** at 450 °C afforded the ketenimine **10a** (isolated in 21% yield) and the quinoline **16a** (56%). Ketenimine **10a** was stable at room temperature for short periods of time and can be stored under N_2 at −5 °C for 1−2 weeks but reacts with atmospheric moisture to give amide **11a**. The ^1H and ^{13}C NMR spectra of this compound indicate that it exists in the amide rather than the tautomeric imide form.

As indicated in Scheme 1, the formation of quinoline **16** is explained in terms of a 1,5-H shift in ketenimine **10** to give the o-quinoid imine **12**. Electrocyclization of **13** affords dihydroquinolines **14** (unobserved) and **15** (observed) prior to oxidation to **16**.

Evidence for the presence of the dihydroquinoline intermediate **15a** was obtained by GCMS and ^1H NMR spectroscopy of the product of the preparative FVT of **6a** at 450 °C; this gave a ratio of ca. 1:2.8 of **15a** to **16a**. The amount of **15a** rapidly decreased, and that of **16a** increased correspondingly due to oxidation by atmospheric oxygen. After ca. 24 h only the quinoline **16a** was present, and it was isolated in 56% yield. The quinoline mixture started forming at 350 °C (preparative FVT), when much of the starting material was recovered unchanged, giving a ratio of **6a:10a:(15a** + **16a)** = 24:33:9.

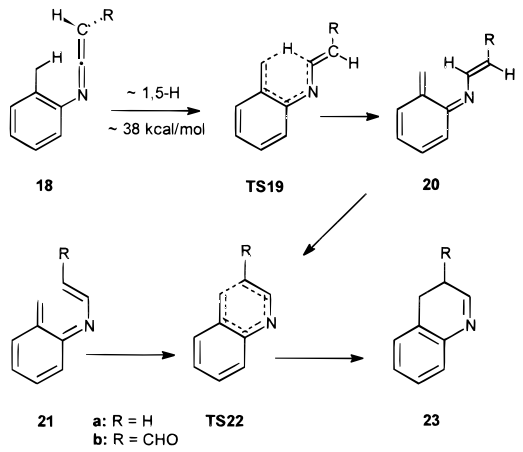
On preparative FVT of **6a** at 700 °C, a mixture of **15a** and **16a** was again obtained. The quinoline **16a** was isolated in 65% yield after full oxidation of **15a**. The ^1H NMR spectrum of **15a** (in admixture with **16a**) features a singlet at 3.71 ppm, ascribed to the CH_2 group, a doublet at 7.34 ppm (H−C(2)), and a broad singlet at 5.85 ppm (NH). Exchange with D_2O caused the latter to disappear and the doublet at 7.34 ppm to collapse to a singlet. The IR spectrum of the mixture of **15a** and **16a** showed a strong, broad signal at 3337 cm^{-1}, assigned to the N−H stretch in the dihydroquinoline **15a**.

The structure of the quinoline **16a** was ascertained by an X-ray crystal structure determination (Figure S1). Crystal data and bond lengths and angles are reported in Tables S1 and S2 (Supporting Information).

FVT of the *N*-mesityl-5-methoxypyrroledione **8** (Scheme 1) produced results similar to those described above (Figures 1d−h). At 300 °C a weak band due to the imidoylketene **9a** appeared in the IR spectrum. When the temperature was increased to 350 °C, the oxoketenimine **10a** appeared, and the imidoylketene **9a** increased in intensity. At 400 °C both oxoketenimine **10a** and imidoylketene **9a** increased in intensity. At 500 °C, there was a strong signal due to oxoketenimine **10a**, together with a weak one due to ketene **9a**. The IR spectrum (Figure 1g) was now similar to the one shown in Figure 1b. The only observable species at 800 °C was the quinoline **16a** (1723 cm^{-1}).

Preparative FVT of the pyrroldione **8** at 450 °C again yielded the oxoketenimine **10** (23%) and a mixture of the dihydroquinoline **15a** and quinoline **16a**. Over a short time period in the presence of air, **15a** was totally converted to **16a** (53%). FVT of **8** at 600 °C gave **15a** and **16a** as the only species, thus indicating that the imidoylketene **9** was converted to oxoketenimine **10** and the latter was totally converted to the cyclized products **15a** and **16a** (combined yield 68%).

Scheme 2



Preparative FVT of the isolated and distilled ketenimine **10a** also resulted in the formation of the quinolines **15a** and **16a**. Direct evidence for the isomerization of ketenimine **10a** to ketene **9a** was obtained by IR spectroscopy of the 77 K pyrolysate resulting from FVT of **7a** at 400 °C: a small amount of the ketene was observed in the presence of a large amount of unchanged ketenimine. The quinoline mixture **15a/16a** also started forming at this mild temperature (400 °C). At 700 °C and after complete oxidation of **15a**, the quinoline **16a** was isolable in 84% yield.

Similar FVT of the analogous 1-mesityltriazole-4-carboxamide **6b** above 500 °C gave rise to an absorption at 2058 cm^{-1} (weak at 500 °C; strong at 600 °C) ascribed to the corresponding ketenimine **10b**, which persisted on warm up to 0 °C. The ketene **9b** was not observable at 77 K, but on Ar matrix isolation at 12 K it appeared at 2133/2138 cm^{-1} (weak at 540 °C; strong at 700 °C FVT temperature). The ketenimine **10b** absorbed strongly at 2061 cm^{-1}.

Preparative FVT of triazole **6b** at 600 °C resulted in quinoline **16b** (56%) together with the unexpected 6,8-dimethylquinoline **17** (29%). The ketenimine **10b** was not isolable at room temparature. GCMS of the crude product gave the ratio of **16b** and **17** as 2.8:1.

FVT of the *N*-(2,6-dimethylphenyl)triazole **6c** under the same conditions as used for **6b** at 600 °C gave rise to a strong absorption at 2059 cm^{-1} in the IR spectrum (77 K), assigned to ketenimine **10c**. Preparative FVT at 600−700 °C afforded only quinoline **16c** (67% isolated yield) and no methylquinoline corresponding to **17**. FVT of quinolinecarboxamide **16b** at temperatures up to 800 °C did not produce the quinoline **17**; the source of this compound in the thermolysis of **6b** remains unknown.

2. Theory. To examine the energy requirement for the rearrangement of oxoketenimines to the quinolines, ab initio molecular orbital calculations[4] were carried out on the 1,5-sigmatropic shift from the ketenimine **18** to the *o*-quinoid imine **20** via the transition state **TS19** (Scheme 2) using the GAUSSIAN 94 system of programs.[5] Structures and energies were examined at the G2(MP2,SVP) level of theory[6] for **18a**, **TS19a**, **20a**, **22a**,

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Table 1. Calculated Relative Energies (kcal mol^{-1}) of Ketenimines, Transition Structures, Vinylimines, and Electrocyclization Products (Schemes 2 and 3)

	computational level	
	MP2/6-31G*// MP2/6-31G*+ZPVE	G2(MP2,SVP)+ZPVE
18a	0	0
TS19a	42.0	40.8
20a	26.8	20.4
18b	0	0
TS19b	39.7	38.6[a]
20b	26.9	20.4[a]
21a		*b*
TS22a		36.5
23a		−23.5
24		0.0
TS25		30.2
26		2.03
27		0.23
TS28		22.6
29		−22.8

[a] Estimated value; see text. [b] Not located as a minimum computationally.

and **TS23a** (R = H). This corresponds effectively to QCISD(T)/6-311+G(3df,2p)//MP2/6-31G* energies together with zero-point vibrational and isogyric corrections. In the G2(MP2,SVP) theory, the basis-set extension energy contribution is calculated at the MP2 level, and the QCISD(T) energy is evaluated using the 6-31G* basis set. It has been shown that the accuracy of the G2(MP2,SVP) method is comparable with that of the G2(MP2) theory[7] but computationally more efficient.[6] The frozen core approximation was employed for all correlated calculations. Zero-point vibrational energy calculations were performed at the HF/6-31G* level.

The influence of a CHO group in **18b**−**20b** was calculated only at the MP2/6-31G*//MP2/6-31G* level of theory. However, estimated G2(MP2,SVP) values for the relative energies of these structures can be obtained by applying the corresponding changes in relative energies for **18a**−**20a** when going from MP2/6-341G* to G2(MP2,-SVP) theory. For this purpose, the difference between the G2(MP2,SVP) and the MP2/6-31G*//MP2/6-31G* energies for **18a**−**20a** without ZPVE corrections is used, since the latter are different in the two cases. The resulting energy increments are then added to the MP2/6-341G*//MP2/6-31G*+ZPVE values for **18b**−**20b**. The calculated relative energies are summarized in Table 1, and selected geometries are given in Figure 2. The MP2/6-31G*//MP2/6-31G* value for the activation barrier (**18b** (**TS19b**) is 39.7 kcal mol^{-1} (166 kJ mol^{-1}), and the estimated G2(MP2,SVP) value is 39 kcal mol^{-1} (161 kJ mol^{-1}).

In the transition structures **TS19**, the migrating hydrogen atom is ca. 0.5 Å above the plane of the molecule. The terminal CH_2 group has twisted to provide

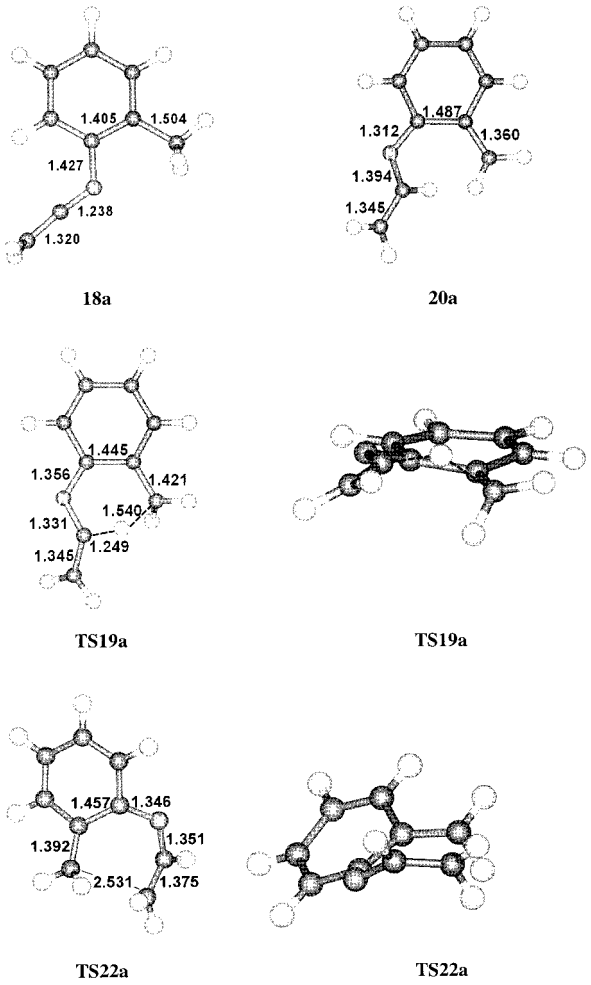

Figure 2. Computed structures of **18a** and **20a** (upper), **TS19a** (middle; planar projection and perspective views; the H atom is migrating ca. 0.5 Å above the molecular plane), and **TS22a** (bottom; planar and perspective views) (MP2/6-31G*). Bond lengths in Å and angles in degrees.

conjugation in the forming C═NC═C moiety in **20** (Figure 2). As the hydrogen atom is being transferred toward the in-plane allenic p orbital, one could expect a pseudopericyclic nature of the reaction.[8] However, **TS19** is not appreciably different from those of ordinary pericyclic reactions such as the 1,5-H shift in 1,3-pentadiene,[9] which we have recalculated at the same level of theory. On the other hand, a comparison of the reaction temperatures required for a 1,5-H shift to an allene (**32**) (170 °C) and to a vinylic carbon in the analogous 1-mesitylpropene (**36**) (> 300 °C) (Scheme 3) reveals a very significant acceleration in the cumulenic systems. The exact nature of this "allene effect"[19] (see Discussion) requires further theoretical investigation. Likewise, the 1,5-H shift in allene **38** has a barrier some 10 kcal mol^{-1} below that in 1,3-pentadiene **40**, as discussed below.

The second step in the formation of dihydroquinolines **23** is formulated as a $[2_\pi + 2_\pi + 2_\pi]$ electrocyclization of the *Z*-vinylimine **21** (Scheme 2). Such reactions are expected to have activation barriers of the order of 26−29 kcal mol^{-1} in simple, i.e., not *o*-quinoid, systems.[9,10]

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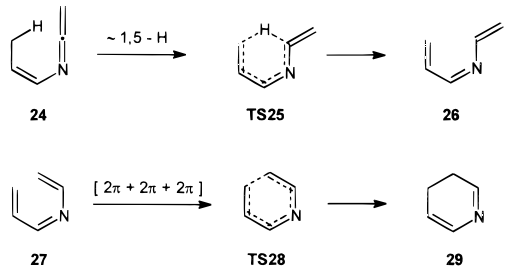
(9) Houk, K. N.; Li, Y.; Evanseck, J. D. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 682−708.

Scheme 3



As mentioned below, only a minimum for *E*-**20a**, not for *Z*-**21a**, was actually located.

To evaluate the consequences of the loss of the benzene resonance energy in **TS19**, **20**, and **21**, we have calculated the activation barriers for the 1,5-H shift in the nonaromatic model *N*-vinylketenimine **24** and the electrocyclization of *Z*-3-azahexa-1,3,5-triene **27** via transition structures **TS25** and **TS28** at the G2(MP2,SVP) level (Scheme 3 and Table 1). The 1,5-H shift barrier of 30 kcal mol^{-1} is ca. 10 kcal mol^{-1} below the aromatic case (**18**−**20**) in Scheme 2.

For the electrocyclization **27** → **29**, the computed activation energy is ca. 23 kcal mol^{-1}, and the reaction is exothermic by ca. 23 kcal mol^{-1}. For the benzo system **20a**, the transition state **TS22a** for electrocyclization lies only ca. 16 kcal mol^{-1} above the *E*-imine **20a**. A minimum for the *Z*-imine **21a** was not located. This cyclization to isoquinoline **23a** is exothermic by ca. 43 kcal mol^{-1} due to the recovery of aromaticity (Scheme 2 and Figure 2). The very low barrier suggests a very early transition state **TS22a** in terms of the Hammond postulate. This is borne out in the calculated structure (Figure 2), which features a distance of 2.53 Å between the two carbon atoms where the new single bond will form. This is only a little shorter than the van der Waals radii (2.9 Å). In the nonbenzo system **27**, the cyclization is much less exothermic (22 kJ mol^{-1}; Table 1; Scheme 3) and the **TS28** is more advanced (the corresponding C−C distance is 2.25 Å). When going from imine **20a** to **23a**, the bonds involved change by an average of 12 pm. In **TS22a** the changes are only ca. 3 pm. In **TS28** they are 5−6 pm (all geometry data are given in Tables S3 and S5 in the Supporting Information).

Discussion

The isomerization of ketenimines **10** to dihydroquinolines **14** (and then **15** and **16**) takes place under very mild FVT conditions. The 1,3-shift of the methoxy group, converting the ketenimine **10a** to ketenes **9a**, is detectable at FVT temperatures > 400 °C. In related earlier work we established such shifts taking place at temperatures > 380 °C from the ketenimine side and > 200 °C from the ketene side.[2a−b] The calculated activation barrier for the 1,3-MeO shift in methoxycarbonylketenimine is ca. 35 kcal mol^{-1} (ca. 32 kcal/mol from the methoxyimidoylketene side; at the G2(MP2,SVP) level of theory).[11] The preparative and analytical experiments with **6** and **10a** reported here reveal that quinolone formation commences at ca. 400 °C (analytical conditions) or 350 °C (preparative conditions), i.e., at temperatures similar to or just a little above those resulting in 1,3-MeO shifts. (These temperatures are upper limits; the 1,3-MeO shifts in ketenes take place as soon as the ketenes can be observed.) The calculated activation barrier of ca. 38 kcal mol^{-1} (ca. 161 kJ mol^{-1}) for the 1,5-H shift leading to quinolone formation is thus in qualitative agreement with the mechanistic interpretation given in Scheme 1.

The ratios of intensities of oxoketenimine (**10**) and imidoylketene (**9**) peaks in the IR spectra (Figure 1) cannot be taken as a true indication of equilibrium ratios (even disregarding the unknown differences in extinction coefficients), because the ketenimines are being removed from the equilibria by cyclization to the quinolones. However, it should be noted that the observed peak ratios are very similar to those found in the analogous *N*-phenyl derivatives, where the ketenes (and not the ketenimines) are being removed from the equilibria by cyclization to quinoline-4-ones.[2a−c] It appears, therefore, that the strong ketenimine peaks in the IR spectra in fact do reflect a preponderance of the ketenimines in equilibrium with the ketenes. This, too, is in agreement with ab initio calculations, which predict the oxoketenimines to be lower in energy than the imidoylketenes by ca. 2 kcal mol^{-1}.[11]

The 1,5-H shifts/electrocyclizations of ketenimines **10** to quinolines **15**−**16** can be compared with analogous reactions in the literature. Motoyoshiya et al. reported rearrangement of *C*-sulfenyl-*C*-ethoxycarbonyl-*N*-phenylketenimines to quinoline-4-ones on reflux in 1,2-dichlorobenzene (180 °C) and postulated imidoylketene intermediates formed by 1,3-shifts of the ethoxy groups.[12] The ketene intermediates could not, however, be observed under such reaction conditions. It was also found that the 2,6-disubstituted ketenimine **30** disappeared on heating to 250 °C, but the product of this reaction could not be identified.[13] The results reported in the present paper suggest that cyclization to the dihydroquinoline **31** took place.

Heimgartner et al. reported thermal cyclization of mesitylallene (**32a**) to dihydronaphthalene (**34**) (Scheme 4), and isomerization of allene **32b** to **35**, taking place at 170 °C in decane with $\Delta H^{\ddagger} = 28.8$ (28.7) kcal mol^{-1} and ($\Delta S^{\ddagger} = 14.0$ (−12.8) cal K^{-1} mol^{-1}, corresponding to $\Delta G^{\ddagger}(298) = 33.0$ (32.5) kcal mol^{-1} or 138 (136) kJ mol^{-1} for **32a** and **32b**, respectively.[14] In contrast, the mesitylpropene **36** required a temperature > 300 °C for the analogous 1,5-H shift equilibrating it with **37**.[14] The open-chain system **38** undergoes a 1,5-H shift to **39** at 100 °C in the gas phase, with $E_a = 24.6$ kcal mol^{-1} [from which $\Delta H^{\ddagger} = 23.9$ kcal mol^{-1}, and $\Delta G^{\ddagger}(298)$ (estimated) ∼28 kcal mol^{-1} (117 kJ mol^{-1})].[15] This is a very low barrier for a 1,5-H shift; the normal value in open-chain 1,3-pentadienes (**40**) is on the order of 36−38 kcal mol^{-1}.[9] The low barrier for **38** has been corroborated by determination of similar activation parameters for cycloalkenylallenes in solution.[16]

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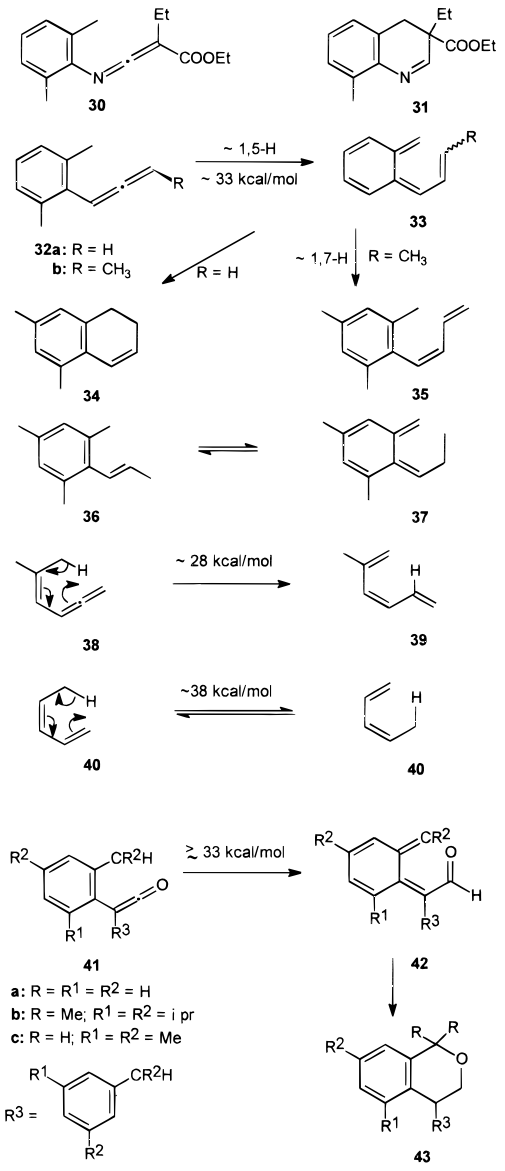
Scheme 4



An analogous cyclization of ketene **41a** to isochromene **43a** was reported as taking place at 250 °C without any further details.[17] Recently, Rappoport et al.[18] described the cyclization of **41b** to **43b** at 170 °C (decane solution, < 1 h). From the reported first-order rate constant, $k \sim 8 \times 10^{-4}$ s^{-1}, the free energy of activation can be derived with the aid of transition state theory ($k = k_B T/h \exp(-\Delta G^{\ddagger}/RT)$), yielding $\Delta G^{\ddagger} \sim 32.6$ kcal mol^{-1} (136 kJ mol^{-1}). Compound **41c** was reported to react ca. 200 times slower than **41b**, from which a rough $\Delta G^{\ddagger} \sim 37.2$ kcal mol^{-1} (155 kJ mol^{-1}) may be derived.

The above data indicate that the penalty for sacrificing the aromaticity in the transition state leading to *o*-quinodimethide **33** is only ca. 5 kcal mol^{-1} (in comparison with **38** → **39**). The calculated difference between the aromatic and open-chain ketenimines (Schemes 2 and 3) was ca. 10 kcal mol^{-1} (section 2). The significantly lower activation energy for **32** → **33** compared with the analogous 1,5-H shift in 1-mesitylpropene (**36**) (reaction > 300 °C in solution),[14] might be ascribed to a pseudopericyclic nature of the former reaction (**32** → **33**). The difference is also seen clearly in the open-chain systems, **38** → **39** versus **40** → **40**. An explanation of the "allene effect" has been given by Jensen,[19] who demonstrated computationally that this effect is specific for 1,3- and 1,5-H shifts but negligible for 1,7- and 1,9-H shifts. Jensen concluded that the allene effect is due to extra conjugation in a biradicaloid transition state.

The activation barriers for allenes **32** and ketenes **41** are similar (32.5−37 kcal mol^{-1}). Our calculated activation barrier for the 1,5-H shift in ketenimine **18**, 38 kcal mol^{-1} (161 kJ mol^{-1}) fits nicely at the upper end of this range. The electrocyclic reactions **13** → **14** (and the model reactions **20** → **23** and **27** → **29**) are normal pericyclic processes of the 3-azahexatriene type with computed activation energies of the order of 16−22 kcal mol^{-1}.

Conclusion

FVT of triazoles **6a**−**c** generates ketenimines **10** (Scheme 1). FVT of pyrroledione **8** generates the isomeric imidoylketene **9a**. Ketenes **9** and ketenimines **10** undergo a facile thermal interconvertion by 1,3-shifts of methoxy and dimethylamino groups. Both **9** and **10** are directly observable by low-temperature IR spectroscopy. When using FVT at temperatures above ca. 400 °C (analytical conditions) or 350 °C (preparative conditions), the ketenimines **10** undergo a 1,5-H shift to *o*-quinone imine methides **12**, followed by electrocyclization to dihydroquinolines **14** and then **15**. Compounds **15** are detectable by NMR spectroscopy but are easily oxidized to quinolines **16** by atmospheric oxygen. Ab initio calculations on model compounds **18**−**20** (Scheme 2) predict an energy barrier of ca. 38 kcal mol^{-1} (161 kJ mol^{-1}) for the 1,5-H shift via the transition state **TS19** and a very early transition state for the cyclization to **23** (Table 1; Figure 2).

The oxoketenimine **10a** is isolable at room temperature. It was fully characterized spectroscopically and chemically via its hydrolysis to amide **11**. FVT of this ketenimine regenerates a small amount of the isomeric imidoylketene **9a**. Both experiments and theory indicate that the oxoketenimines **10** dominate in the equilibria with imidoylketenes, **10** ⇄ 9.

Experimental Section

The pyrolysis apparatus was as previously reported for Ar matrix (12 K),[20] neat film (77 K) deposition,[21] and preparative scale work (77 K isolation).[22] BaF_2 disks were used for depositions. Due to different designs, temperatures required for a reaction to occur are often ca. 100 °C lower in the preparative than in the analytical (spectroscopic) apparatus. Details of the X-ray crystal structure analysis of **16a** are given in the Supporting Information. Reactions with azides (described below) are potentially hazardous, and due precautions against explosions should be taken. No adverse observations were made.

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Methyl 1-(2,4,6-Trimethylphenyl)-1*H*-1,2,3-triazole-4-carboxylate (6a). This compound was prepared[23] from 2,3,4-trimethylphenyl azide (3.5 g; 21.7 mmol) and methyl propiolate (1.7 g; 20.2 mmol), yielding 4.05 g (75%), mp 158−160 °C: IR (KBr) ν 3137, 2953, 1740, 1545, 1442, 1374, 1340, 1261, 1248, 1229, 1195, 1143, 1048 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.93 (s, 6H) 2.34 (s, 3H), 3.98 (s, 3H), 6.98 (s, 2H), 8.12 (s, 1H); ^{13}C NMR δ 17.3, 21.2, 52.4, 129.3, 129.6, 133.0, 134.9, 140.1, 140.7, 161.3; MS *m*/*z* 245 (M^+), 214, 185, 158, 143, 115, 91, 77, 55; HRMS calcd for $C_{13}H_{15}N_3O_2$ *m*/*z* 245.1164; found 245.1161. Anal. Calcd for $C_{13}H_{15}N_3O_2$: C, 63.67; H, 5.17; N, 17.14. Found: C, 63.79; H, 5.14; N, 17.34.

***N*,*N*-Dimethyl-1-(2,4,6-trimethylphenyl)-1*H*-1,2,3-triazole-4-carboxamide (6b).** A mixture of compound **6a** (1.2 g, 4.63 mmol) and 20% aqueous KOH (20 mL) was stirred overnight at room temperature. The reaction mixture was diluted to 50 mL and acidified with dilute HCl, and the solid which separated was filtered, washed with water, and dried to yield a white solid (1.0 g, 94%). GCMS analysis of this product indicated that the corresponding carboxylic acid had been formed. Without further purification, a mixture of this acid (0.9 g; ca. 3.9 mmol) and $SOCl_2$ (10 mL) was refluxed for 1 h. The excess thionyl chloride was removed on a rotary evaporator, and the residue was dissolved in CH_2Cl_2 (20 mL) and cooled to 10 °C in an ice−water bath. A solution of dimethylamine (2 equiv) in CH_2Cl_2 (15 mL) was added dropwise with stirring. After addition, stirring was continued for 30 min at 20 °C. The reaction mixture was washed with water (50 mL). The organic phase was dried over anhydrous $MgSO_4$, and the solvent was removed under reduced pressure at 40 °C. The residue was stirred with hexane (10 mL), and the solid was filtered, washed with hexane, and dried to afford a white solid (0.9 g, 90%), mp 116−118 °C: IR (KBr) ν 1624, 1537, 1391, 1209, 1109, 1039, 858, 763, 685 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.97 (s, 6H), 2.36 (s, 3H), 3.17 (s, 3H), 3.67 (s, 3H), 7.00 (s, 2H), 8.15 (s, 1H); ^{13}C NMR ($CDCl_3$) 17.2, 21.0, 36.4, 38.7, 129.1, 130.1, 132.8, 134.8, 140.2, 144.5, 161.1; HRMS calcd for $C_{14}H_{18}N_4O$ *m*/*z* 258.1481, found 258.1480. Anal. Calcd for $C_{14}H_{18}N_4O$: C, 65.08; H, 7.03; N, 21.70. Found: C, 64.99; H, 7.04; N, 21.66.

***N*,*N*-Dimethyl-1-(2,6-dimethylphenyl)-1*H*-1,2,3-triazole-4-carboxamide (6c).** The procedure was similar to that used above except for the purification of the final product. The crude product was stirred with hexanes−ether (4:1) to yield a white solid (1.14 g, 85%), mp 89−91 °C: IR (KBr) ν 1615, 1538, 1390, 1204, 1120, 1039, 772, 686 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.01 (s, 6H), 3.17 (s, 3H), 3.67 (s, 3H), 7.17−7.34 (m, 3H), 8.18 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 17.3, 36.4, 38.7, 128.4, 130.0, 130.2, 135.1, 135.3, 144.6, 161.0; HRMS calcd for $C_{13}H_{16}N_4O$ *m*/*z* 244.1324, found 244.11324. Anal. Calcd for $C_{13}H_{16}N_4O$: C, 63.92; H, 6.60; N, 22.93. Found: C, 63.96; H, 6.57; N, 22.81.

5-Methoxy-1-(2,4,6-trimethylphenyl)pyrrole-2,3-dione (8). The procedure was analogous to that used in ref 24. To a stirred and cooled (0 °C) mixture of *N*-2,4,6-trimethylphenylacetimidic ester[25] (1.4 g, 7.3 mmol) and dry triethylamine (1.5 g, 14.6 mmol) in dry ether (50 mL) was added a solution of oxalyl chloride in dry ether (10 mL) over 30 min. After the solution was stirred for 3.5 h at 0 °C, hexane (50 mL) was added and stirring continued for 30 min at room temperature. The separated solid was filtered, washed quickly with ice-cold water, and crystallized from benzene to give yellow crystals, yield 70%: mp 146−148 °C; IR (KBr) ν 2956, 2925, 1772, 1714, 1578, 1573, 1488, 1449, 1395, 1320, 1245, 942 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.09 (s, 6H), 2.29 (s, 3H), 4.03 (s, 3H), 4.95 (S, 1H), 6.94(s, 2H); ^{13}C NMR δ 17.9, 21.1, 59.0, 96.5, 126.4, 129.2, 136.9, 139.7, 159.3, 179.4, 179.8; HRMS calcd for $C_{14}H_{15}NO_3$ *m*/*z* 245.1052, found 245.1052. Anal. Calcd for $C_{14}H_{15}NO_3$: C, 68.54; H, 6.17; N, 5.71. Found: C, 68.64; H, 6.31; N, 5.58.

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FVT of Triazole 6a. (a) The compound (100 mg) was subjected to preparative FVT at 450 °C, being sublimed into the apparatus at 50−60 °C in the course of 2 h. The products were collected in a U-tube cooled in liquid N_2. Upon completion of the pyrolysis, the system pressure was equalized with N_2, and the U-tube warmed to room temperature. The oily residue in the U-tube was dissolved in CCl_4 and immediately subjected to vacuum distillation using a Kugelrohr apparatus. Distillation at 50 °C (4.5×10^{-5} mbar) afforded 16 mg (21%) of the oxoketenimine **10a** as a clear oil: IR (CCl_4) ν 2951, 2077, 2069, 1710, 1445, 1238, 1145 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.27 (s, 3H), 2.34 (s, 6H), 3.69 (s, 3H), 4.24 (s, 1H), 6.88 (s, 2H); ^{13}C NMR ($CDCl_3$) δ 18.8, 21.0, 45.4, 51.3, 129.2, 129.7, 134.4, 138.3, 165.7, 170.1 (see also Supporting Information); HRMS calcd for $C_{13}H_{15}NO_2$ *m*/*z* 217.1103, found 217.1103. Anal. Calcd for $C_{13}H_{15}NO_2$: C, 71.85; H, 6.96; N, 6.45. Found: C, 71.46; H, 6.91; N, 6.51.

A pink solid which had deposited at the entrance of the U-tube was found to be a mixture of two compounds having R_f values of 0.49 and 0.29 (TLC, SiO_2, hexane/$CHCl_3$ 3:2). Column chromatography (hexane/$CHCl_3$ 3:2) yielded only a yellow solid, 42 mg (56%), mp 98−100 °C which was identified as methyl 6,8-dimethylquinoline-3-carboxylate (**16a**): IR ($CDCl_3$) ν 2955, 1723, 1605, 1440, 1275, 1237, 1115, 1007 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.49 (s, 3H), 2.77 (s, 3H), 3.99 (s, 3H), 7.50 (s, 2H), 8.69 (d, 1H), 9.36 (d, 1H); ^{13}C NMR ($CDCl_3$) δ 18.0, 21.5, 52.4, 122.6, 125.8, 127.0, 134.4, 136.8, 137.1, 138.3, 147.5, 148.0, 166.2; HRMS calcd for $C_{13}H_{13}NO_2$ *m*/*z* 215.0946, found 215.0943.

(b) To determine the composition of the above pink solid, the products of a similar pyrolysis of **6a** at 450 °C were examined by GCMS. This allowed the identification of quinoline **16a** (t_R 10.04 min, *m*/*z* 215) and the dihydroquinoline **15a** (t_R 11.70 min, *m*/*z* 217). The ratio of intensities of the peaks at *m*/*z* 215 and 217 was ca. 2.8:1, variable because **15** is rapidly oxidized to **16a**. Spectral data for **15a** in admixture with **16a**: ^{1}H NMR ($CDCl_3$) δ 2.11 (s, 3H), 2.19 (s, 3H), 3.70 (s, 2H), 3.71 (s, 3H), 5.85 (bs, 1H), 6.70 (s, 2H), 7.34 (d, 1H); IR (KBr) ν 3337, 1719, 1663, 1640 cm^{-1}; ^{13}C NMR ($CDCl_3$) δ 16.6, 20.6, 25.9, 51.0, 97.9, 120.7, 121.8, 128.1, 129.1, 132.1, 136.9, 150.0, 168.8; HRMS calcd for $C_{13}H_{15}NO_2$ *m*/*z* 217.1103, found 217.1095. The ^{1}H NMR spectra of **15a** and **16a** are reproduced in the Supporting Information.

(c) Similar FVT at 350 °C afforded a mixture of **6a**, **10a**, and (**15a** + **16a**) in the ratio 24:33:9 as determined by ^{1}H NMR spectroscopy.

(d) Compound **6a** (80 mg) was pyrolyzed at 700 °C as above to yield 40 mg of **16a** (65%) after complete oxidation of **15a**.

Reactions of Ketenimine 10a. (a) The freshly distilled ketenimine **10a** (60 mg) was subjected to FVT at 400 °C. The products were collected on the BaF_2 disk at 77 K. The IR spectrum revealed the presence of a large amount of ketenimine **10a** as well as a small amount of ketene **9a** (if the extinction coefficients of **10a** and **9a** were identical, less than 10% of **9a** was formed). The quinoline **16a** (<5% yield) was identified in the yellow material deposited between the pyrolysis tube and the 77 K BaF_2 disk by ^{1}H NMR spectroscopy and comparison with the previously described sample.

(b) Preparative FVT of **10a** (18 mg) at 700 °C gave an 84% yield of **16a** after complete oxidation of **15a** (initial mixture of **15a** and **16a** = ca. 1:3 by ^{1}H NMR).

(c) Following a similar pyrolysis of **6a** (100 mg) at 450 °C, the pure, distilled oxoketenimine **10a** (15 mg) was left exposed to the atmosphere for 18 h at room temperature, whereby it reacted with H_2O to give *N*-mesitylmalonamide monomethyl ester **11a** as yellow crystals, 17.5 mg (95%), mp 132−134 °C: IR (CCl_4) ν 3351, 3275, 2956, 1752, 1647, 1535, 1324, 1232, 1157, 1057, 1025 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.17 (s, 6H), 2.27 (s, 3H), 3.51 (s, 2H), 3.80 (s, 3H), 6.88 (s, 2H), 8.35 (bs, 1H); ^{13}C NMR ($CDCl_3$) δ 18.3, 20.9, 40.9, 52.6, 128.9, 130.8, 134.9, 137.1, 163.3, 170.4; HRMS calcd for $C_{13}H_{17}NO_3$ *m*/*z* 235.1208, found 235.1211. Anal. Calcd for $C_{13}H_{17}NO_3$: C, 66.35; H, 7.29; N, 5.96. Found: C, 66.29; H, 7.27; N, 6.11.

FVT of Pyrroledione 8. The compound (75 mg) was pyrolyzed at 450 °C, being sublimed into the apparatus at 75

°C in the course of 3 h. Similar workup as with **6a** yielded the oxoketenimine **10a** (15 mg, 23%) along with the quinoline **16a** (35 mg, 53%) after complete oxidation of **15a** (initial mixture of **15a** and **16a** = ca. 1:3 by ^{1}H NMR). At 600 °C, **16a** was obtained analogously in 68% yield. The spectral data for **10a**, **15a**, and **16a** were as reported above.

***N,N*-Dimethyl-6,8-dimethylquinoline-3-carboxamide (16b) and 6,8-Dimethylquinoline (17). (a) FVT of 6b.** This compound (200 mg) was pyrolyzed as described for **6a**. At 600 °C an oil was obtained on the coldfinger. GCMS indicated the presence of two compounds, **16b** (*m*/*z* 228) and **17** (*m*/*z* 157). Column chromatography of the oil (SiO_2, hexane/benzene 1:1) gave **17** as an oil (36 mg, 29%), followed by **16b** as an oil (100 mg, 56%, eluting with $CHCl_3$). Spectral data for **16b**: IR (CCl_4) ν 2926, 1645, 1605, 1490, 1392, 1266, 1099, 1001 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.49 (s, 3H), 2.78 (s, 3H), 3.07 (s, 3H), 3.18 (s, 3H), 7.46 (s, 2H), 8.14 (d, 1H), 8.91 (d, 1H); ^{13}C NMR ($CDCl_3$) δ 17.9, 21.5, 35.5, 39.6, 125.0, 127.1, 128.7, 133.2, 134.7, 136.6, 140.0, 145.8, 146.3, 169.4; HRMS calcd for $C_{14}H_{16}N_2O$ *m*/*z* 228.1262, found 228.1261.

17 is a known compound:[26] spectral data: IR (CCl_4) ν 2926, 1590, 1495, 1373, 1125, 858 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.47 (s, 3H), 2.77 (s, 3H), 7.31−7.39 (s, 2H), 7.98−8.02 (dd, 2H), 8.85−8.87 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 18.0, 21.4, 120.8, 124.6, 128.3, 131.9, 135.6, 135.9, 136.5, 145.9, 148.3; HRMS calcd for $C_{11}H_{11}N$ *m*/*z* 157.0891, found 157.0879.

(b) Conversion of 16a to 16b. For proof of the structure of **16b**, this compound was also synthesized from the fully characterized ester **16a** (30 mg) which was hydrolyzed with 10% aqueous KOH at 80 °C for 30 min. After cooling to room temperature, the mixture was acidified with 6 M HCl, the solid was filtered and washed with water to give 20 mg of the carboxylic acid, this was taken up in 2 mL of freshly distilled $SOCl_2$, and the mixture was refluxed for 30 min under N_2. After removal of excess $SOCl_2$ on the rotatory evaporator, the residue was dissolved in CH_2Cl_2 and cooled to 10 °C, and 2 equiv of dimethylamine in CH_2Cl_2 was added slowly. The resulting mixture was stirred at 20 °C for 30 min. Water was added (20 mL) and the organic phase was separated and washed successively with water and brine, dried over $MgSO_4$, concentrated in vacuo, and chromatographed on SiO_2. The desired amide **16b** (15 mg) was eluted with $CHCl_3$−MeOH (1:1). Its NMR spectra were identical with the ones reported in (a) above.

FVT of Triazole 6c. This compound (100 mg) was similarly pyrolyzed at 600 °C to give compound **16c** (60 mg, 67%): IR (CCl_4) ν 2928, 1645, 1548, 1492, 1392, 1261, 1095, 1008 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.75 (s, 3H), 3.01 (s, 3H), 3.12 (s, 3H), 7.34−7.67 (m, 3H), 8.17 (d, 1H), 8.92 (d, 1H); ^{13}C NMR ($CDCl_3$) δ 18.0, 35.6, 39.7, 126.3, 127.0, 127.1, 127.6, 128.8, 130.8, 135.4, 137.2, 147.3, 169.3; HRMS calcd for $C_{13}H_{14}N_2O$ *m*/*z* 214.1106, found 214.1103.

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Supporting Information Available: X-ray crystal structure and packing diagram, crystal data, and bond lengths and angles for **16a** (Figure S1, Tables S1 and S2). Calculated geometries of **18a**, **TS19a**, and **20a** (MP2/6-31G*), absolute energies and zero-point vibrational energies for **18**−**20a,b** and **22**−**29** (Tables S3−S6). ^{1}H and ^{13}C NMR spectra of **10a**, and ^{1}H NMR spectra of **15a** and **16a** (12 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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