Imidoylketene−Oxoketenimine Interconversion. Rearrangement of a Carbomethoxyketenimine to a Methoxyimidoylketene and 2-Methoxy-4-quinolone

Belinda E. Fulloon and Curt Wentrup*

Department of Chemistry, The University of Queensland, Brisbane, Qld 4072, Australia

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FVP of triazole **13** produces the isolable ketenimine **11** together with indole **15**. **11** undergoes reversible interconversion with imidoylketene **10** above 380 °C. The latter cyclizes to quinolone **12**. Meldrum's acid derivative **16** produces the same ketene **10** above 200 °C, and the latter isomerizes to ketenimine **11** at 200 °C by a 1,3-shift of a MeO group. A competing elimination of MeOH from **16** produces (phenylimino)propadienone **20**.

Introduction

The interconversion of α-oxoketenes involves a degenerate intramolecular 1,3-shift of the group R (**1a** ⇆ **2a**).[1] This rearrangement was first reported for benzoylketene (**1a**, R = Ph) and established by ^{13}C scrambling in the specifically labeled ketene, both by direct IR spectroscopic observation of the ketenes and by ^{13}C NMR analysis of the trapping product with methanol, methyl benzoylacetate. In this case, the interconversion **1a** ⇆ **2a** is complete under flash vacuum pyrolysis (FVP) conditions at 800 °C (*ca.* 10^{-4} mbar; contact times ≈ ms).[1] An analogous ^{13}C labeling experiment demonstrated that a methyl group does not undergo this 1,3-shift in acetylketene (**1a,** R = CH_3) at FVP temperatures up to 1100 °C.[2]

1 **2**

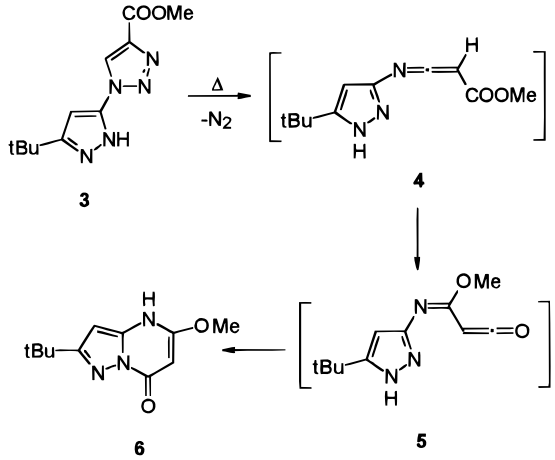
a: X = O, Y = O
b: X = NR′, Y = O
c: X = O, Y = CR_2'

The same type of rearrangement interconverts imidoylketenes and oxoketenimines (**1b** ⇆ **2b**).[3−5] For R = aryl, FVP temperatures of 600−700 °C are required,[4,5] but the reaction is dramatically accelerated for R = SMe (*ca.* 400 °C) and, by implication, also for R = NMe_2.[3,4]

Ab initio calculations have provided a comprehensive rationale for these observations.[6] The most important factor governing the 1,3-shift of the group R is electron donation from this group into the ketene LUMO, which has a large coefficient at the central ketene C atom to which the migration takes place. Thus, the accelerated migration of electron-donating groups is readily understood. The calculated migratory aptitudes follow the order $CH_3 \ll Ph < H < OH < MeO < NH_2 < SH < NHMe$ $MeS < NMe_2$.[6,7]

We have recently found that a similar interconversion of vinylketenes and oxoallenes (**1c** ⇆ **2c**) becomes observable when an electron-donating group is employed (R = OMe, NMe_2, or Cl).[8] Further calculations confirmed the very facile 1,3-migration of halogen atoms (Br > Cl ∼ NMe_2).[8b]

Although predicted by theory to be facile, there has been little or no *direct* evidence for the interconversion of carboxylic acid derivatives of ketenes and ketenimines (**1b** ⇆ **2b**, R = OR′ or Cl), except for the thioesters[4] (R = SMe). McNab *et al.* concluded from ^{13}C labeling studies of the rearrangement of pyrazolyltriazole **3** to pyrazolopyrimidinone **6** that a ketenimine−imidoylketene rearrangement **4** → **5** was involved.[9]



3 **4** **5** **6**

An analogous mechanism was postulated for the conversion of ethyl 1-phenyltriazole-4-carboxylate (**7**) to 2-hydroxy-4-quinolone (**8**),[9] thought to arise by ethene elimination from an initially formed 2-ethoxyquinolone.

[⊗] Abstract published in *Advance ACS Abstracts,* February 1, 1996.

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(3) Ben Cheikh, A.; Chuche, J.; Manisse, N.; Pommelet, J. C.; Netsch, K.-P.; Lorencak, P.; Wentrup, C. *J. Org. Chem.* **1991**, *56*, 970.

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(6) Wong, M. W.; Wentrup, C. *J. Org. Chem.* **1994**, *59*, 5279.

(7) (a) Related isomerization of thioacyl isocyanates to acyl isothiocyanates, and of guanyl isocyanate to carbamoylcarbodiimide have been reported by Goerdeler et al.;[7b] the migratory aptitudes were similar to the ones calculated by us:[6] $(Alk)_2N$, Alk(Ar)N > ArS > AlkS ≫ ArO > AlkO. (b) Goerdeler, J.; Jonas, G. *Chem. Ber.* **1966**, *99*, 3572. Goerdeler, J.; Bartsch, H.-J. *Chem. Ber.* **1985**, *118*, 2294, 4196. Goerdeler, J.; Raddatz, S. *Chem. Ber.* **1980**, *113*, 1095.

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(9) Clarke, D.; Mares, R. W.; McNab, H. *J. Chem. Soc., Chem. Commun.* **1993**, 1026.

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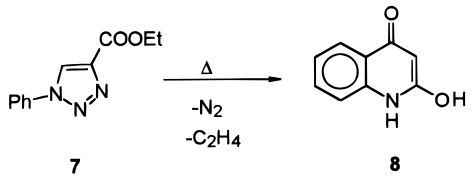
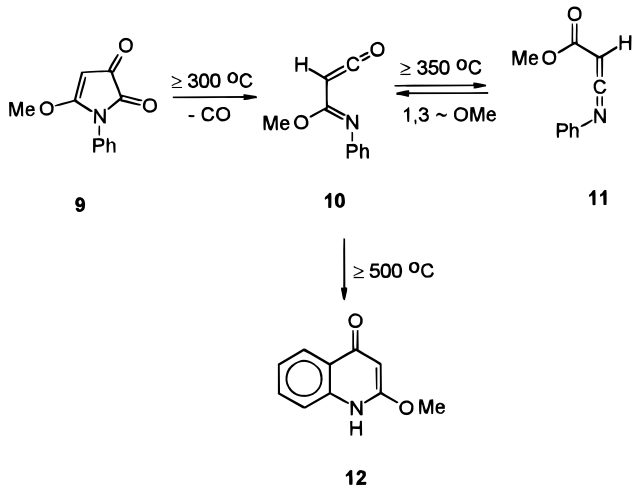


7 **8**

By using the pyrroledione precursor **9**, we were able to observe both the imidoylketene **10** and the ketenimine **11**, which are related through a 1,3-shift of the methoxy group, taking place at *ca.* 350 °C under FVP conditions; this interconversion is so facile that it competes with the cyclization of ketene **10** to 2-methoxy-4-quinolone (**12**).[10]



9 **10** **11** **12**

We now report further studies of these ketene and ketenimine intermediates, demonstrating the extraordinarily facile 1,3-shift of the methoxy group at a temperature as low as 200 °C under FVP conditions and even proceeding in solution in boiling diphenyl ether (242 °C).

Results and Discussion

Preparative FVP of triazole **13** with isolation of the products on a liquid N_2 cooled cold finger resulted in three products: the ketenimine **11**, the indole **15**, and the quinolone **12** (Scheme 1). In parallel experiments, the FVP products were isolated on a BaF_2 disk at 77 K for IR spectroscopic observation of the primary reaction products. N_2 elimination from **13** commenced at 380 °C, and both a ketenimine **11** and a ketene **10** were immediately observable as very weak peaks by IR spectroscopy. At 450 °C, a much stronger signal due to the ketenimine **11**, together with a weak signal due to the ketene **10**, were observed (Figure 1a). The ketenimine was isolable as a neat liquid by Kugelrohr distillation of the product of the preparative pyrolyses; a 29% isolated yield was obtained at 600 °C. The residue from the distillation was separated by column chromatography to give indole **15** (13%) and quinolone **12** (44%). Analogous FVP of **13** at 800 °C gave **15** (4%) and **12** (93%). The ketenimine was no longer present. The yields are summarized in Table 1.

The formation of indoles from triazoles has been investigated previously under both thermal and photochemical conditions.[11] The cyclization of an initially formed imidoylcarbene **14** to give indole **15** is the fully expected normal outcome.[11,12] The 1,2-H shift in imidoylcarbenes to give ketenimines is also well docu-

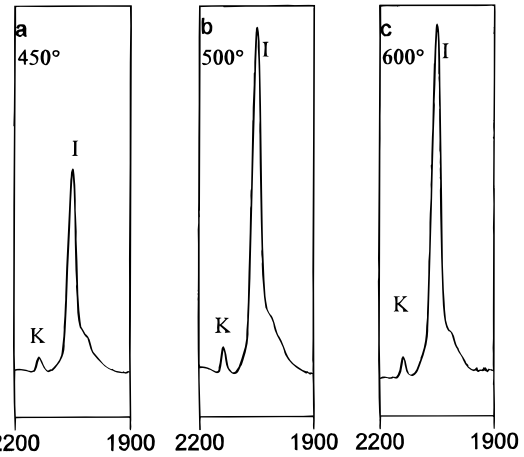


Figure 1. Partial FTIR spectra (1900−2200 cm^{-1} range) of the products (77 K) of FVP of **13.** K = ketene **10** (2135 cm^{-1}); **I** = ketenimine **11** (2050 cm^{-1}).

Scheme 1

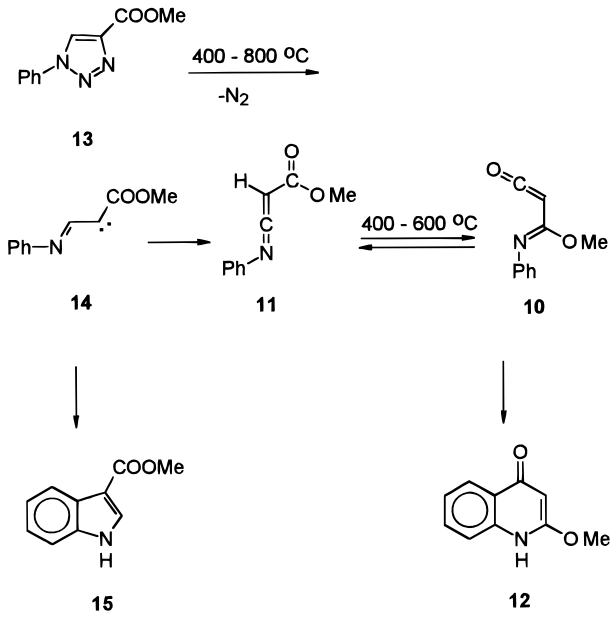


Table 1. Products of FVP of Ketene/Ketenimine Precursors as a Function of Temperature

		yield, %[a]			
precursor	temp, °C	**11**	**12**	**15**	**21**[b]
9[c]	500	30	64		
9[c]	800		97		
11	500		75		
11	700		91		
13	600	29	44	13	
13	800		93	4	
16	350	26	48[d]		
16	600		67		33
16	700		50		50
16	800		33		67

[a] Absolute yields by isolation. The ratios of **12** and **21** were determined by ^1H NMR spectroscopy. [b] By trapping of **20** with MeOH on the cold finger. [c] Data from ref 10. [d] 20% starting material **16** was recovered.

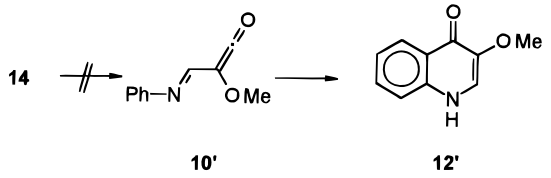
(10) Fulloon, B.; El-Nabi, H. A. A.; Kollenz, G.; Wentrup, C. *Tetrahedron Lett.* **1995**, *36*, 6547.

(11) Gilchrist, T. L.; Rees, C. W.; Thomas, C. *J. Chem. Soc., Perkin Trans 1* **1975**, 8. Mitchell, G.; Rees, C. W. *J. Chem. Soc., Perkin Trans 1* **1987**, 413.

mented.[12] The surprising observation is that, as soon as the ketenimine **11** starts to form (380−450 °C), it isomerizes to the ketene **10**. As shown in Figure 1, the ketene peak (K) is present throughout the temperature range 450−600 °C. It never increases significantly in intensity because the ketene is removed from the equilibrium by cyclization to the quinolone **12**, which is always formed, even under the mildest conditions of FVP, where very little decomposition of **13** occurs. Compounds **10** and **11** are much more volatile than quinolone **12** and therefore are deposited on the cold disk (77 K) free of any quinolone until a FVP temperature of 800 °C. At lower FVP temperatures (400−700 °C), the quinolone (with small amounts of indole **15**) condenses on the cool surface between the pyrolysis zone and the deposition disk.

We conclude from these experiments that an equilibrium between ketenimine **11** and ketene **10** is established as soon as **11** is formed (≥400 °C). While **10** is only observable by low temperature spectroscopy (up to +15 °C), its structure is given by that of the derived quinolone **12** as well as by independent generation from the pyrroledione **9**.[10] **9** gave only ketene **10** at 300 °C, but the ketenimine **11** dominated in the IR spectrum already at 350 °C. A ketene:ketenimine ratio similar to that shown in Figure 1b was achieved from **9** at 500 °C. Ketenimine **11** was isolable in 30% yield following FVP of **9** at 500 °C; quinolone **12** was obtained in 64% yield under these conditions, and in 97% yield at 800 °C.[10] The combined results from **13** and **9** demonstrate that the interconversion of ketenimine **11** and ketene **10** takes place in both directions, starting at 350 °C or lower.

It is necessary also to consider an alternative Wolff rearrangement in imidoylcarbene **14** which, by a 1,2-shift of the methoxy group would give ketene **10′**, isomeric with **10**. Cyclization of ketene **10′** would yield the quinolone **12′**, isomeric with **12**.

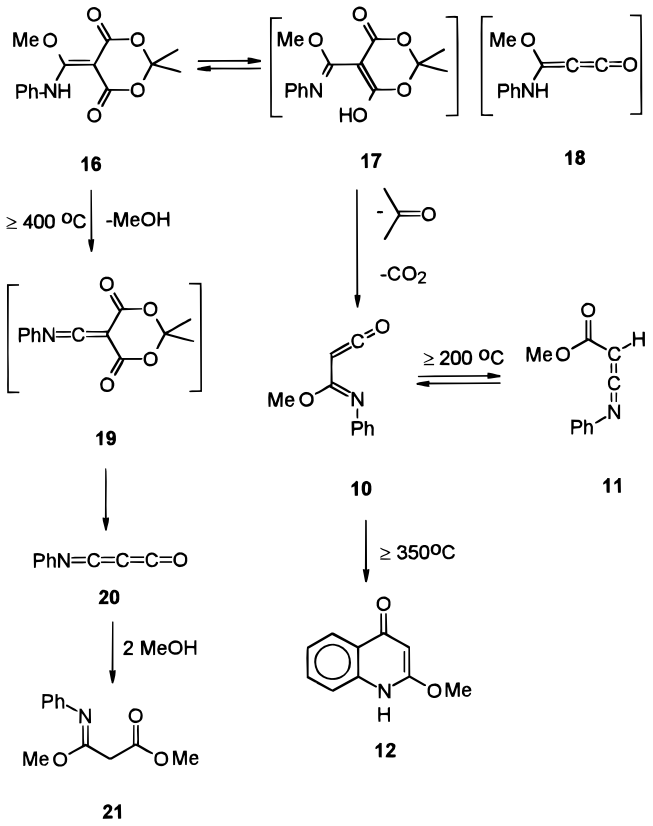


10′ **12′**

A careful search by 500 MHz ^{1}H NMR failed to reveal the presence of **12′** (a known compound[13]) in either the crude product of FVP of **13** or in the chromatography fraction containing all of quinolone **12**. Therefore, if this Wolff rearrangement takes place at all, it could only be to the extent of a few percent.

It was shown previously that 5-aminomethylene derivatives of Meldrum's acid (2,2-dimethyl-1,3-dioxane-4,6-dione) are excellent precursors of imidoylketenes.[3,4,14a] The requisite methoxy-substituted Meldrum's acid **16** was prepared by displacement of the methylthio analogue[4] with methanol in the presence of a $HgO/HgCl_2$ catalyst (either HgO or $HgCl_2$ alone[15] does not suffice). FVP of **16** proceeds with elimination of acetone and CO_2,

Scheme 2



probably via the tautomer[4,14b,16] **17** (Scheme 2), starting already at 200 °C. The first detectable intermediate is the imidoylketene **10** (2135 cm^{-1}). A methyleneketene **18**, which could have formed directly from **16** by loss of acetone and CO_2, was not detectable. Importantly, even at the lowest temperature where **16** reacts (200 °C), there was already formation of a small amount of the ketenimine **11** (2050, 1712, 1696 cm^{-1}) (Figure 2a). The amount of ketenimine rapidly increased, and that of the ketene decreased as a function of temperature, so that at 400 °C their ratio approached that seen earlier using **13** and **9** as precursors (Figure 2c). At the same time, quinolone **12** was being formed; this was isolable in 48% yield at 350 °C and in 67% yield at 600 °C. The ketenimine **11** was again isolated by distillation (26% from FVP at 350 °C). **10** and **11** were shown by spectral comparison to be identical with the materials described above.

It is seen in Figure 2 that a new peak starts appearing in the IR spectrum near 2200 cm^{-1} at 400 °C. At 700 °C this species has replaced everything else in the ketene region, giving rise to a very strong and complex signal with maxima at 2222 and 2140 cm^{-1} (Figure 2d,e). This new compound is (phenylimino)propadienone (**20**), formed in a competing elimination of MeOH from **16**, a reaction that starts at 400 °C (Scheme 2). Cumulene **20** was identified by comparison of its IR spectrum, both as a neat film at 77 K and in Ar matrix at 12 K (2247 (vs), 2140 (w) cm^{-1}), with samples prepared from other precursors.[17] Furthermore, trapping of **20** with MeOH produced the malonic ester imide **21**. The yield of **21** increased, and that of quinolone **12** decreased with rising

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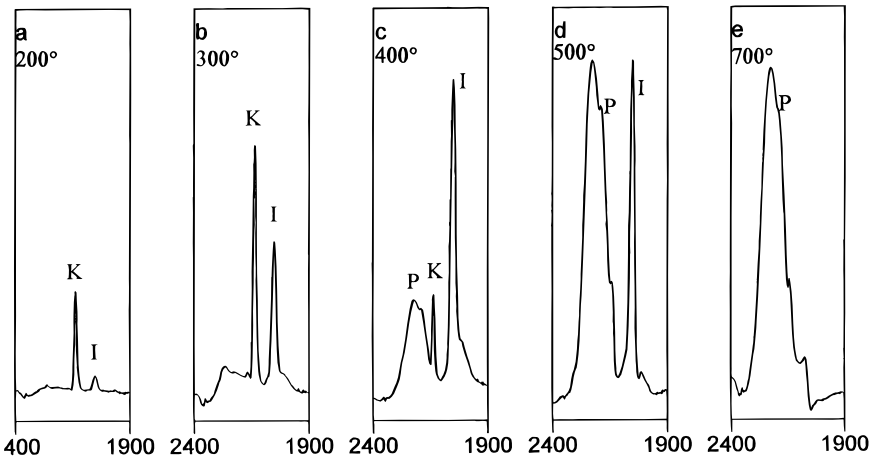

Figure 2. Partial FTIR spectra (1900−2200 cm^{-1} range) of the products (77 K) of FVP of **16**. K = ketene **10** (2135 cm^{-1}); I = ketenimine **11** (2050 cm^{-1}); P = propadienone **20** (2222, 2140 cm^{-1}).

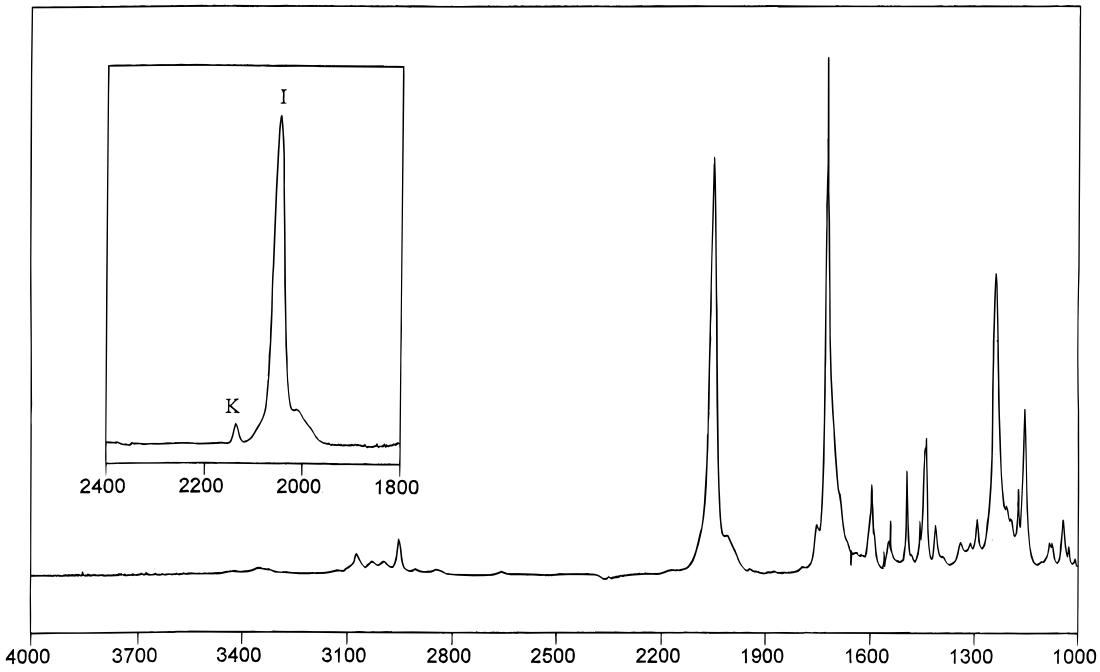

Figure 3. FTIR spectrum of ketenimine **11** in CCl_4. Inset: partial FTIR spectrum (77 K) showing the formation of a small amount of ketene **10** (K, 2135 cm^{-1}) on FVP of **11** (I, 2050 cm^{-1}) at 450 °C.

temperature, in agreement with the results of the IR spectroscopic observation. The yields are reported in Table 1.

The ketenimine derivative of Meldrum's acid (**19**) is not detectable in this reaction. However, by using an analog of **16** with Me_2N in place of OMe, the corresponding elimination of Me_2NH at 300 °C gave **19**, which was detectable by IR and MS as a fleeting intermediate, decomposing to **20** already at 310 °C.[17a]

The most important conclusion from this section is that ketene **10** isomerizes to ketenimine **11** already at 200 °C on FVP, indicating a very low barrier for the 1,3-shift of the MeO group. It is also remarkable that this 1,3-shift can compete with the cyclization to quinolone **12**. The ab initio calculated activation barrier for the rearrangement **10** → **11** is 155 kJ mol^{-1}; for **11** → **10** it is *ca.* 165 kJ mol^{-1}.[8b]

Since ketenimine **11** is isolable from the reactions of **13**, **16**, or **9**, we were able to examine its own behavior on FVP. **11** (2050 cm^{-1}) was recovered unchanged at temperatures below 400 °C. At 450 °C, a weak signal at 2135 cm^{-1} due to ketene **10** appeared (Figure 3). The ratio of the two peaks remained essentially unchanged between 400 and 600 °C, the reason being removal of the ketene **10** to form quinolone **12**. The latter was isolated from these analytical pyrolyses from 450 °C onwards and identified by comparison with the material from earlier experiments. In a preparative FVP of **11** at 500 °C, a 75% yield of **12** was isolated; at 700 °C the yield was 91%.

The reaction of ketenimine **11** with methanol gave imide **21** in 83% yield (Scheme 3).

The decomposition of **13** and **16** can also be carried out in diphenyl ether solution, as has been reported for related Meldrum's acid derivatives[15] and pyrroldiones.[10] The results are given in Table 2, with data for **9** included

(17) (a) Mosandl, T.; Kappe, C. O.; Flammang, R.; Wentrup, C. *J. Chem. Soc., Chem. Commun.* **1992**, 1571. (b) Mosandl, T.; Stadtmüller, S.; Wong, M. W.; Wentrup, C. *J. Phys. Chem.* **1994**, *98*, 1080. (c) Wentrup, C.; Kappe, C. O.; Wong, M. W. *Pure Appl. Chem.* **1995**, *67*, 749.

Scheme 3

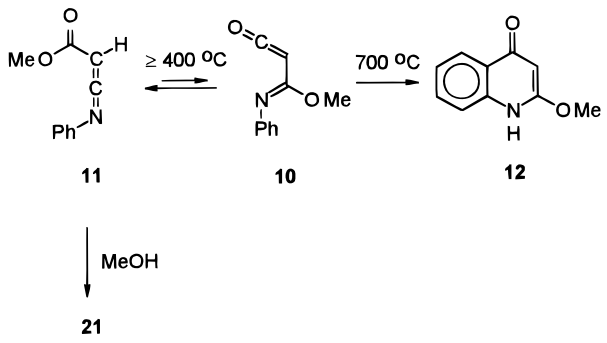

Table 2. Products of Reaction in Diphenyl Ether Solution

			yield %	
precursor	temp, °C	time	**12**	**15**
13	242	19 h	30	7
16	242	15 min	30	−
16	150	2 d	40	−
9	242	15 min	36[a]	−
9	150	1 wk	0[b]	−

[a] Data from ref. 10. [b] Starting material recovered unchanged.

for comparison. Although the yields are much inferior to those achieved by FVP, it is noteworthy that the triazole **13** yields quinolone **12** in solution, thereby implying that the ketenimine−imidoylketene rearrangement (**11** → **10**) also takes place in solution.

Conclusion

We have demonstrated a facile 1,3-shift of the methoxy group, interconverting the imidoylketene **10** and the isolable ketenimine **11**. From the ketene side (**10**), this reaction is observable already at 200 °C under FVP conditions. From the ketenimine side, the reaction is observable from 380 °C onward. The ketene **10** can be detected by IR spectroscopy but readily cyclizes to quinolone **12**. These reactions also proceed in boiling diphenyl ether solution. The facile methoxy group shift is in accord with predictions from ab initio calculations of the activation barriers for this type of reaction.[6,8]

Experimental Section

The pyrolysis apparatus was as previously reported for Ar matrix (12 K),[18] neat film (77 K) deposition,[14a] and preparative scale work (77 K isolation).[19] BaF_2 disks were used for depositions. FTIR spectra were in all cases recorded on a Perkin Elmer 1720X spectrometer. Chromatography was on Kieselgel 100 (Merck). Methyl 1-phenyl-1,2,3−triazole-4-carboxylate (**13**) was prepared according to the literature.[20]

2,2-Dimethyl-5-[methoxy(phenylamino)methylene]-1,3-dioxane-4,6-dione (16) was prepared by a modification of the procedure used by Ye *et al.*[15] for the preparation of different Meldrum's acid derivatives. To a solution of 2,2-dimethyl-5-[methylthio(phenylamino)methylene]-1,3-dioxane-4,6-dione (0.147 g; 0.5 mmol) in MeOH (5 mL) was added yellow HgO (0.109 g; 0.5 mmol) and $HgCl_2$ (0.135 g; 0.5 mmol), and the mixture was refluxed for 20 min. The mixture was then cooled to rt and filtered, and the filtrate was concentrated *in vacuo*. H_2O (10 mL) was added to the residue, causing precipitation of the product, which was recrystallized from THF/hexane: yield 0.11 g (79%), mp 162−164 °C; ^{1}H NMR ($CDCl_3$) δ 1.75 (s, 6 H), 4.13 (s, 3 H), 7.26−7.43 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 26.2; 62.8, 75.8, 103.1; 123.3; 127.0; 129.3; 135.0; 164.2; 171.4; IR (KBr) ν 1722, 1659, 1575 cm^{-1}; HRMS m/z calcd for $C_{14}H_{15}NO_5$ 277.0949; found: 277.0948. Anal. Calcd for $C_{14}H_{15}NO_5$: C, 60.64; H, 5.45; N, 5.05. Found: C, 60.72; H, 5.51; N, 5.03.

FVP of 13. The compound (80 mg; 0.39 mmol) was subjected to preparative FVP at 600 °C, being sublimed into the apparatus at 85 °C in the course of 2 h. Products were isolated on a cold finger at 77 K. Upon completion of the pyrolysis, the system pressure was equalized with N_2, the cold finger was allowed to warm to room temperature, and the oily product mixture was collected in a receiving flask by washing the cold finger with CCl_4 and immediately subjected to vacuum distillation using a Kugelrohr apparatus. Distillation at 50 °C (2.4×10^{-4} mbar) afforded 20 mg (29%) of the ketenimine **11** as a clear liquid: ^{1}H NMR ($CDCl_3$) δ 3.71 (s, 3 H), 4.59 (s, 1 H), 7.27−7.40 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 51.8, 52.3, 124.5, 128.7, 129.7, 136.5, 168.6, 176.4; IR (CCl_4) ν 2952, 2050, 1712, 1696 cm^{-1}. HRMS m/z calcd for $C_{10}H_9NO_2$ 175.06333; found: 175.0629. This compound decomposed in the course of 1−2 d at room temperature; a satisfactory elemental analysis was not obtainable.

The residue from the distillation was subjected to column chromatography (ether/hexane 40:60). Two compounds were isolated. The first fraction (R_f 0.20) was identified as methyl indole-3-carboxylate (**15**) (9 mg; 13%) by comparison with an authentic sample prepared according to ref 21: mp 144−146 °C (lit.[21] 144−145.6 °C); ^{1}H NMR ($CDCl_3$) δ 3.91 (s, 3 H), 7.38, 8.19 (m, 4 H), 7.91 (d, 1 H).

The second fraction (R_f 0.07) was identified as 2-methoxy-4-quinolone (**12**) (30 mg; 44%) by comparison with the material described previously:[10] mp 170−172 °C. Anal. Calcd for $C_{10}H_9NO_2$: C, 68.56; H, 5.18; N, 8.00. Found: C, 68.71; H, 5.17; N, 7.95.

The results of an analogous pyrolysis at 800 °C are given in Table 1. A 20:1 ratio of **12** and **15** was determined by ^{1}H NMR spectroscopy.

FVP of 16. (a) The compound (60 mg; 0.22 mmol) was pyrolyzed at 350 °C, being sublimed into the apparatus at 135 °C in the course of 3 h. Workup as above yielded the ketenimine **11** (10 mg; 26%), identified by ^{1}H NMR and IR comparison with the previously isolated material. Column chromatography (ether/hexane 80:40) yielded **16** (12 mg; 20%; R_f 0.15) and **12** (18 mg; 48%; R_f 0.31). No trace of **15** was formed. (b) In a similar pyrolysis of **16** (48 mg; 0.17 mmol) at 600 °C, the cold finger was coated with MeOH (1 mL) prior to the experiment and again with 1 mL of MeOH after the completion of the deposition of the pyrolysate. After warming to rt and evaporating excess MeOH, the residue (32 mg) was shown by ^{1}H NMR to consist of **12** (67%) and **21** (33%). **21** was identical with the material described previously[17a] (see also reaction of **11** with methanol below). (c) The results of analogous experiments at 700 and 800 °C are given in Table 1.

FVP of 11. (a) The freshly distilled ketenimine (20 mg; 0.11 mmol) was subjected to pyrolysis at 500 °C, being distilled into the apparatus at 50 °C (30 min). Quinolone **12** (15 mg; 75%) was isolated from the cold finger and identified as the exclusive product by TLC and ^{1}H NMR comparison of previously prepared samples. A similar experiment with 80 mg of **11** at 700 °C gave a 91% yield of **12**. (b) FVP of **11** with IR spectroscopic observation of the rearrangement product, the ketene **10**, was carried out as described in the text. Figure 3 shows that a small amount of the ketene is present above 400 °C. The degree of conversion to quinolone **12** is very low under these conditions. **12** was identified in the white material deposited between the pyrolysis tube and the 77 K BaF_2 disk in an experiment at 450 °C by TLC and GC comparison with the previously described sample.

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Reaction of 11 with Methanol. Freshly distilled **11** (20 mg) was added to MeOH (5 mL), and the mixture was allowed to stir overnight. Evaporation of the solvent afforded **21** as a yellow oil (20 mg; 83%). Its identity was established by comparison with previously described material:[17a] ^{1}H NMR ($CDCl_3$) δ 3.21 (s, 2 H), 3.68 (s, 3 H), 3.80 (s, 3 H), 6.77−7.31 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 35.9, 52.3, 53.8, 120.9, 123.4, 129.1, 147.9, 156.8, 168.2; IR (CCl_4) ν 1751, 1683, 1598, 1160 cm^{-1}.

Pyrolysis in Diphenyl Ether Solution. The appropriate compound (**13**, **16**, or **9**) (80 mg) was heated in boiling diphenyl ether (242 °C) (5 mL) under N_2. After a given time (see Table 2), the mixture was cooled and diluted with hexane (30 mL). The precipitate was filtered and purified by column chromatography. After eluting remaining diphenyl ether with ether/hexane 40:60, the products were eluted with pure ether. The results are given in Table 2.

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Supporting Information Available: ^{1}H and ^{13}C NMR spectra of ketenimine **11** (2 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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