

## Novel heterocumulene (RN=C=C=C=X) and ketene rearrangements

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**Abstract:** The novel iminopropadienones RN=C=C=C=O (**8**) and the corresponding thione **21** have been synthesized by FVP of isoxazole or Meldrum's acid derivatives. Bisimines **16** and the unusual, linear ketenimine **18** were generated in related reactions. In the Meldrum's acid series, a competing fragmentation leads to imidoylketenes (R'N=CR-CR''=C=O) (**28**).  $\alpha$ -Oxoketenes (O=CR-CR'=C=O) (**22**), imidoylketenes (**28**), and vinylketenes (**39c**) undergo reversible interconversion with  $\alpha$ -oxoketenes (**23**), oxoketenimines (**29**), and acylallenes (**40c**), respectively, via a thermal 1,3-shift of the group R. This is favored by electron-donating substituents R by means of interaction with the ketene LUMO.

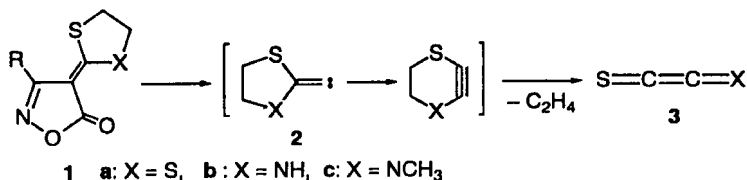
### INTRODUCTION

We have used flash vacuum pyrolysis (FVP) to generate a variety of reactive intermediates and unusual molecules. Isolation of the products in low temperature matrices allows their investigation by IR and UV, and when necessary also ESR spectroscopy. Direct on-line monitoring of the FVP reactions with mass spectrometry is also of crucial importance. In many cases, matrix photolytic generation and/or bleaching of the species of interest can give additional valuable information.

Thus, in recent years, we have described the generation, direct detection, and chemistry of several unusual and/or unstable ketenes, including  $\alpha$ -oxoketenes (**1**); imidoylketenes (**2**), carboxy(vinyl)ketenes (**3**), and alkylideneketenes (**4**). Extension of this work led to the discovery of highly unstable cumulenes of the type X=C=C=Y as well as the much more stable iminopropadienone derivatives RN=C=C=C=O. This chemistry is intimately linked to investigations of ketene—ketene rearrangements as summarized herein.

### ETHENEDIONE DERIVATIVES

Ethenedithione, C<sub>2</sub>S<sub>2</sub> (**3a**) was generated by FVP of the isoxazolones **1a** (R = CH<sub>3</sub> or C<sub>6</sub>H<sub>5</sub>), whereby the crucial step is the breaking of the relatively weak N-O bond, resulting in the formation of the (unobserved) vinylidene **2a**. C<sub>2</sub>S<sub>2</sub> was characterized by matrix isolation IR and UV spectroscopy as well as mass spectrometry (**5**).



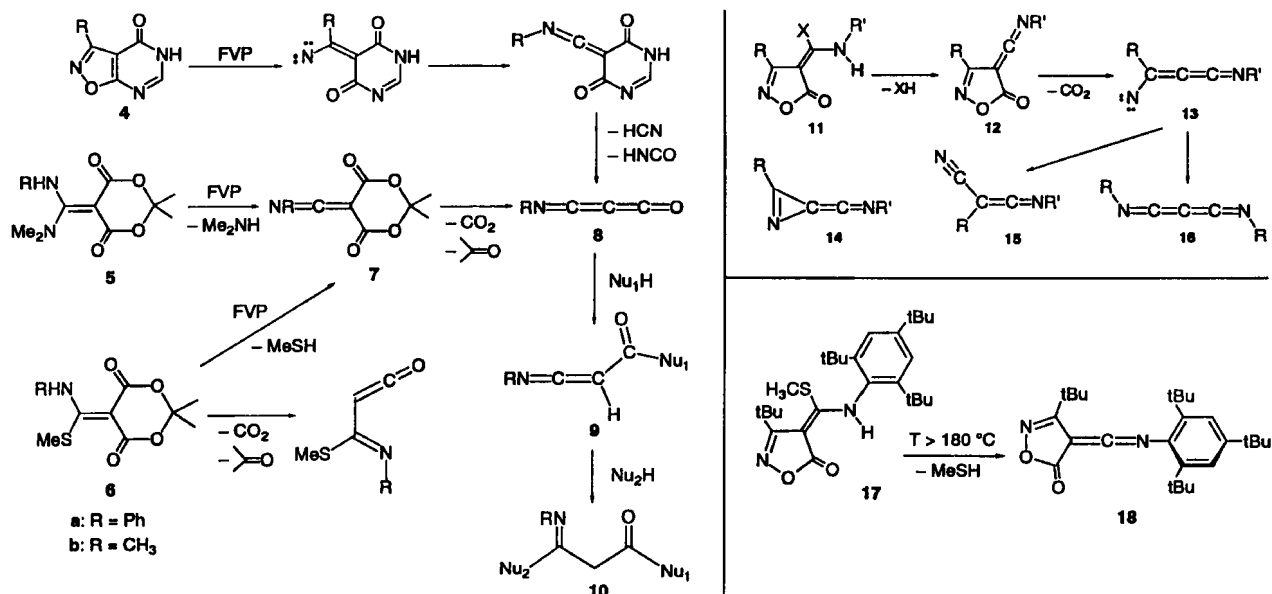
The imine analogs **3b** and **3c** are significantly less stable than **3a**. **3b** rearranges to thioformyl cyanide under FVP conditions, but both **3b** and **3c** have been shown to exist by neutralization-reionization mass spectrometry (NRMS) (**6**). The oxygen analog, O=C=C=NH, does not even survive NRMS (**7**).

### IMINOPROPADIENONES

Breaking of the N-O bond in isoxazolopyrimidinone **4** is the first step in the efficient, almost quantitative formation of phenyliminopropadienone (**8a**) (**8,9**). This compound is also obtained in high yield by FVP of the Meldrum's acid derivative **5a** via initial loss of dimethylamine, and in lower yield from the methylthio analog **6a** by loss of MeSH (**8-10**). In the latter case, the imidoylketene—oxoketenimine rearrangement intervenes (*vide infra*). Methyliminopropadienone (**8b**) is obtained analogously from **5b** or **6b**, but not from **4b** because this reaction would require a 1,2-shift of the methyl group in a vinylnitrene.

The cumulenes **8** react with nucleophiles such as amines and alcohols at the ketene-like carbon atom to furnish ketenimines **9**. The latter are often long-lived enough to be investigated by NMR spectroscopy, and sometimes isolable at room temperature. Further addition of nucleophile leads to malonic ester imides **10** (**8,11**).

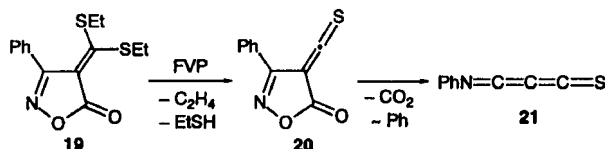
For the generation of bisiminopropadienes (**16**), the thermal elimination of amines and thiols (XH) from isoxazolones **11** has been investigated. For these leaving groups, formation of the transient ketenimine **12** can compete with the habitual N-O bond cleavage in **11**. Breaking the N-O bond in **12** formally generates nitrene **13**, which can cyclize to azirine **14** or rearrange to ketenimines **15** ( $R = H$ ) or **16** ( $R = \text{aryl}$ ). Examples of **12**, **14**, **15**, or **16** have been observed by matrix isolation IR spectroscopy and/or mass spectrometry (**12**).



By using the 2,4,6-tri-*tert*-butylphenyl derivative **17**, it was possible to isolate the ketenimine **18**. Not only is **18** stable at room temperature (albeit sensitive to water and nucleophiles); it also possesses a most unusual structure for a ketenimine, with a linear C-C-N-C backbone (**13**). Ab initio calculations provide a rationale for the unusual structure and spectroscopic properties of **18** in terms of stabilization of the linear structure by a combination of electronic and steric effects (**13**).

While the bisimines like **16** can be observed by MS and matrix isolation IR in certain cases, their transient nature has so far precluded detailed studies of their chemical reactions.

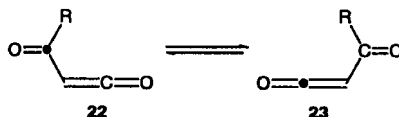
Phenyliminopropadienethione (**21**) proved difficult to synthesize (**14**) and even harder to trap with nucleophiles, but both of these challenges have now been mastered (**15**). A thermal elimination reaction provides the transient



thioketene **20**, and familiar isoxazolone chemistry involves loss of CO<sub>2</sub> via opening of the N-O bond, followed by 1,2-migration of the phenyl group in the putative vinylnitrene. The thiocumulene **21** has been thoroughly characterized by MS and by matrix isolation IR in conjunction with ab initio calculation of the spectrum; it reacts sluggishly with amines at the thiocarbonyl and imine carbon atoms (**15**).

### KETENE—KETENE REARRANGEMENTS

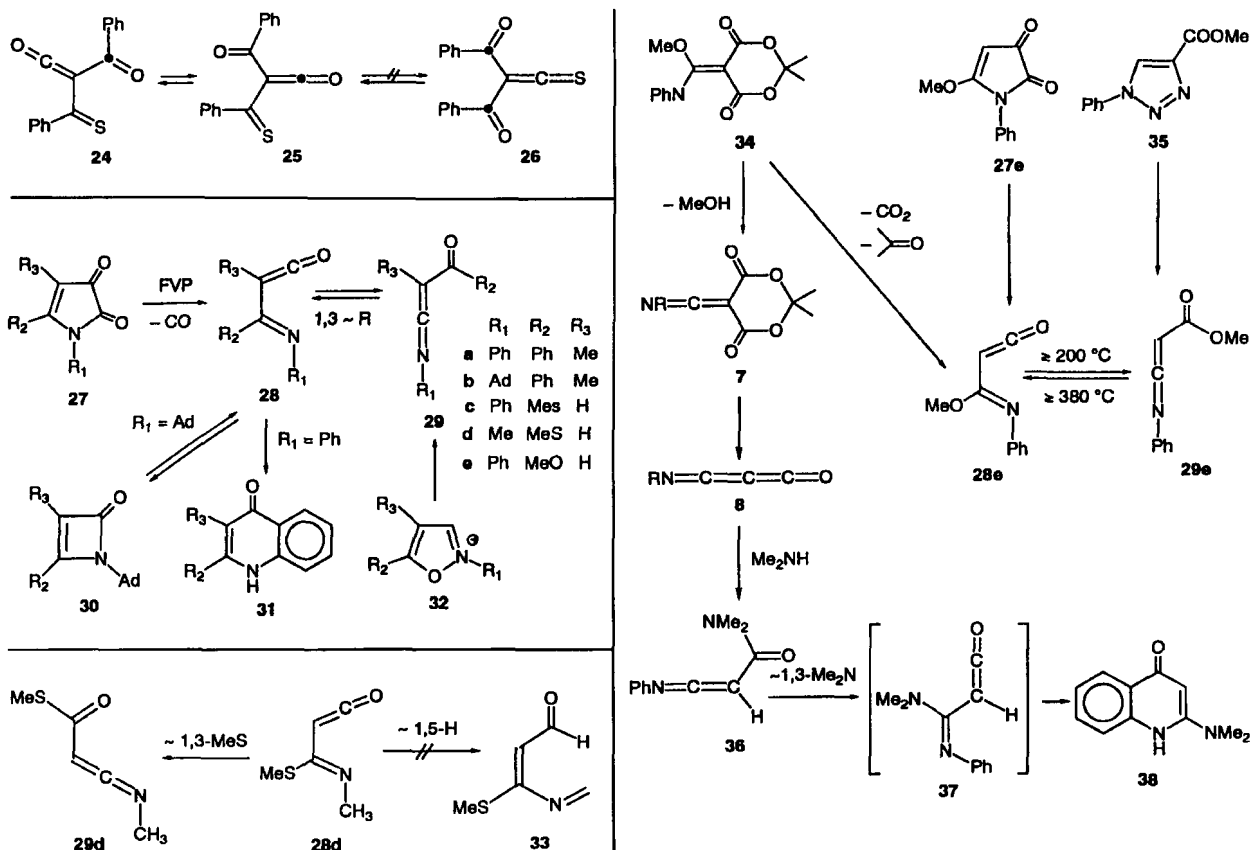
In the FVP of some of the Meldrum's acid derivatives, such as **6**, a competing reaction leads to an imidoalketene—oxoketenimine rearrangement. This is a variant of the  $\alpha$ -oxoketene— $\alpha$ -oxoketene interconversion (**22**  $\rightleftharpoons$  **23**), first established in the case of benzoylketene (**22**, R = Ph) and demonstrated by <sup>13</sup>C



labeling to involve a 1,3-shift of the phenyl group, starting at *ca* 500 °C and being complete at 800 °C under FVP conditions (16). Subsequent work revealed that a methyl group does not undergo this 1,3-shift even at 1000 °C (17). In contrast, as shown below, electron rich groups will readily undergo this migration.

An analogous 1,3-phenyl shift interconverts <sup>13</sup>C-labeled benzoyl(thiobenzoyl)ketenes **24** and **25**, but the isomeric thioketene **26** was not detectable, probably because of the reversibility of the reaction together with the *ab initio* computational finding that thioformylketene is of lower energy than formylthioketene (18,19).

Imidoylketenes **28** have been generated from pyrroldiones **27** and, in some cases, also from the isomeric ketenimines **29** (**a** and **e**). Ketenes **28 a, c, and e** readily cyclize to quinolones **31** in high yields. Nevertheless, the interconverting ketenes and ketenimines (cases **b-e**) can be observed directly by low temperature IR spectroscopy. **29a** and **29e** are isolable and rearrange on mild FVP to the quinolones **31** via ketenes **28**. In the adamantyl case, a separate equilibrium with the azetin-2-one **30b** was observed (20-23).



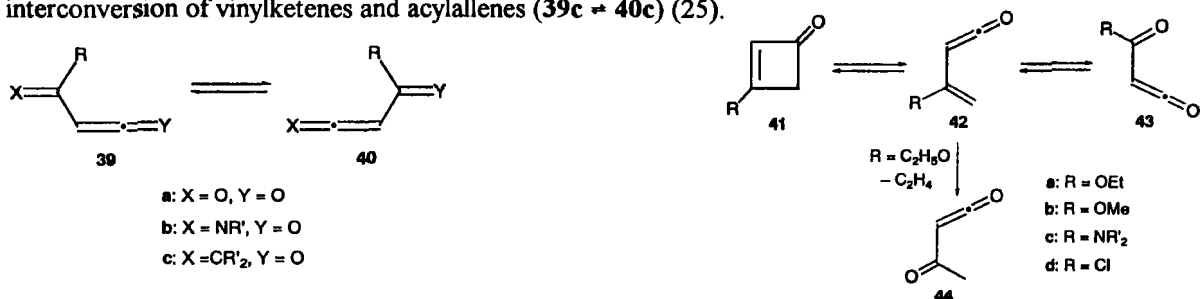
The 1,3-shifts of MeS and MeO groups are extremely facile. The MeO shift **28e** → **29e** is observable already at 200 °C; the reverse reaction, **29e** → **28e** is observable from 380 °C onwards (23). *Ab initio* calculations indicate that **29** is of lower energy than **28** (19). The MeO and MeS shifts are able to compete with the cyclization of **28** to quinolones **31**, so much so that **29e** can be isolated from the FVP of **27e**. The MeS shift in **28d** also competes successfully with the normally expected (2, 24) 1,5-H shift to **33**.

Ketenes **28c** and **d** can also be generated from the Meldrum's acid **6** (R = Ph or Me) in competition with RNCCCO (**8**) formation (*vide supra*). **8** is not formed from **28** or **29**.

Similarly, ketene **28e** is formed from Meldrum's acid **34** together with PhNCCCO (**8**), the proportion of the latter increasing with the temperature. The ketenimine **29e** can also be approached from the triazole **35**; in each case the equilibrium between **28e** and **29e** is established, and **28e** finally cyclizes to **31e** (23).

Amide-substituted ketenimines, e.g. **36**, are obtainable by low temperature addition of amines to iminopropadienones **8**. The ketenimine **36** rearranges at room temperature to quinolone **38**, thus implying an extraordinarily facile 1,3-migration of the dimethylamino group to the intermediate ketene **37** (11).

The generality of ketene rearrangements of the type **39**  $\rightleftharpoons$  **40** is further illustrated by the recently discovered interconversion of vinylketenes and acylallenes (**39c**  $\rightleftharpoons$  **40c**) (25).



For example, ethoxyvinylketene **42a** is obtainable from cyclobutenone **41** and interconverts with allene **43a** on FVP at *ca* 600°. At higher temperature, irreversible loss of ethylene causes formation of *Z*- and *E*-acetylketene **44a** (25). The analogous rearrangements of amino- and chloro-substituted derivatives (**42/43c,d**) have also been observed (26).

The facile migration of electron donating groups R can be understood in terms of a favourable interaction between a filled lone pair orbital on R with the vacant atomic p orbital of the ketenic carbon atom, forming part of the ketene LUMO (27). Ab initio calculations provide the following sequence of migratory aptitudes: NMe<sub>2</sub> > Br > Cl > MeS > NHMe > SH > OCH<sub>3</sub> > NH<sub>2</sub> > OH > H > Ph > CH<sub>3</sub> (25,27). Halogen atoms are also predicted to undergo this remarkable 1,3-shift very easily (19,26).

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