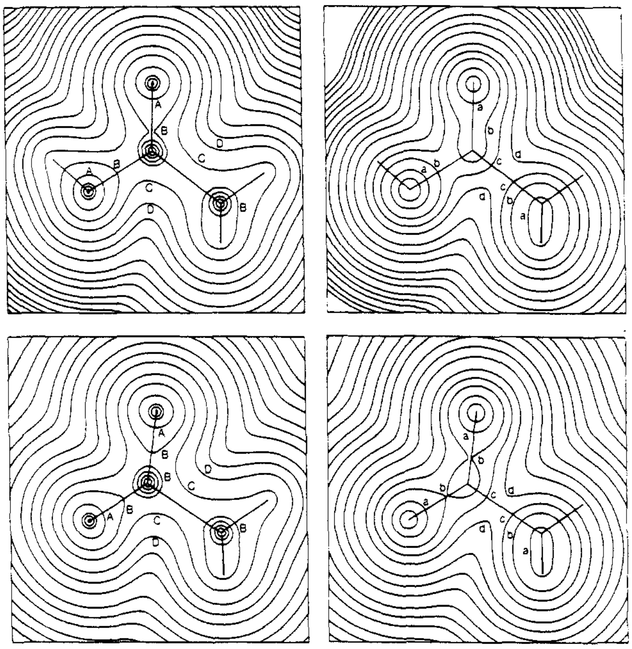

Figure 4. Projection density functions for acetic acid (upper left = total density, upper right = π density) and acetate ion (lower left = total density, lower right = π density). The contour values are the same as for Figure 3.

the result is presented as a contour plot. Plots of this type are shown for (*Z*)-methyl acetate and its anion in Figure 3. The corresponding plots for the *E* ester and anion appear quite similar. In the plots, one might first note how the oxygens dominate the charge distribution. The carbonyl carbon has been stripped of much of its valence electron distribution, and this agrees well with the strong polarization found in the population analysis.

When the ester and anion are compared, it will be seen that the total density contours are not much different. One might expect the main change to be found with the π (out-of-plane) electrons, and their projected densities also are shown in Figure 3. Contrary to common expectation, there is relatively little shift in π density to the carbonyl oxygen on going from the ester to the anion. One must conclude that the origin of the acidity of the esters is the strong polarization of the carbonyl group caused by its oxygen.

It is interesting to compare the results for the ester and its anion with the acetic acid and acetate ion, since the process involved is essentially the same and since the electron populations for methyl acetate and acetic acid are essentially the same (Table II). Charge density projection plots for acetic acid and acetate ion are given in Figure 4. If one were to overlay the total density plots for the acid and the ion, one would find that the locations of the oxygens and the methyl group are essentially unchanged on ionization; only the carbonyl carbon moves. Again, the contours do not change much on going from the acid to the anion. This also is seen on examining just the π charge density plot. There is not a large shift in charge to the carbonyl oxygen on ionization. These results are completely in accord with the conclusions of Siggel and Thomas[9] that the difference in acidity between ethanol and acetic acid results from the polarization of the carbonyl group in the acid.

One may also note that whereas the electron population at the carbonyl carbon of the esters increases on ionization, that for acetic acid decreases. The latter is what one might expect for an allyl anion of the type O–C–O. Here one π MO will have a node at the carbon, and the other will have a relatively small coefficient at carbon because of the electronegativity of the adjacent oxygens. In addition, the electron population at the hydroxy hydrogen is quite small, and so there is not a large amount of charge to be distributed after ionization. On the other hand, an allyl anion of the type O–C–C would be expected to have an increased population at the central carbon because the node in the higher energy π MO will be between the carbon and oxygen, giving the former a significant coefficient. The terminal carbon will be electropositive with respect the central carbon and should donate charge density both via the σ and π MOs. Considerations of these types are important for many carbon acids, and we shall subsequently report similar studies of a wide range of these acids.

Acknowledgment. The calculations were carried out with GAUSSIAN-82.[10] The post-Hartree–Fock calculations were carried out at the Pittsburgh Supercomputing Center with the aid of a grant of computer time from that center. The projection density functions were calculated with a CSPI array processor, which was provided by a DOD instrument grant. The electron populations were calculated with PROAIMS.[11] The investigation was supported by NIH Grant 1GM11629.

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(10) Binkley, J. S.; Frisch, M. J.; DeFrees, D. J.; Raghavachari, K.; Whiteside, R. A.; Schlegel, H. B.; Fluder, E. M.; Pople, J. A. *GAUSSIAN-82*; Carnegie-Mellon University: Pittsburgh, PA, 1982.

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Benzyne, Cyclohexyne, and 3-Azacyclohexyne and the Problem of Cycloalkyne versus Cycloalkylideneketene Genesis

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Received July 29, 1987

Abstract: Benzyne, cyclohexyne, and 3-azacyclohexyne have been obtained by flash vacuum pyrolysis of phthalic anhydride, 4-cyclopentylidene-3-methylisoxazol-5(4*H*)-one (**34**), and 3-methyl-4-(2-pyrrolidinylidene)isoxazol-5(4*H*)-one (**37**), respectively, isolated at 77 K and observed by IR spectroscopy. Trapping and fragmentation reactions are described, and the implications for the mechanism of benzyne formation from phthalic anhydride via cyclopentadienylideneketene (**9**) are discussed.

The formation of benzyne (**1**) in the high-temperature pyrolyses[2] of phthalic anhydride (**3**) and benzocyclobutenedione (**4**) continues to attract vigorous attention, particularly because of the possibility of interconversion of benzyne and cyclopentadienylidenecarbene

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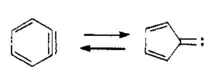
(**2**).[3] Evidence for the formation of **1** from **2** has been reported,[4,5]



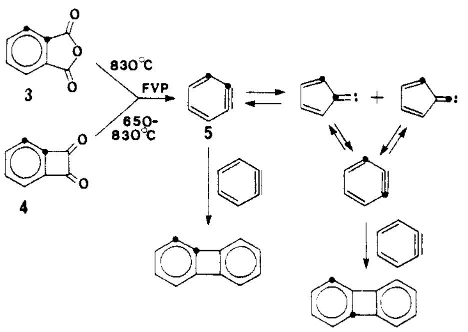
and theoretical calculations[6] indicate that this process is exothermic. Evidence for the forward reaction **1** → **2**, based on the observation of ^{13}C scrambling in the biphenylene product from the flash vacuum pyrolyses (FVP) of labeled phthalic anhydride and benzocyclobutenedione, has also been reported (Scheme I).[3]

C.W. has pointed out[7] that this evidence is insufficient proof of the reaction **1** → **2**. We do not, in fact, doubt that the reaction **1** → **2** may be possible; we maintain that it has not been proven beyond reasonable doubt. The reason that the evidence is insufficient is illustrated in Scheme II. There is no evidence so far published that labeled benzyne **5** is the *initial* product of FVP of **3** and **4**. Rather, we expect a reaction sequence leading eventually to the carbenic ketene **8a**. **8a** may undergo a Wolff-type ring contraction[8] to cyclopentadienylideneketene **9**. If this is so, CO loss from **9** will give cyclopentadienylidenecarbene **10** as the first-formed C_6H_4 species, and hence automatically a 1:1 mixture of the two benzynes **5** and **11**, which would give rise to the biphenylenes **12** and **13** actually isolated. The *reversible* reaction **9** ⇄ **8a** + **8b** + **8c** also considered by us would have the same consequences.[9e] Thus, we need to distinguish the reactions **8a** → **5** directly, **8** → **5** + **11** via **9**, and **8a** → **9** → **10** → **5** + **11**. The problem, but not necessarily the mechanism, is the same in the case of benzocyclobutenedione **4**.

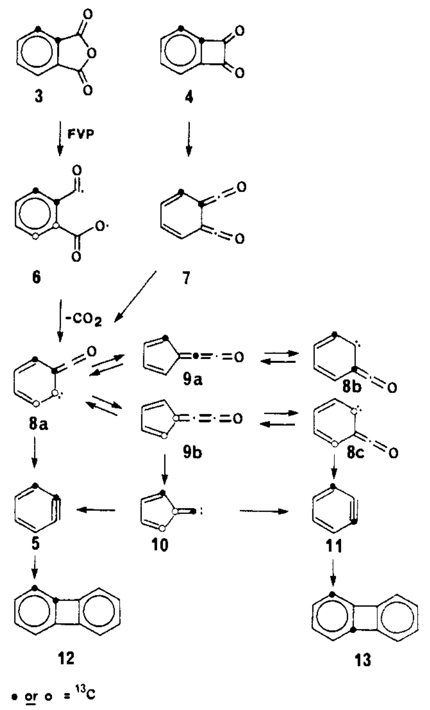
Although we have not published our proposal before, it has sparked intense experimentation and debate and is being frequently quoted.[3,9] The latest information[9f] is that the problem is still not solved. In this paper we wish to add some weight to the credibility of the reactions shown in Scheme II.

In this context there is also a problem with the photoelectron (PE) spectrum of benzyne.[10] Remarkably, a PE spectrum at-

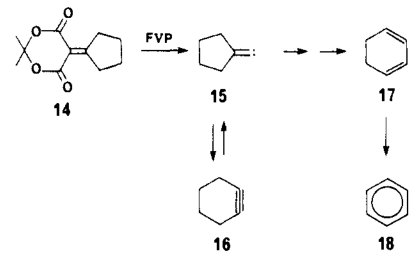
Scheme I



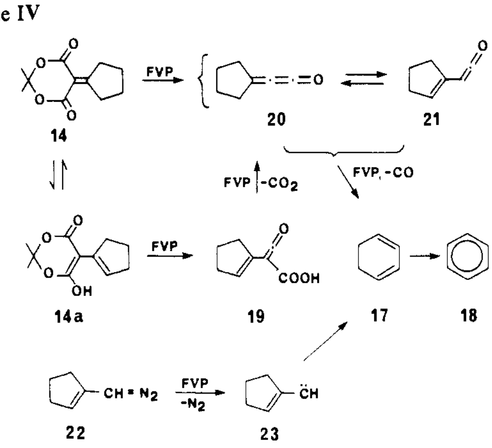
Scheme II



Scheme III



Scheme IV



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[1] (a) Briehl, H. Ph.D. Thesis, University of Marburg, 1984. (b) Gross, G. Ph.D. Thesis, University of Marburg, 1983.

[2] (a) Fields, E. K.; Meyerson, S. *Chem. Commun.* **1965**, 474–476. (b) Brown, R. F. C.; Gardner, D. V.; McOmie, J. F. W.; Solly, R. K. *Aust. J. Chem.* **1967**, *20*, 139–148. (c) Cava, M. P.; Mitchell, M. J.; De Jongh, D. C.; Van Fossen, R. Y. *Tetrahedron Lett.* **1966**, 2947–2951. (d) For the photolysis of **4** to **7** and benzyne (unlabeled case), see: Chapman, O. L.; Mattes, K.; McIntosh, C. L.; Pacansky, J.; Calder, G. V.; Orr, G. *J. Am. Chem. Soc.* **1973**, *95*, 6134–6135. (e) For an alternative route and IR of benzyne (C≡C, 2085 cm^{-1}) see: Chapman, O. L.; Chang, C.-C.; Kolc, J.; Rosenquist, N. R.; Tomioka, H. *Ibid.* **1975**, *97*, 6586–6588. (f) For the microwave spectrum of benzyne from **4**, see: Brown, R. D.; Godfrey, P. D.; Rodler, M. *Ibid.* **1986**, *108*, 1296–1297.

[3] Barry, M.; Brown, R. F. C.; Eastwood, F. W.; Guanawardana, D. A.; Vogel, C. *Aust. J. Chem.* **1984**, *37*, 1643–1657.

[4] Armstrong, R. J.; Brown, R. F. C.; Eastwood, F. W.; Romyn, M. E. *Aust. J. Chem.* **1979**, *32*, 1767–1774.

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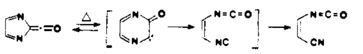
[6] Apeloig, Y.; Schreiber, R.; Stang, P. J. *Tetrahedron Lett.* **1980**, *21*, 411.

[7] Wentrup, C. (1983), quoted in ref 3.

[8] (a) For extensive references see e.g.: Wentrup, C. *Reactive Molecules*; Wiley: New York, 1984. (b) A possible example of a *reversible* Wolff rearrangement of the type **9** ⇌ **8** (cf. Scheme II) is given (Bender, H.; Wentrup, C., unpublished work, 1986) by the reaction



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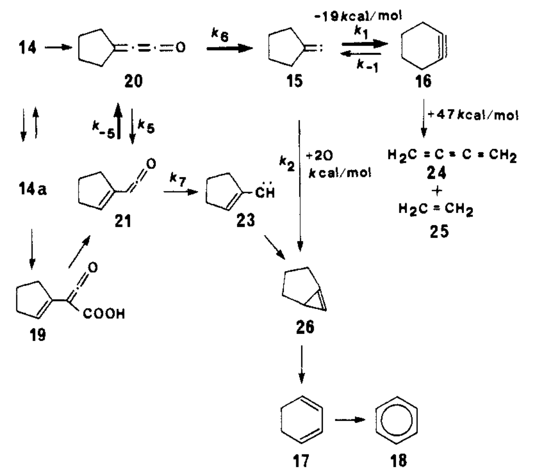
Scheme V



tributed to benzyne is obtained on FVP of unlabeled **3** or **4**, *but not* from other precursors, viz. iodobenzene, *o*-diiodobenzene, and benzoyl bromide.[10] Again, we do not doubt that benzyne is actually formed, but we maintain that the attribution of the PE spectrum to benzyne has not been proved beyond reasonable doubt. It could be that part of the spectrum is due to e.g., cyclopentadienylideneketene **9** (unlabeled). Very recently, computational evidence has cast serious doubt on the assignment of the 9.24-eV PE band to benzyne.[11] This of course adds considerable weight to our scepticism. Even the interpretation of the PE spectra of simple methyleneketenes and vinylketenes[12] is subject to serious doubt,[13] because the underlying chemistry was not known at the time. We are substantiating this claim in a separate publication.[14]

There are other, related problems as well.

The Cyclohexyne Problem

Albeit a well-known *reactive intermediate*, cyclohexyne (**16**) has not, so far, been observed. It was postulated as an intermediate in the FVP of the Meldrum's acid derivative **14** (Scheme III)[15] en route to cyclohexadiene and thence benzene. Here we showed that much more complicated chemistry is involved,[13] as set out in simplified form in Scheme IV. The three ketenes **19**, **20**, and **21**, where **19** constitutes a new type, were all observable and trappable. Although the exact interrelationship between the three is more involved than shown in Scheme IV, in simpler cases each individual ketene is selectively and sequentially obtainable as shown in an accompanying paper.[14] The products **17** and **18** were also obtained from diazo compound **22**, but significantly, *no trace* of cyclohexyne or its trimer dodecahydrotriphenylene could be found in the pyrolyses of **14**. We thought it would be important to find a means of synthesizing cyclohexyne (**16**); the results are reported below.

More recently still, Shevlin has invoked cyclohexyne in an important contribution to the pyrolysis of **14** and shown experimentally that butatriene and ethylene are formed as well (Scheme V).[16] These products were missed in previous investigations, but we have confirmed their presence by inspection of our old spectra. It should be noted that our pyrolysis apparatus operates at much lower pressures and hence shorter contact times than that used in Shevlin's work. Therefore, butatriene and ethylene are very minor products in our experiments ($\geq$800 °C, ca. 10^{-5} Torr, 5-cm quartz pyrolysis tube), not because of the stability of cyclohexyne, but because of the stability of the ketenes. Shevlin[16] lends support to his mechanism (Scheme V) by identifying a high-energy (ΔH^{*} = 46.8 kcal/mol) fragmentation of cyclohexyne to **24** and **25** computationally (MP2/STO 6-31G*). The significant conclusions[16] are that the conversion of cyclopentylidenecarbene (**15**) to cyclohexyne (**16**) is exothermic by ca. 19 kcal/mol, that cyclohexadiene and benzene (**17**, **18**) are formed not from cyclohexyne but from carbene **15**, and that methyleneketene **20** *fragments more rapidly* to **15** than it interconverts with **21** ($k_6 \gg k_5$). This possibility (**21** → **20** → **15** → **16**) is valid, and in fact, it has been suggested before.[17] The problem is again that cyclohexyne (**16**) has not actually been identified.

Results and Discussion

Benzyne. The difficulty of the benzyne problem is due to the fact that phthalic anhydride does not decompose to any significant extent below 900 °C in our apparatus. At these temperatures, however, ketenes decarbonylate. Phthalic anhydride was pyrolyzed at 10^{-5} Torr by using the double-pyrolysis technique (see the Experimental Section) with the two heated sections (5 cm each) at 700 and 800 °C, respectively. In order to be able to perform warmup experiments, the products were not trapped in Ar matrices but isolated directly on KBr windows at 77 K. Very little decomposition occurred. Thus, the products are actually isolated in a solid matrix of phthalic anhydride. Below the temperatures indicated, no perceptible decomposition took place. At these temperatures, the IR bands of benzyne[2d,e] were detected at 720, 815, 1020, 1045, 1440, and 2080 cm^{-1}. Other bands due to benzyne[2d,e] at 1607 and 1627 cm^{-1} would be obscured by phthalic anhydride. All bands were shifted toward lower frequency due to the use of phthalic anhydride rather than argon as the host. This effect is normal. The very weak[2e] C≡C stretching vibration of benzyne appeared as a rather broad peak at 2080 cm^{-1} at 77 K (2085 cm^{-1} in Ar at 8 K[2e]). Warming the matrix to 120 K caused this peak to split into a doublet with maxima at 2090 and 2080 cm^{-1}. On further warming to 180 K, one band had disappeared, leaving a single, weak peak at 2080 cm^{-1}. A shift to lower frequencies is the normal outcome of a warm-up experiment, presumably because of increased intermolecular interaction and aggregation. Therefore, the band position alone does not necessarily reflect its origin. However, benzyne does not survive at 180 K,[18] and the remaining species absorbing at 2080 cm^{-1} may, therefore, be due to cyclopentadienylideneketene **9** (unlabeled). Cyclopentadienylideneketene **9** is a known species,[9a] and we generated it for comparison from the original precursor[4] and also from 5-[7-(2-norbornenylidene)] Meldrum's acid[19] and confirmed the ketene absorption at 2090 (Ar, 12 K) or 2080 cm^{-1} (neat). Since the C≡C stretch of benzyne is very weak, whereas ketenes absorb strongly in this region, the amount of **9** possibly isolated in the pyrolysis of phthalic anhydride was very small and the proof of its structure is not straightforward. We hope to shed more light on this issue with the aid of FT-IR spectroscopy. Since ketenes decarbonylate efficiently under the conditions of the experiment, it is no surprise that the detection of **9** is difficult. We therefore sought an analogous reaction where the ketene, if formed, would have another escape route, thus permitting its indirect detection. The results follow.

Cyclopentylideneketene and Cyclopentenylketene. Cyclohexene-1,2-dicarboxylic anhydride (**27**) is similar to phthalic anhydride in that little or no decomposition took place on FVP below 880 °C. FVP at 880 °C (5 × 10^{-2} Torr) with isolation of the product on a KBr disk at 77 K for IR spectroscopy gave rise to a ketene as signaled by the appearance of a strong and sharp peak at 2110 cm^{-1} (Figure 1, bottom), deposited in the presence of large amounts of undecomposed starting material. This ketene

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(10) Dewar, M. J. S.; Tien, T.-P. *J. Chem. Soc., Chem. Commun.* **1985**, 1243–1244.

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(12) Mohmand, S.; Hirabayashi, T.; Bock, H. *Chem. Ber.* **1981**, *114*, 2609–2621.

(13) Wentrup, C.; Gross, G.; Berstermann, H.-M.; Lorenčak, P. *J. Org. Chem.* **1985**, *50*, 2877–2881.

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(15) Baxter, G. J.; Brown, R. F. C. *Aust. J. Chem.* **1978**, *31*, 327–339.

(16) Tseng, J.; McKee, M. L.; Shevlin, P. B. *J. Am. Chem. Soc.* **1987**, *109*, 5474–5477.

(17) Wentrup, C. *Reactive Molecules*; Wiley: New York, 1984; p 283.

(18) Cf.: Chapman, O. L.; McIntosh, C. L. *J. Chem. Soc. D* **1971**, 1162. Kolc, J. *Tetrahedron Lett.* **1972**, 5321.

(19) Wiersum, U. E., to be published.

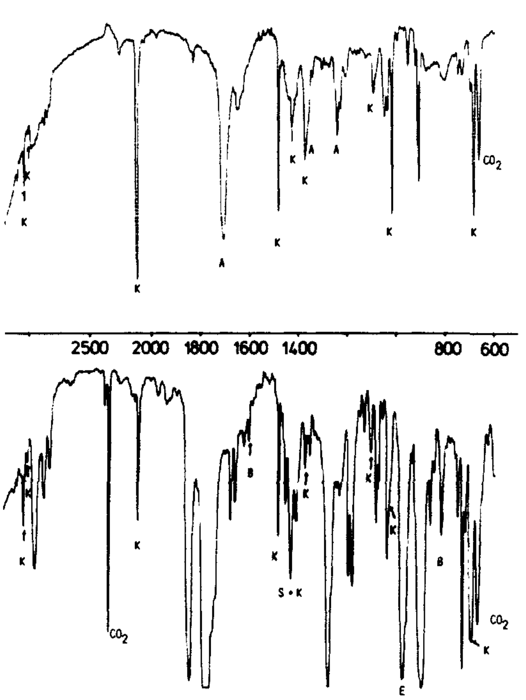
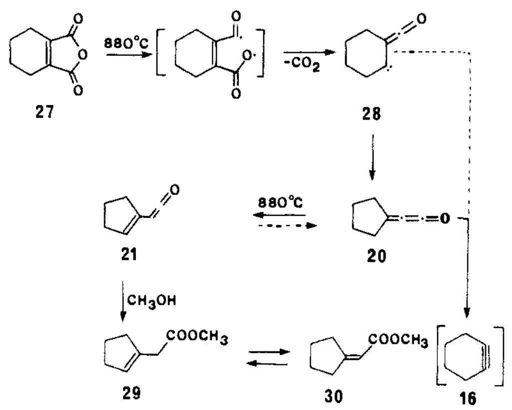
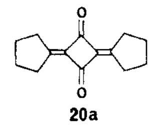


Figure 1. IR spectra at 77 K. Top: cyclopentenylketene **21** obtained by FVP of **14** at 750 °C. Bottom: cyclopentenylketene **21** in the presence of **27**, obtained by FVP of **27** at 880 °C. Key: K = ketene **21**; A = acetone; E = ethylene; B = butatriene; S and unmarked peaks = starting material.

Scheme VI



was found to be identical with cyclopentenylketene **21**, which we had characterized previously[13] (see Schemes IV and VI and Figure 1). Ketene **21** formed according to Scheme VI had numerous IR bands in common with that formed according to Scheme IV (Figure 1) [3030 (w), 3005 (w), 2110 (s), 1480 (s), 1435 (m; partly obscured by **27**), 1370 (m), 1100 (m), 1020 (s), 680 (s) cm^{-1}]. Both ketenes disappeared on warm-up at −90 to −70 °C, causing all the abovementioned bands to vanish. For further identification, cyclopentenylketene **21** was also generated by FVP of the dimer[13] of **20** (**20a**) at 700 °C. Again the abovementioned IR bands were observed, and again the monomer **20** did not survive due to isomerization to **21**.



20a

Finally, ketene **21** produced from the anhydride **27** was trapped with methanol on the cold finger at 77 K. Warm-up followed by ^{1}H NMR and GC–MS analysis confirmed that ester **29** (Scheme VI) was formed together with a few percent of the isomer **30**, indicating that a little of the methyleneketene **20** had survived the experiment,[20] even though the amount was too small for direct observation by IR (2087 cm^{-1}; ref 13). **29** interconverts with **30** on heating, but not in the cold.[13]

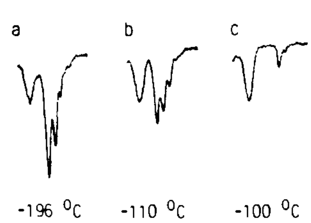
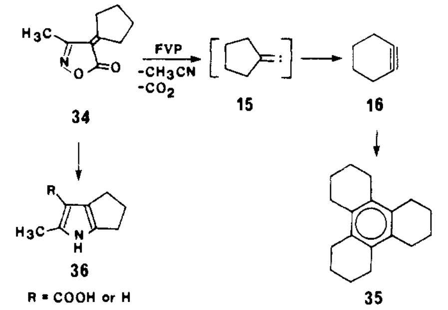


Figure 2. IR spectra (2200–2000 cm^{-1}) of cyclohexyne obtained by FVP of **34** at 850 °C, showing disappearance of peaks at 2090 and 2105 cm^{-1} on warming to −100 °C.

Scheme VII



Nor was cyclohexyne directly detectable by IR (vide infra), and no trace of the trimer dodecahydrotriphenylene or a methanol addition product was detectable by meticulous GC–MS. This does not mean that cyclohexyne is not produced: at the temperature of 880 °C the Shevlin mechanism[16] (Scheme V) operates, so that any cyclohexyne formed would be rapidly removed as cyclohexadiene, benzene, butatriene, and ethylene. Indeed, the ^{1}H and ^{13}C NMR spectra of the liquid pyrolyzate from **27**, obtained in the preparative apparatus (see the Experimental Section) at 900 °C, demonstrated that it consisted of benzene, butatriene, and a smaller amount of 1,3-cyclohexadiene. The IR spectrum of the gaseous product revealed CO$_2$ and ethylene. The presence of ethylene and butatriene is also clearly visible in the low-temperature IR spectrum in Figure 1 (bottom) [ethylene 970 (vs) cm^{-1}; butatriene 810 (s), 1600 (m), 2000 (vw) cm^{-1}]. These products are not visible when **21** is generated from the Meldrum's acid precursor **14** at 750–840 °C (Figure 1, top).

The results solidly confirm the formation of vinylketene **21** from anhydride **27**, and they have important bearing on the benzyne problem of Scheme II. In Scheme II, the ketenes **9** have no other escape routes: they must lead to benzyne; the high temperature required makes either of the reactions **9** → **10** → **5** or **9** → **8** → **11** so rapid that a direct isolation of significant quantities of **9** becomes nearly impossible (vide supra). In Scheme VI, in contrast, the analogous ketenes **28** and/or **20** lose CO to give cyclohexyne, but methyleneketene **20** *has a new escape route*, making it indirectly detectable in the form of **21**. The conclusiveness of our experiment is thanks to the fortunate circumstance that vinylketenes such as **21** are thermally very stable. We have recently discovered another such case, namely the equilibration of imidoylketene (**31**) and 3-aminopropadienone (**32**) where the latter decarbonylates to ethynamine (**33**) (directly detectable and isolable at low temperatures), whereas the imidoylketene is thermally very stable above 800 °C.[21]

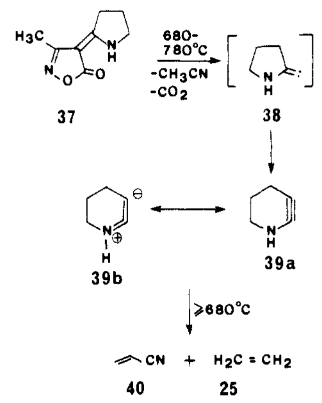
$$\underset{\textbf{31}}{\mathrm{HN{=}CHCH{=}C{=}O}} \rightleftarrows \underset{\textbf{32}}{\mathrm{H_2NCH{=}C{=}C{=}O}} \rightarrow \underset{\textbf{33}}{\mathrm{H_2NC{\equiv}CH}} + \mathrm{CO}$$

---

[20] (a) No ketene was observed on similar FVP of cyclohexene-2,3-dicarboxylic anhydride, thus demonstrating that hydrogen 1,3-shifts do not occur in this substance at 880 °C. In contrast, 1,3-shifts in ketenes occur thermally at much lower temperatures.[13,14,20b] (b) Wentrup, C.; Netsch, K.-P. *Angew. Chem.* **1984**, *96*, 792; *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 802.

[21] Wentrup, C.; Briehl, H.; Lorenčak, P.; Vogelbacher, U. J.; Winter, H.-W.; Maquestiau, A.; Flammang, R. *J. Am. Chem. Soc.*, in press.

Scheme VIII



Cyclohexyne. Isoxazol-5(4*H*)-ones are excellent precursors of a variety of unusual and otherwise inaccessible acetylenes, including ethynamine (**33**).[21-23] FVP of 4-cyclopentylidene-3-methylisoxazol-5(4*H*)-one (**34**) (Scheme VII) at 700–850 °C (10^{-4} Torr) gave CO_2, acetonitrile, and a compound absorbing at 2090 and 2105 cm^{-1} in the IR (Figure 2; precision of measurement, ±2 cm^{-1}). These signals disappeared on warm-up between −110 and −100 °C (Figure 2b). After warming to room temperature, the trimer of cyclohexyne, dedecahydrotriphenylene (**35**), was rigorously identified, first by GC–MS, and then by preparative GC and ^1H NMR. The yield is low, and the signals ascribed to cyclohexyne are weak, but they are expected to be weak because of the high symmetry.[24] Futhermore, cyclohexyne formation has to compete with production of the pyrroles **36**, a process described in detail elsewhere.[25] Therefore, the yield of cyclohexyne, as measured by the intensity of the 2090–2105 cm^{-1} peaks, increases over the temperature range 700–850 °C. The "real" yield of cyclohexyne must be much higher than 2% because much of it is removed as benzene, butatriene, and ethylene at these temperatures. Once again, these products were identified just as described for the pyrolysis of **27** above.

The observed C≡C stretching vibration of cyclohexyne is in excellent agreement with our MNDO calculated value[26] and with predictions based on ab initio calculations for cyclopentyne (1828 cm^{-1}),[27a] cyclohexyne,[27b] and the known 3,3,7,7-tetramethylcycloheptyne (2190, 2170 cm^{-1}).[28] Since the strain energy should increase nonlinearly as the rings become smaller, the C≡C stretching vibrations should move to progressively lower frequencies. A double absorption band is not unexpected: whereas normal allenes, for example, give single sharp lines in the IR, the strained cyclic allene cycloheptatetraene possesses a double band of low intensity.[29] Disubstituted acetylenes often feature double bands.[28,30] Cyclooctyne shows two bands, at 2260 and 2206 cm^{-1}.[24]

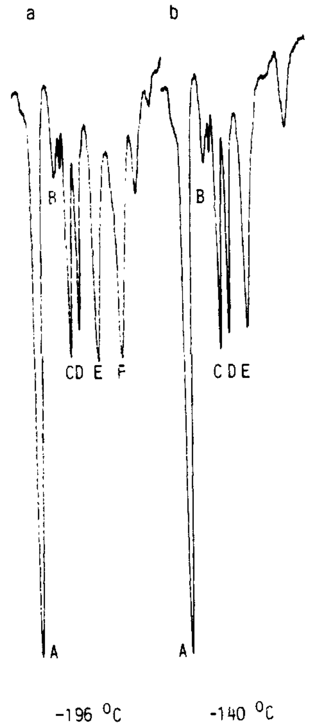
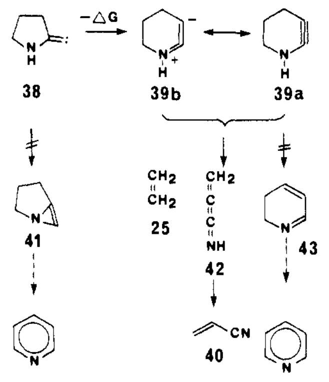


Figure 3. IR spectra (2400–2000 cm^{-1}) of 3-azacyclohexyne **39** produced by FVP of **37** at 780 °C: (a) at −196 °C; (b) at −140 °C. Key: A = CO_2 (2338 cm^{-1}); B and C = acetonitrile; D = acrylonitrile (2228 cm^{-1}); E = polymer (2180 cm^{-1}); F = **39** (2114 cm^{-1}); minor bands, 2074 and 2034 cm^{-1}.

Scheme IX



Is cyclohexyne formed from the Meldrum's acid derivative **14** at all? It probably is, but its presence is very difficult to establish directly. At temperatures where **20** is stable, no cyclohexyne is formed. When **20** starts decomposing, so does cyclhexyne, and its detection in the presence of **20** is impossible since the ketene absorbs very strongly and masks any signals due to **16**. Conditions where the rate of formation of cyclohexyne is high enough, and the rate of its decomposition slow enough to permit both its detection and the isolation of the trimer, were found only in the case of the isoxazolone **34**, and then only because no ketenes are produced to obscure the IR region of interest.

Given sufficient time and patience, this methodology (Scheme VII) ought to permit a microwave spectroscopic detection and hence full structural elucidation of cyclohexyne. Such work is being planned.

3-Azacyclohexyne. The strategy is illustrated in Scheme VIII. FVP of isoxazolone **37** in the temperature range 680–780 °C produced CO_2, acetonitrile, and a new, sharp peak at 2114 cm^{-1} (77 K), which was as strong as those of acetonitrile at the optimal temperature of 780 °C (Figure 3). New peaks at 2228 and 2180

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(24) Cf.: Meier, H.; Petersen, H.; Kolshorn, H. *Chem. Ber.* **1980**, *113*, 2398–2409.

(25) Wollweber, H.-J.; Wentrup, C. *J. Org. Chem.* **1985**, *50*, 2041–2047.

(26) Our corrected MNDO calculated value for the cyclohexyne C≡C stretching vibration, 2092 cm^{-1}; ΔH_f, 88 kcal/mol.

(27) (a) Olivella, S.; Pericàs, M. A.; Riera, A.; Solé, A. *J. Am. Chem. Soc.* **1986**, *108*, 6884–6888. (b) A corrected GVB/3-21G calculated value for cyclohexyne is 2003 cm^{-1}: Olivella, S.; Pericas, M. A.; Riera, A.; Solé, A. *J. Org. Chem.* **1987**, *52*, 4160–4163. (c) The corrected GVB/3-21G calculated value for the C≡C stretch of 3,6-dioxacyclohexyne (1897 cm^{-1}) is surprisingly low in view of the normal behavior of 3-azacyclohexyne (**39**): Olivella, S.; Pericas, M. A.; Riera, A.; Serratosa, F.; Solé, A. *J. Am. Chem. Soc.* **1987**, *109*, 5600–5605.

(28) Krebs, A.; Kimling, H. *Angew. Chem.* **1971**, *83*, 540; *Angew. Chem., Int. Ed. Engl.* **1971**, *10*, 509. Unsubstituted cycloheptyne reportedly absorbs weakly at 2121 cm^{-1} (Ar, 17 K), and bands at 2107 and 2116 cm^{-1} were tentatively assigned to 3,3,6,6-tetramethylcyclohexyne: Krebs, A.; Cholcha, W.; Müller, M.; Eicher, T.; Pielartzik, H.; Schnöckel, H. *Tetrahedron Lett.* **1984**, *25*, 5027–5030.

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cm^{-1} also grew over the whole temperature range, and the 2228-cm^{-1} peak continued growing after first the 2114-cm^{-1} and then the 2180-cm^{-1} signals had disappeared at pyrolysis temperatures above 780 °C. The 2180-cm^{-1} band belonged to a polymer and hence remained stable at room temperature. The 2228-cm^{-1} band was shown by ^1H and ^{13}C NMR spectroscopy to be due to acrylonitrile. The IR spectrum obtained by expanding the pyrolyzate into a gas cell demonstrated the presence of ethylene and CO_2 only. Apart from the polymer, CO_2, ethylene, acrylonitrile (**40**), acetonitrile, and starting material were the *only* detectable products at room temperature.

The 2114-cm^{-1} band is ascribed to 3-azacyclohexyne (**39**) for the following reasons: (i) it is very unstable, disappearing on warming to −150 to −130 °C; (ii) the polymer signal grows in concert with the 2114-cm^{-1} species up to 780 °C; (iii) when the 2114-cm^{-1} species disappears above 780 °C, so does the polymer; (iv) the polymer is similar to but different from the one obtained from ethynamine;[21] (v) when the 2114-cm^{-1} species *and* the polymer disappear at 800 °C, **25** and **40** are the *only* products apart from acetonitrile, CO_2, and unchanged starting material; (vi) the frequency of the $C\equiv C$ stretching vibration is a little higher than that of cyclohexyne; this is the expected effect of an amine substituent;[21] (vii) the strength and sharpness of the band is typical of aminoacetylenes.[21,27c,31]

The peculiarities of **39** will be discussed with reference to Scheme IX. Resonance (**39a** $\leftrightarrow$ **39b**) is expected to lower the energy of the acetylene significantly with respect to cyclohexyne itself. This makes the reaction **38** → **39** even more exothermic than the all-carbon case in Scheme V. Moreover, the reaction **38** → **41** will also be more endothermic than its analogue in Scheme V because **41** is a formally antiaromatic 1*H*-azirine, thus making this route to pyridine very unfavorable. Like cyclohexyne,[16] **39** does not, apparently, isomerize directly to dihydropyridine (**43**) either. Although open-chain secondary ethynamines isomerize to ketenimines,[21,32] such a route is unattractive for **39** for reasons of ring strain. Although canonical structure **39b** is expected to contribute to the stabilization of this acetylene, it is also a dipole, thereby accounting for the extreme ease of polymerization of this material. In the dilute gas phase, no other escape route than fragmentation to propadienone imine (**42**) and ethylene seems open. **42** is too unstable to be isolated from this reaction: it undergoes the expected[21] isomerization to a nitrile, viz. acrylonitrile (**40**). Ketene and ketenimine[33a] absorb in the IR at 2131 and 2040 cm^{-1}, respectively, and propadienone[33b] at ca. 2100 cm^{-1} under the solid-state conditions used here. Compound **42** would then be expected near 2010 cm^{-1}. In fact, the IR spectrum (Figure 3) does show very weak and transitory bands at 2034 and 2074 cm^{-1}. The 2034-cm^{-1} band disappears at the same time as **39**, but the 2074-cm^{-1} band only at −130 °C. However, any assignment of these minor bands at the present time would be hazardous.

Conclusion. Benzyne is produced by FVP of phthalic anhydride, but its inverconversion with cyclopentadienylidenecarbene is yet to be proven. Nothing forbids the reaction **1** $\rightleftarrows$ **2** from occurring, but its operation in the pyrolysis of phthalic anhydride, benzocyclobutenedione, and other sources of benzyne remains to be established.

Flash vacuum pyrolysis of cyclohexene-1,2-dicarboxylic anhydride (**27**) produces isolable and trappable cyclopentenylketene **21** as well as the cyclohexyne fragmentation products, i.e., ethylene, butatriene, and benzene. These facts demonstrate that similar pathways in the FVP of phthalic anhydride and benzocyclobutenedione are extremely likely (Scheme II). The FVP of Meldrum's acid derivative **14** may well lead to cyclohexyne (**16**), but this compound is not directly observable in this reaction because of rapid fragmentation to butatriene and ethylene at the high temperatures required. However, cyclohexyne (**16**) is directly observable in the pyrolyses of isoxazolene **34** where no ketenes are formed; here, the trimer **35** of cyclohexyne is isolable (Scheme VII). 3-Azacyclohexyne (**39**) is generated in a similar manner from isoxazolene **37**. **39** is directly observable at 2114 cm^{-1} but highly reactive. In the gas phase it undergoes exclusive fragmentation to ethylene and acrylonitrile. These results directly support the Shevlin methanism[16] of cyclohexyne fragmentation. The isoxazolone route opens the road to a more detailed spectroscopic study of cycloalkynes and heteroanalogues.

Experimental Section

Apparatus. The pyrolysis apparatus used for low-temperature IR studies consists of a 10-cm-long (0.8-cm-i.d.) quartz tube divided into two heating zones, each of 5-cm length and individually wrapped with Kanthal wire and equipped with thermocouples. The tube is suspended in the center of a 5.6-cm-i.d. stainless steel cooling mantle, which is flanged to the shroud of an Air Products liquid N_2 cryostat (for 77 K) or a Leybold-Heraeus closed-cycle liquid He cryostat (for 10 K). The quartz tube is surrounded by a vacuum and terminates ca. 2 cm from the cold end of the cryostat where the products are deposited, usually on KBr disks. The pyrolysis temperature given is that of the second 5-cm length of the tube. In such cases, the first heating zone serves only to sublime the starting material and is maintained at a suitable temperature, usually not higher than 200 °C. In dual pyrolysis experiments, the two 5-cm lengths are both used for pyrolysis at individual temperatures. The second heating zone is surrounded by a silver-mirrored quartz radiation shield, which maintains constant temperature of the tube to within a few millimeters of the exit end and at the same time serves to minimize infrared radiation that would otherwise arrive on the cold end of the cryostat and cause significant temperature increase. The vacuum is maintained with a Pfyffer TSH 101 turbomolecular pump flanged to the opposite side of the cold end through a 5-cm-o.d. stainless steel "chimney" to minimize the pressure gradient, i.e., the pumping line is linear in the direction of the pyrolysis tube and only interrupted by the KBr disk in the center of the cold head. The operating pressure is 10^{-5} Torr or better or as stated. The actual pressures quoted for pyrolyses are those measured at the inner wall of the reactor mantle farthest removed from the pump. This construction allows for extremely short contact times (10^{-3} s or less), and consequently, very high nominal temperatures are required in order to bring about any reaction. The nominal temperatures required are often up to 200 °C higher than those quoted by other workers in the field. At the risk of stating the obvious, this implies that our conditions are actually very significantly milder.

For preparative experiments not involving direct observation of intermediates, a 20 × 2 cm (o.d.) quartz tube and an Edwards Diffstak two-stage oil diffusion pump capable of a vacuum of 10^{-3}–10^{-5} Torr was used and products were trapped in liquid N_2 traps in a conventional manner. The tubes were unpacked.

IR spectra were recorded on a Perkin-Elmer 281 instrument at a resolving power of 1 cm^{-1} and a precision of 2 cm^{-1}. ^1H and ^{13}C NMR spectra were recorded at 400 and 100 MHz, respectively. Mass spectra quoted are 70-eV electron ionization spectra obtained with direct insertion.

Pyrolysis of phthalic anhydride was carried out as described in the general text. Benzyne was identified by comparison with the reported IR spectrum.[2d,e] Cyclopentadienylideneketene **9** was generated by FVP of 5-[7-(2-norbornenylidene)] Meldrum's acid, which was provided to us by Dr. U. E. Wiersum at Akzo Research, Arnhem, Holland.

Pyrolyses of 5-cyclopentylidene-2,2-dimethyl-1,3-dioxane-4,6-dione (14) and cyclohexene-1,2-dicarboxylic anhydride (27) were carried out at the temperatures given in the text and employing the single pyrolysis zone of the apparatus for low-temperature IR spectroscopy. Spectra are given in Figure 1. Trapping with methanol was performed in the same apparatus by codepositing the pyrolyzates with methanol followed by warm-up to room temperature and analysis by ^1H and ^{13}C NMR spectroscopy. Methyl cyclopentenylacetate (**29**) and methyl cyclopentylideneacetate (**30**) were identified by comparison with authentic samples previously described.[13] Dodecahydrotriphenylene was searched by GC and GC-MS (SE 30), and the search was negative. Benzene, cyclohexa-1,3-diene, and butatriene[34] were determined by ^1H and ^{13}C NMR spectroscopy; butatriene was also determined by IR spectroscopy[34] at 77 K. Cyclohexa-1,4-diene was not detectable. The presence of CO_2 and/or acetone was determined from the low-temperature IR spectra and CO_2 also from gas-phase IR spectra. When ethylene was assayed, the

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preparative pyrolysis apparatus was used with two liquid N_2 traps, and at the end of the experiment the contents of the traps were allowed to expand into a gas cell for IR spectroscopy. Yields of products from **14** were as previously described,[13] except that traces of butatriene and ethylene were detected as well. In the preparative pyrolysis of **27** at 900 °C, 50% of the starting material was recovered unchanged. The liquid product showed strong signals at δ 95.7 and 170.9 (butatriene) and 128.3 (benzene) in the ^{13}C NMR. The gas-phase IR spectrum of the volatile product was due to a mixture of CO_2 and ethylene, identified by comparison with the spectra of authentic samples.

4-Cyclopentylidene-3-methylisoxazol-5(4*H*)-one (34)[25] (200 mg, 1.21 mmol) was sublimed at 85 °C and pyrolyzed at 800 °C (10^{-3} Torr), collecting the products at 77 K. The pyrolyzate was warmed to room temperature and analyzed by GC on two columns: (i) SE 52, 80 °C, programmed at 12 °C/min to 250 °C, 29 psi He; (ii) SE 30, isothermal, 180 °C, 30 psi He. The following products [retention time on column (i) and yield in parentheses] were identified by comparison of retention times and GC–MS with those of authentic samples: 4,5-dihydro-2-methylcyclopenta[*b*]pyrrole (**36**, R = H) (721 s, 71%), 4,5-dihydro-2-methyl-cyclopenta[*b*]pyrrole-3-carboxylic acid (**36**, R = COOH) (796 s, 17%), dodecahydrotriphenylene (**35**) (1597 s, ca. 2%). On column (ii) **35** had a retention time of 1038 s.

3-Methyl-4-(2-pyrrolidinylidene)-3-methylisoxazol-5(4*H*)-one (37). 3-Methylisoxazol-5(4*H*)-one (1.98 g, 20 mmol) and 2-methoxy-1-azacyclopent-1-ene[35] (1.98 g, 20 mmol) were dissolved in 50 mL of toluene, and 1.8 mL of acetic acid and 0.7 mL of piperidine were added. The mixture was stirred for 10 min at 50 °C, which caused a white solid to precipitate. The mixture was then heated at reflux for 20 min. The dark red to brown mixture was cooled and filtered and the solid recrystallized from either ethanol or water to give 1.5 g (45%) of long, white needles: mp 200–201 °C; IR (KBr) 3480 (m), 3230 (m), 2975 (w), 2930 (w), 1695 (s), 1595 (s), 1545 (s), 1415 (m), 1310 (s), 1145 (m), 1080 (m), 1010 (s), 960 (s), 870 (s), 830 (m) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.20 (s, 3 H, CH_3), 2.21–2.28 (m, 2 H), 3.02 (t, 2 H), 3.76 (t, 2 H), 9.33 (br, NH); ^{13}C NMR ($CDCl_3$) δ 13.5 (CH_3), 86.9 (C-4), 158.4 (C-6), 168.7 (C-3), 175.3 (C-5); MS *m/z* (relative intensity) 167 ($[M + 1]^+$, 9), 166 ($[M]^{\cdot +}$, 100), 165 ($[M - 1]^+$, 65), 109 (15), 108 (37), 95 (22), 92 (15), 53 (12), 41 (12), 39 (13). Anal. Calcd for $C_8H_{10}N_2O_2$: C, 57.82; H, 6.07; N, 16.86. Found: C, 58.07; H, 6.04; N, 16.94.

Pyrolyses of this compound were carried out in the temperature range 680–790 °C as described fully in the text. For identification of the stable products, the pyrolysis was carried out at 700 °C in the preparative apparatus collecting the products in two liquid N_2 traps. The gaseous products were allowed to expand into a gas cell for IR spectroscopy. A strong spectrum due to CO_2 and ethylene resulted, and these were the only constituents (ratio ~1:1, i.e., 100% pyrolysis yield). The liquid product was taken up in $CDCl_3$ and determined by IR, ^1H NMR, and ^{13}C NMR spectroscopy to consist of acetonitrile and acrylonitrile (1:0.9). No other products were detectable. Thus, the pyrolysis yield of acrylonitrile was 90%.

Acknowledgment. This research was supported by the Deutsche Forschungsgemeinschaft, Fonds der Chemischen Industrie, and Australian Research Grants Scheme. We are grateful to Dr. U. E. Wiersum, Akzo Research, Arnhem, Holland, for a gift of 5-[7-(2-norbornenylidene)] Meldrum's acid, and to Professor P. B. Shevlin, Auburn University, for a preprint of his paper.

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Interrelationship between Carboxy(vinyl)ketenes, Methyleneketenes, Vinylketenes, and Hydroxyacetylenes

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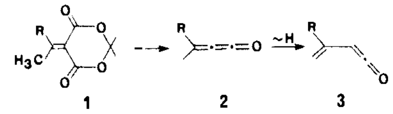
Abstract: Carboxy(vinyl)ketenes, alkylideneketenes, and vinylketenes have been obtained selectively, sequentially, and isomerically pure for the first time by flash vacuum pyrolysis of 2,2-dimethyl-5-alkylidene-1,3-dioxane-4,6-diones (Meldrum's acid derivatives) under controlled conditions. Each of the ketenes was directly observed by IR spectroscopy and trapped with methanol or aniline. Highly unstable compounds believed to be the hydroxyacetylene isomers of the alkylidene- and vinylketenes have been observed for the first time.

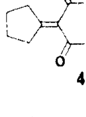
It was thought until recently that 5-alkylidene derivatives of Meldrum's acid (2,2-dimethyl-1,3-dioxane-4,6-dione) **1** decompose thermally to alkylideneketenes **2** which then, given the presence of a δ-hydrogen atom, isomerize in a second step at higher temperatures to vinylketenes **3**. Photoelectron spectra of ketenes **2** and **3** were assigned on the basis of this assumption.[1] We have shown that the assumption is a vast oversimplification[2] and now report that the chemistry of simple Meldrum's acid derivatives is even more complicated than previously thought, involving no less than four different species: a carboxy(vinyl)ketene, a methyleneketene, a hydroxyacetylene, and a vinylketene.



1 **2** **3**

a R = CH_3
b R = H

The flash vacuum pyrolysis (FVP) of the 5-cyclopentylidene derivative **4** of Meldrum's acid to the three ketenes **5–7** was described previously.[2a] Carboxy(vinyl) ketenes had never been observed before, let alone isolated. Although all three ketenes could be observed, a completely sequential generation was not achieved, and their generic relationship therefore remained uncertain. We have now succeeded in a strictly sequential generation of such ketene triads and thus in establishing their exact relationships. The results are reported herein.



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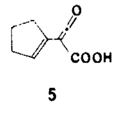

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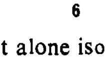

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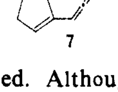

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Results

FVP of **1a** at 400 °C gave strong new bands at 2125 (C=C=O), 2500–3400 (COOH), 1770 (C=O), and 1630 (C=C)

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