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Reactive nitrogenous molecules from Meldrum's acid derivatives, pyrrole-2,3-diones, and isoxazolones

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rahydropyranyloxy)methyl]-2-isoxazoline, 90344-27-7; 5(*R*)-*syn*-5-(2,2-dimethyl-1,3-dioxolan-4-yl)-3-[(tetrahydropyranyloxy)methyl]-2-isoxazoline, 90410-13-2; 5(*S*)-*anti*-5-(2,2-dimethyl-1,3-dioxolan-4-yl)-3-phenyl-2-isoxazoline, 90410-14-3; 5(*R*)-*syn*-5-(2,2-dimethyl-1,3-dioxolan-4-yl)-3-phenyl-2-isoxazoline, 90410-15-4; 5(*S*)-*anti*-5-(2,2-dimethyl-1,3-dioxolan-4-yl)-3-[(1-methoxy-1-cyclohexyloxy)methyl]-2-isoxazoline, 90344-28-8; 5(*S*)-*anti*-5-(2,2-dimethyl-1,3-dioxolan-4-yl)-3-ethyl-2-isoxazoline, 90344-29-9; 5(*R*)-*syn*-5-(2,2-dimethyl-1,3-dioxolan-4-yl)-3-ethyl-2-isoxazoline, 90344-30-2; 5(*S*)-*anti*-5-(2,2-dimethyl-1,3-dioxolan-4-yl)-3-[(1,3-dioxolan-2-yl)methyl]-2-isoxazoline, 90344-31-3; 5(*R*)-*syn*-5-(2,2-dimethyl-1,3-dioxolan-4-yl)-3-[(1,3-dioxolan-2-yl)methyl]-2-isoxazoline, 90344-32-4; *anti*-3-methyl-5-[1(*tert*-butyldiphenylsilyloxy)ethyl]-2-isoxazoline, 90344-54-0; *syn*-3-methyl-5-[1(*tert*-butyldiphenylsilyloxy)ethyl]-2-isoxazoline, 90344-55-1; ethyl *anti*-5-(1-benzyloxyethyl)-2-isoxazoline-3-carboxylate, 90344-56-2; ethyl

syn-5-(1-benzyloxyethyl)-2-isoxazoline-3-carboxylate, 90344-57-3; *anti*-3-ethyl-5-[1(*tert*-butyldimethylsilyloxy)ethyl]-2-isoxazoline, 90344-58-4; *syn*-3-ethyl-5-[1(*tert*-butyldimethylsilyloxy)ethyl]-2-isoxazoline, 90344-59-5; *anti*-3-methyl-5-[1(*tert*-butyldimethylsilyloxy)ethyl]-2-isoxazoline, 90344-60-8; *syn*-3-methyl-5-[1(*tert*-butyldimethylsilyloxy)ethyl]-2-isoxazoline, 90344-61-9; ethyl *anti*-5-[1(*tert*-butyldimethylsilyloxy)ethyl]-2-isoxazoline-3-carboxylate, 90344-62-0; ethyl *syn*-5-[1(*tert*-butyldimethylsilyloxy)ethyl]-2-isoxazoline-3-carboxylate, 90344-63-1; *anti*-3-phenyl-5-[1(*tert*-butyldimethylsilyloxy)ethyl]-2-isoxazoline, 90270-62-5; *syn*-3-phenyl-5-[1(*tert*-butyldimethylsilyloxy)ethyl]-2-isoxazoline, 90270-63-6; *anti*-3,α-dimethyl-2-isoxazoline-5-methanol acetate, 90344-64-2; *syn*-3,α-dimethyl-2-isoxazoline-5-methanol acetate, 90344-65-3; *anti*-3-phenyl-2-isoxazoline-5-methanol, 90270-51-2; *syn*-3-phenyl-2-isoxazoline-5-methanol, 90270-52-3.

Reactive Nitrogenous Molecules from Meldrum's Acid Derivatives, Pyrrole-2,3-diones, and Isoxazolones

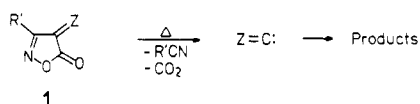
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Received January 10, 1984

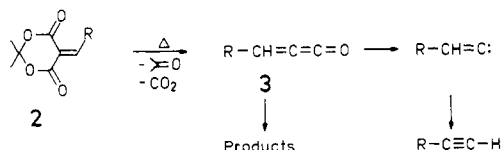
Flash vacuum pyrolysis of 5-(aminomethylidene)-2,2-dimethyl-1,3-dioxane-4,6-diones (Meldrum's acid derivatives) 12 gives 4-hydroxyquinolines/4-quinolones 15 or 3-enaminoacroleins 22 in good to excellent yields. Intermediate (aminomethylene)ketenes and imidoyleketenes are directly observed and their transformation into product 22 monitored by low-temperature IR spectroscopy. Imidoyleketenes are also formed and observed upon thermal CO extrusion from pyrrole-2,3-diones 16. Isocyanamines and fulminates are generated by pyrolysis of hydrazono- or oximino-Meldrum's acid derivatives 32 and 39, monitored by IR spectroscopy, and found to rearrange to cyanamides and cyanates, depending on substituents. The thermal reactions of isoxazol-5(4*H*)-ones and Meldrum's acid derivatives are compared and discussed.

The thermal decomposition of isoxazolones of the general formula 1 under flash vacuum pyrolysis conditions allows the preparation of a large number of interesting molecules, viz., acetylenes ($Z = RCH$),¹ aminoacetylenes

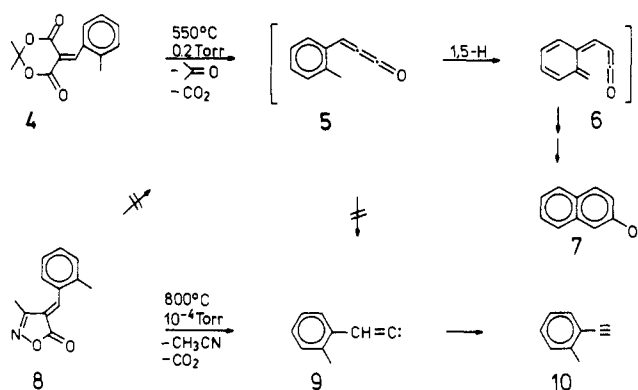


($Z = RNHCH$ or R_2NCH),² isocyanides ($Z = RN$),³ isocyanamines ($Z = RNHN$),^{4,5} fulminic acid ($Z = HON$),⁶ organic fulminates ($Z = RON$),⁷ the CNO radical (by flash photolysis of 1, $Z = HON$),⁸ and annelated pyrroles.⁹

Concurrently with these investigations, the pyrolysis of derivatives of Meldrum's acid (2) has been shown to lead



Scheme I



to methyleneketenes 3 as primary products; in many instances, these decarbonylate with concomitant rearrangement to acetylenes, thus giving the same products as obtained from 1 ($Z = RCH$).¹⁰

However, there are differences in behavior of isoxazolones and Meldrum's acid derivatives. For example, the pyrolysis of the (*o*-methylbenzylidene)dioxanedione 4 did not give any *o*-tolylacetylene (10) but instead a quantitative yield of 2-naphthol (7), formed after tautomerization of the methyleneketene 5 to the vinylketene 6.¹¹ In sharp contrast, the corresponding 4-(*o*-methylbenzylidene)isoxazol-5(4*H*)-one 8 furnished a 95% yield of the desired acetylene 10 at 800 °C (10^{-4} torr) (Scheme

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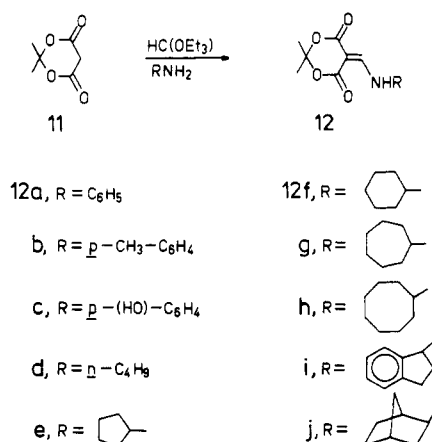
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Scheme II

Table I. 5-(Aminomethylidene)-Meldrum's Acids 12^a

| 12 | reaction temp, °C | reaction time, min | yield, % | mp, °C | analysis ^b |
|----------------|-------------------|--------------------|----------|----------------------|---|
| a ^c | | | | | |
| b | 50 | 60 | 86 | 152–153 | C ₁₄ H ₁₅ NO ₄ |
| c | 60 | 10 | 21 | 207–209 | C ₁₃ H ₁₃ NO ₄ |
| d | 5 | 15 | 36 | 112–114 | C ₁₁ H ₁₇ NO ₄ |
| e | 70 | 15 | 64 | 140 | C ₁₂ H ₁₇ NO ₄ |
| f | 50 | 30 | 60 | 152–153 ^c | C ₁₃ H ₁₉ NO ₄ |
| g | 80 | 10 | 41 | 126–128 | C ₁₄ H ₂₁ NO ₄ |
| h | 25 | 30 | 44 | 152–154 | C ₁₆ H ₂₃ NO ₄ |
| i | 80 | 15 | 20 | 95 | C ₁₆ H ₁₇ NO ₄ |
| j | 20 | 30 | 67 | 150 | C ₁₄ H ₁₉ NO ₄ |

^a Prepared according to Scheme II (see also Experimental Section). ^b Correct elemental C, H, N analysis (deviation <0.4%) was obtained. ^c Reference 17.

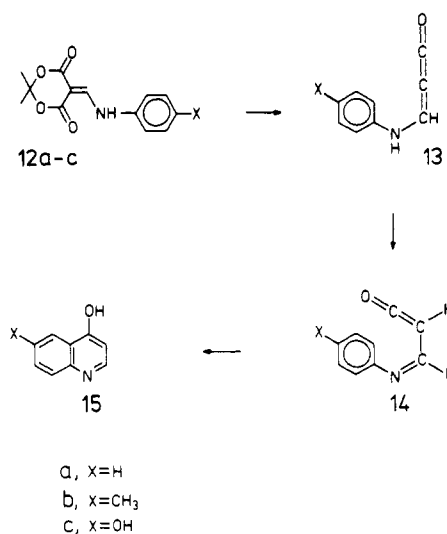
I).¹² Accordingly, in all cases where the intermediate methyleneketene can tautomerize, disparate products may be expected from Meldrum's acids and isoxazolones. Several further examples have been published.¹³ Moreover, other cases are known in which acetylenes are obtained from Meldrum's acid derivatives but not from the corresponding isoxazolones, because tautomerization involving 4-alkylidene side chains in the latter prevent the formation of the requisite vinylidene.^{9,14,15}

In view of these differences, and because little was known concerning the behavior of nitrogenous Meldrum's acid derivatives,¹⁶ we have undertaken a comparative study of such compounds and report the results herein.

Results and Discussion

1. 5-(Aminomethylidene)-2,2-dimethyl-1,3-dioxane-4,6-diones 12. These compounds were prepared from Meldrum's acid (11) in a three-component reaction with ethyl orthoformate and the appropriate amine (Scheme II). This method was first used by Polansky and co-workers¹⁷ in Meldrum's acid chemistry, and has been

Scheme III



thoroughly studied by Wolfbeis for other systems.¹⁸ The same procedure can be applied to prepare 4-(aminomethylidene)isoxazol-5(4H)-ones (1, Z = RR'NCH)² and 3-(aminomethylidene)furan-2(3H)-ones.^{18,19} Reaction conditions and yields of the compounds 12 b-j are indicated in Table I. All products were fully characterized by elemental analysis and spectroscopic data. Some characteristic ¹³C NMR chemical shifts and coupling constants are collected in Table II.

2. 4-Hydroxyquinolines/4-Quinolones 15 from 12a-c. It is known²⁰ that the thermal decomposition of 5-[(arylamino)methylidene]-1,3-dioxane-4,6-diones (e.g., 12a) in solution leads to the formation of 4-hydroxyquinolines/4-quinolones 15, a reaction that was rediscovered recently,²¹ but nothing was known about the mechanism of this transformation. To this end, we first confirmed the clean, high-yield formation of the 4-hydroxyquinolines 15a-c on flash vacuum pyrolysis of 12a-c at temperatures between 400 and 600 °C (10⁻⁵–10⁻³ torr), a reaction that can be carried out on a preparative scale. In order to obtain evidence pertaining to the intermediates 13 and 14, postulated in Scheme III, the pyrolysis products were isolated at -196 °C on KBr or BaF₂ windows in an apparatus^{2,12} allowing the direct IR spectroscopic examination of the pyrolysates. Under these conditions, the pyrolysis of 12b resulted in IR absorptions at 2079 and 2123 cm⁻¹ (-196 °C; stable up to -80 and -100 °C, respectively), which we ascribe to 13b and 14b, respectively. The first of these (2079 cm⁻¹) is obtained without contamination by the 2123-cm⁻¹ species upon very slow pyrolysis at 540 °C (10⁻⁵ torr). At the same time, CO₂ (2330 cm⁻¹) and acetone (1705 cm⁻¹) are formed. Under less carefully controlled pyrolysis conditions, particularly at higher pressures, both 13b and 14b are observed, and above 600 °C both disappear; at this stage the quinoline 15 is the only product, and its identity was confirmed by isolation following the IR experiments. The assignment of the 2079-cm⁻¹ absorption to the methyleneketene 13b is in agreement with the IR frequencies of benzylideneketenes reported by Brown et al. (2080–2094 cm⁻¹).²² In

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(13) Dehmlow, E. V.; Slopianka, M. *Angew. Chem.* 1979, 91, 163; *Angew. Chem., int. Ed. Engl.* 1979, 18, 170. Besida, J.; Brown, R. F. C.; Colmanet, S.; Leach, D. N. *Aust. J. Chem.* 1982, 35, 1373. Besida, J.; Brown, R. F. C. *Ibid.* 1982, 35, 1385.

(14) Wollweber, H.-J., Ph.D. Dissertation, University of Marburg, 1980.

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(16) McNab, H. *Chem. Soc. Rev.* 1978, 7, 345; *J. Org. Chem.* 1981, 46, 2809. For reactions of 5-(aminomethylidene)-2,2-dimethyl-1,3-dioxane-4,6-diones under basic conditions, see: Ziegler, E.; Wipfler, H.; Knieringer, A.; Wolfbeis, O. S. *Z. Naturforsch.* 1978, 33b, 1550. For antiallergic activity of related derivatives, see: Leshner, G. Y.; Singh, B.; Mielens, Z. E. *J. Med. Chem.* 1982, 25, 837.

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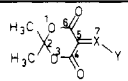
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Table II. ^{13}C NMR Spectral Data for Meldrum's Acid Derivatives^a

| compd |  | | | | | | other carbons ^b |
|------------------|---|-------|---------------------------|---------------------------|-------|---------------------------|--|
| | CH_3 | C-2 | C-4 ($^3J_{\text{CH}}$) | C-6 ($^3J_{\text{CH}}$) | C-5 | C-7 ($^1J_{\text{CH}}$) | |
| 11 | 27.0 | 105.8 | 164.1 | 164.1 | 36.6 | | |
| 12b ^c | 26.4 | 104.0 | 163.9 (9.4) | 162.7 (3.8) | 86.2 | 152.9 (171.4) | 136.1, 118.8, 130.0, 135.7, 20.4 |
| 12c ^c | 26.4 | 104.0 | 164.1 (9.2) | 162.9 (3.7) | 85.5 | 152.9 (171.3) | 130.4, 120.7, 116.0, 156.1 |
| 12d | 26.7 | 104.5 | 165.6 (9.3) | 163.9 (3.3) | 84.2 | 159.1 (168.9) | 50.1, 32.1, 19.4, 13.4 |
| 12e | 26.7 | 104.4 | 165.5 (9.4) | 163.9 (3.2) | 83.9 | 158.0 (168.2) | 61.5, 33.4, 23.4 |
| 12f | 26.5 | 104.1 | 165.3 (8.9) | 163.7 (3.5) | 83.7 | 157.2 (168.1) | 58.6, 33.0, 24.0, 24.5 |
| 12g | 26.6 | 104.3 | 165.4 (9.2) | 163.9 (3.1) | 83.8 | 157.4 (167.6) | 61.5, 35.4, 27.4, 23.4 |
| 12h | 26.7 | 104.3 | 165.4 (9.1) | 163.9 (3.2) | 83.7 | 157.4 (167.6) | 60.6, 32.6, [26.7], [23.0], 25.1 |
| 12i | 26.9 | 104.6 | 165.5 (9.7) | 163.9 (3.2) | 84.7 | 158.1 (169.0) | 65.4, [34.3], [30.0], 139.7, [127.3], [124.1], [125.2], [129.2], 143.2 |
| 12j | 26.7 | 104.4 | 165.5 (9.5) | 163.9 (3.2) | 83.9 | 157.6 (168.4) | 43.5, 63.0, [35.6], 39.8, [27.8], [35.2], [26.1] |
| 32a | 26.8 | 103.2 | 154.4 | 161.1 | 110.3 | | 49.4, 52.7 |
| 32b | 26.9 | 105.2 | 158.6 | 159.2 | 112.6 | | 141.1, 117.2, 129.6, 126.7 |
| 32c | 25.4 | 103.6 | 152.7 | 160.6 | 116.7 | | |
| 38 | 27.4 | 105.2 | 151.2 | 158.0 | 134.5 | | |
| 39a | 27.9 | 105.8 | 151.1 | 156.9 | 133.1 | | 67.8 |
| 39b | 27.8 | 105.5 | 151.1 | 157.1 | 132.9 | | 76.7, 14.3 |
| 39c | 28.0 | 106.0 | 150.8 | 156.5 | 134.7 | | 158.7, 115.3, 129.6, 125.7 |
| 39d | 28.0 | 106.0 | 150.6 | 156.6 | 134.8 | | 156.9, 115.2, 130.0, 135.5, 20.7 |
| 39e | 28.1 | 106.5 | 150.5 | 155.8 | 136.1 | | 158.6, 110.8, 149.0, 120.4, 130.6, 121.4 |

^a The solvent was CDCl_3 unless otherwise stated. Given are chemical shifts in ppm relative to Me_4Si and coupling constants, J , in hertz, with the proton at C-7 in compounds 12b–j ($X = \text{CH}$, $Y = \text{NHR}$). ^b These are listed in the sequence of IUPAC numbering of the substituents, Y, whereby ring carbon atoms come first. For values in brackets the assignment is uncertain. ^c The solvent was $(\text{CD}_3)_2\text{SO}$.

Table III. IR Absorptions of Imidoalkenes 17 from Pyrrole-2,3-diones 16 (Scheme IV)

| 16–17 | R^1 | R^2 | R^3 | ketene absorption, ^a cm^{-1} |
|-------|---------------|---------------|---------------|---|
| a | Ph | Ph | Ph | 2122 |
| b | Ph | CH_3 | Ph | 2140 |
| c | Ph | CH_3 | CH_3 | 2130 |
| d | CH_3 | Ph | Ph | 2123 |
| e | H | Ph | Ph | 2140 |

^a At -196°C ; from pyrolysis of 16 at 500°C (10^{-4} torr).

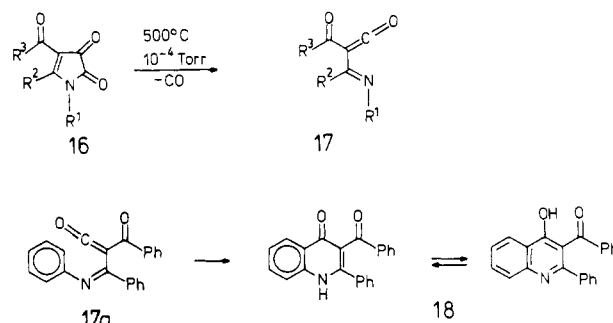
order to confirm the assignment of the 2123 cm^{-1} peak to the imidoalkene 14b, we have generated such ketenes in a different manner, as described in the following section, and found that they absorb generally in the range $2122\text{--}2140\text{ cm}^{-1}$ and also cyclize to quinolones in the gas-phase.

3. Imidoalkenes from Pyrrole-2,3-diones.¹² The pyrrole-2,3-diones 16, prepared by Ott,²³ decompose in solution with evolution of CO .²⁴ By carrying out this decomposition in the gas phase at 500°C and isolating the products on a KBr disk at -196°C , strong absorptions due to the imidoalkenes 17 are observed by IR spectroscopy (Scheme IV and Table III). These absorptions, at $2122\text{--}2140\text{ cm}^{-1}$, disappeared on warming between -105 and -70°C .

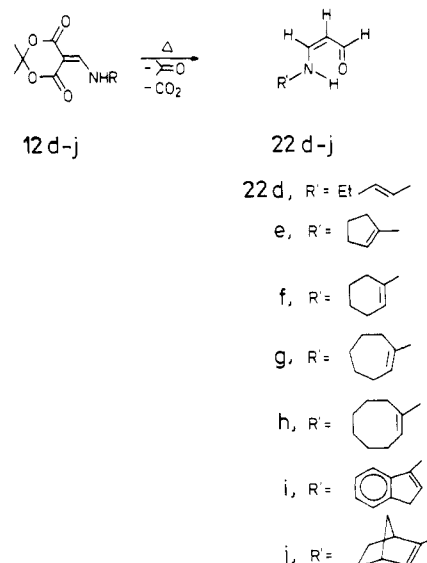
In the case of 17a, the ketene absorption was absent at pyrolysis temperatures above 600°C , and isolation of the product confirmed its identity with the quinolone-4-hydroxyquinoline tautomeric pair 18 previously isolated from a solution thermolysis of 16a.²⁴ This result implies a gas-phase cyclization of the ketene 17a to 18 (Scheme IV), completely analogous to the cyclization $14 \rightarrow 15$ shown in Scheme III.

A few other imidoalkenes have been matrix isolated by other workers and found to absorb at $2130\text{--}2140\text{ cm}^{-1}$.²⁵

Scheme IV



Scheme V



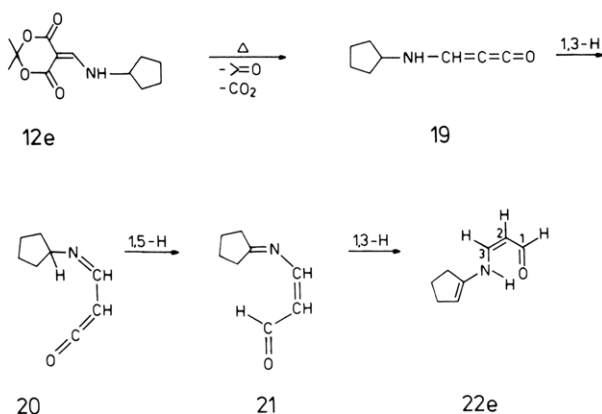
4. Enaminoacroleins from 12d–j. The preparative pyrolyses of the Meldrum's acid derivatives 12d–j at $500\text{--}600^\circ\text{C}$ gave results entirely different from those described for 12a–c in Section 2: no cyclization products were formed, but instead, enaminoacroleins 22d–j (Scheme V) were isolated in yields between 44% and 91%. The

(23) Ott, W. *Synthesis* 1976, 478.

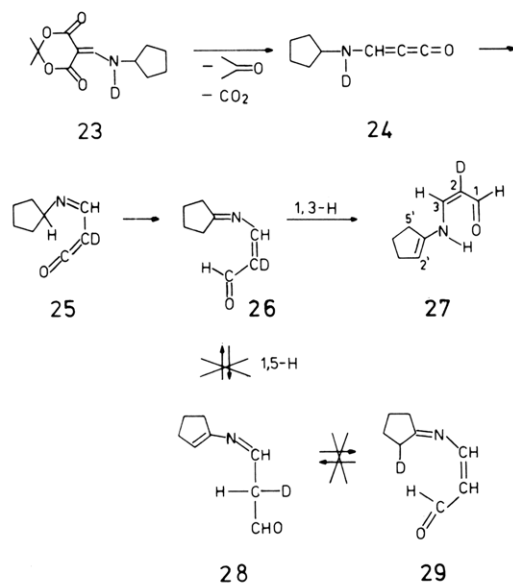
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Scheme VI



Scheme VII



mechanism of this reaction is illustrated for the cyclopentenyl derivative **22e** in Scheme VI.

The formation of the methyleneketene **19** by pyrolysis of **12e** at 500 °C (6×10^{-6} torr) is supported by the IR absorption at 2086 cm^{-1} , recorded at -196 °C (Figure 1). This peak disappeared on warming to -90 °C, and on further warming to room temperature the IR spectrum gradually transformed into that of the end product **22e** (Figure 1). The imidoalkene **20** (2122 cm^{-1}) was observable only as a weak band (together with a stronger band for **19**) at a pyrolysis temperature of 370 °C. At higher temperatures **20** was absent, presumably because of the occurrence of rapid 1,5-hydrogen shifts to give **21**. Since no ketene is present above -90 °C, and the end product **22e** is not yet formed at this temperature, the final rearrangement **21** \rightarrow **22e** must occur between -90 °C and +25 °C. Under preparative conditions involving longer contact times, the whole sequence **12e** \rightarrow **22e** may take place in the gas phase (vide infra).

For further information on the nature of the hydrogen shifts, the *N*-deuterio compound **23** (Scheme VII) was pyrolyzed and found to give the product **27**, specifically deuterated in position 2 of the side chain. This was shown by ^1H NMR spectroscopy, whereby the signal for H-2 at 5.09 ppm was missing, as were the couplings with the aldehydic proton, $^3J_{\text{H1,H2}} = 2.1$ Hz, and with H-3, $^3J_{\text{H2,H3}} = 7.3$ Hz. In fact, the ^1H NMR spectrum of deuterated compound **27** was identical with that obtained from **22e** upon spin-decoupling of H-2. Furthermore, in the ^{13}C

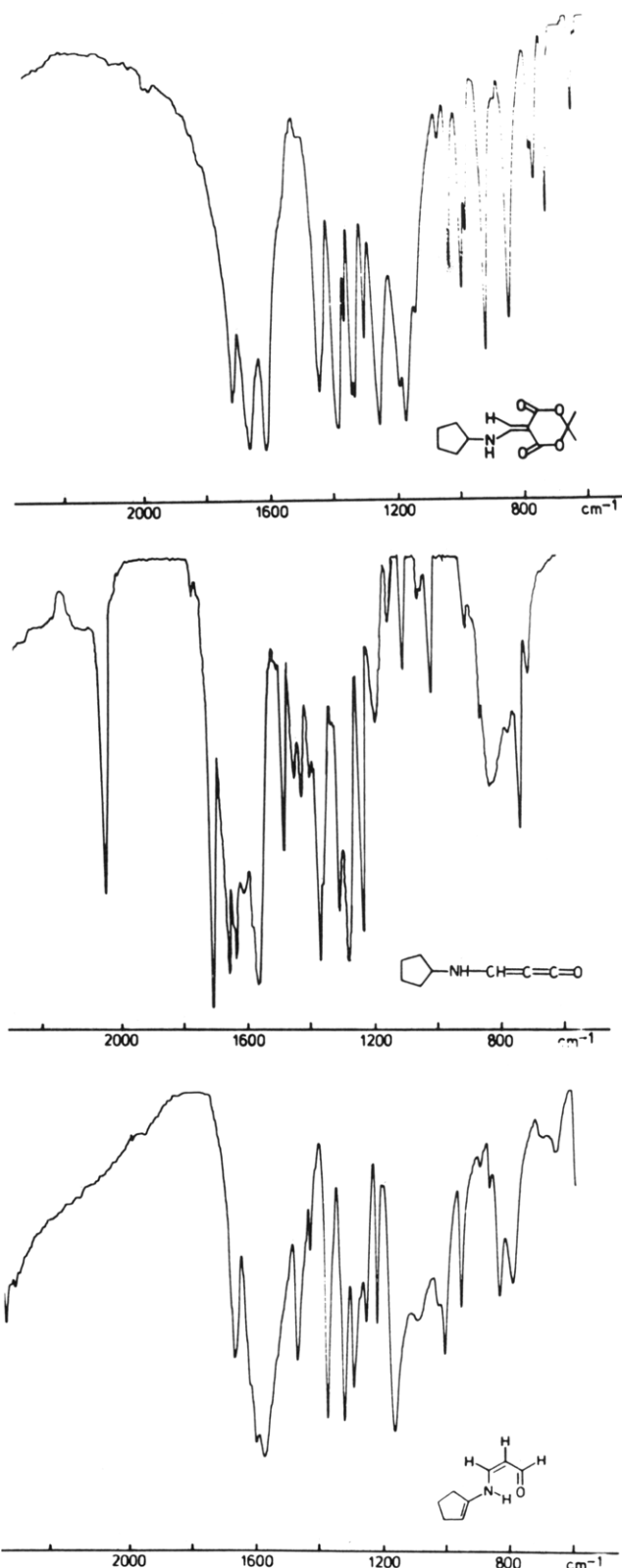
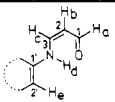


Figure 1. Infrared spectra of **12e** (KBr) (top), **19** (-196 °C) (center), and **22e** (KBr, 25 °C) (bottom).

NMR spectrum, the signal for C-2 in **22e** (104.8 ppm) had disappeared in **27**, having moved upfield to 104.4 ppm (the α -shift due to deuterium) and transformed into a very low intensity 1:1:1 triplet due to coupling with deuterium and absence of the nuclear Overhauser effect.

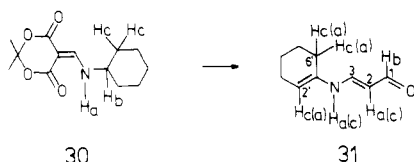
The sequence **24** \rightarrow **25** \rightarrow **26** \rightarrow **27** therefore constitutes a necessary and sufficient number of steps. This is in contrast to a recent communication by McNab and co-workers,²¹ who in a study of the analogous formation of

Table IV. Proton and Carbon-13 NMR Chemical Shifts and Coupling Constants for (Z)-3-Enaminoacroleins 22^a

| compd | |  | | | | | other Hs other Cs | J_{ab} $^1J_{C_1H}$ | J_{ac} $^2J_{C_1H}$ | J_{bc} $^1J_{C_2H}$ | J_{cd} $^2J_{C_2H}$ | $^1J_{C_3H}$ | $^1J_{C'_2H}$ |
|-------|----------------|---|----------------------------------|----------------------------------|-----------------------------------|-----------------------------------|--|--------------------------|--------------------------|--------------------------|--------------------------|--------------|---------------|
| | | H _a C ₁ | H _b C ₂ | H _c C ₃ | H _d C' ₁ | H _e C' ₂ | | | | | | | |
| 22d | δ^1H | 9.14 dd | 5.07 dd | 6.76 ddd | 11.22 | 5.26 m | 0.99 t, CH ₃ ; 2.04 m, CH ₂ ; 6.02 t, CH | 2.1 | 3.0 | 7.2 | 12.4 | | |
| | $\delta^{13}C$ | 188.6 | 96.0 | 147.6 | 128.0 | 116.3 | 14.1 (CH ₃); 22.8 (CH ₂) | | | | | | |
| 22e | δ^1H | 9.15 dd | 5.09 dd | 6.85 ddd | 11.45 | 5.14 m | 1.97 t; 2.40 m; 2.46 m | 2.1 | 3.1 | 7.3 | 12.7 | | |
| | $\delta^{13}C$ | 189.2 | 104.8 | 153.4 | 141.0 | 104.5 | 21.4; 30.1; 30.4 | 169.6 | 6.2 | 155.7 | 24.6 | 163.8 | 156.6 |
| 22f | δ^1H | 9.13 dd | 5.05 dd | 6.79 ddd | 11.34 | 5.32 m | 1.73 m, 2 H; 2.07–2.16 m, 4 H | 2.2 | 3.0 | 7.2 | 12.9 | | |
| | $\delta^{13}C$ | 188.8 | 104.0 | 151.7 | 135.9 | 105.1 | 21.8; 21.8; 23.4; 24.8 | 162.5 | 6.4 | 156.8 | 24.3 | 163.4 | 153.7 |
| 22g | δ^1H | 9.15 dd | 5.09 dd | 7.00 ddd | 11.04 | 5.45 m | 1.51 m; 1.60 m; 1.72 m; 2.13 q; 2.30 m | 2.1 | 3.1 | 7.3 | 12.7 | | |
| | $\delta^{13}C$ | 189.1 | 104.8 | 152.4 | 141.2 | 108.5 | 25.2; 25.7; 26.9; 30.8; 31.1 | 163.3 | 6.4 | 156.5 | 24.2 | 162.6 | 154.6 |
| 22h | δ^1H | 9.14 dd | 5.08 dd | 7.02 ddd | 11.23 | 5.27 t | 1.48–1.59 m, 8 H; 2.14 m, 2 H; 2.37 m, 2 H | 2.1 | 3.1 | 7.3 | 12.8 | | |
| | $\delta^{13}C$ | 189.4 | 104.6 | 152.6 | 138.6 | 107.3 | 25.4; 25.5; 25.7; 26.3; 27.5; 30.7 | 163.4 | 6.0 | 156.9 | 23.2 | 163.8 | 154.4 |
| 22j | δ^1H | 9.1 dd | 5.1 dd | 7.1 ddd | 10.3 | 5.48 m | 1.0–3.1 m, 8 H | 2.1 | 3.1 | 7.4 | 11.7 | | |

^a All 1H NMR spectra were measured in $CDCl_3$ solution, at 400 MHz, and the ^{13}C NMR spectra in $(CD_3)_2SO$ solution at 25.16 MHz, except for 22d, where the solvent was $CDCl_3$ in both cases. Chemical shifts δ in ppm; coupling constants J in hertz. For reference data supporting the *Z*-*s*-*Z* structures shown, see: McNab, H. *J. Chem. Soc., Perkin Trans. 2* 1981, 1283. Skötsch, C.; Haffmanns, G.; Breitmaier, E. *Chem. Ber.* 1977, 110, 2872.

22f from 12f using deuterium-labeled precursors (30) reported scrambling of deuterium between positions, 2, 2', and 6' in the product 31:



To explain this, a series of hydrogen shifts corresponding to $26 \rightleftharpoons 28 \rightleftharpoons 29$ (Scheme VII) was proposed. From the 1H and ^{13}C NMR data described for 27 above, we can exclude the occurrence of these additional hydrogen shifts (Scheme VII) under our conditions. Consequently, the hydrogen shifts observed by McNab et al. must succeed the formation of the enaminoacrolein. A likely explanation of this behavior is found in the fact that the pressure in the flash vacuum pyrolysis apparatus used by McNab (10^{-2} torr) was significantly higher than in ours (10^{-4} – 10^{-6} torr). This leads to longer contact times and more collisions with the walls, which may catalyze the hydrogen shifts. Our observation that the formal 1,3-shift $26 \rightarrow 27$ is faster than the 1,5-shift $26 \rightarrow 28$ also indicates that the 1,3-shift is auto- or wall-catalyzed.

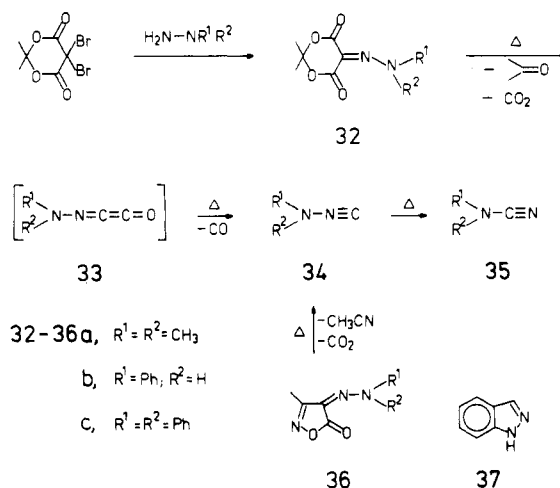
The pyrolyses of 12d and 12f–j to give 22d and 22f–j proceeded as described above for 12e. Only in the case of 22j was the product so unstable that a complete characterization including elemental analysis was not possible.

The 1H and ^{13}C NMR spectra of the enaminoacroleins in $CDCl_3$ solution (see Table IV) conclusively demonstrate that these compounds exist in the *Z*-*s*-*Z* forms shown.

5. Isocyanamines from Hydrazones 32. The hydrazone derivatives 32 of Meldrum's acid were prepared from 5,5-dibromo-2,2-dimethyl-1,3-dioxane-4,6-dione and the appropriately substituted hydrazines. 32b has been prepared previously by coupling of Meldrum's acid with phenyldiazonium salts.^{26,27}

The pyrolysis of the dimethyl compound 32a at 400–520 °C (10^{-4} – 10^{-3} torr) gave dimethylisocyanamine (34a) (IR neat) 2080 cm^{-1}) which had the chemical properties previously described for the compound prepared in a different

Scheme VIII



manner.²⁸ At higher pyrolysis temperatures partial isomerization to dimethylcyanamide (35a) occurred. Thus, at 680 °C the IR spectrum of the cold (-196 °C) product showed two bands of equal intensity at 2080 (34a) and 2220 (35a) cm^{-1} . 35a was identified by comparison with the spectrum of the authentic material.

The phenylhydrazone 32b gave, at 400 °C, strong IR signals for the isocyanide 34b (2120, 2155 cm^{-1}) and phenylcyanamide (35b) (2220 cm^{-1}). Most importantly, the doublet assigned to *N*-isocyananiline (34b) was exactly identical with that previously observed for the compound generated by pyrolysis of the isoxazolone 36b and therefore confirms this assignment.⁵ Also, the temperature dependence of the 2120–2155- cm^{-1} peaks was as observed⁵ for the compound generated from 36b: these signals disappeared above -100 °C, whereas those due to phenylcyanamide (35b) remained unaffected.

A preparative pyrolysis of 32b at 500 °C (10^{-3} torr) furnished an 85% yield of phenylcyanamide (35b) together with 15% of indazole (37), the latter being due to a gas-phase cyclization of the isocyanide 34b.^{4,5}

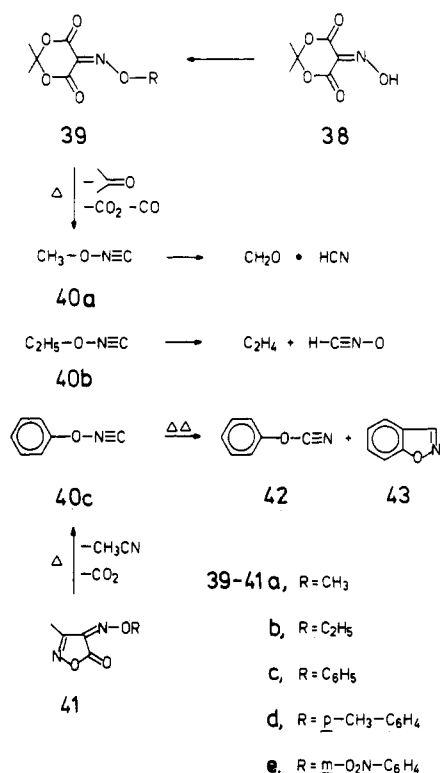
We have previously found that the introduction of a second phenyl group as in 34c accelerates the isonitrile-

(26) Eistert, B.; Geiss, F. *Chem. Ber.* 1961, 94, 929.

(27) See also: Regitz, M.; Stadler, D. *Liebigs Ann. Chem.* 1965, 687, 214. Regitz, M.; Liedhegener, A.; Stadler, D. *Ibid.* 1968, 713, 101.

(28) Brederick, H.; Föhlich, B.; Walz, K. *Liebigs Ann. Chem.* 1965, 686, 92.

Scheme IX



nitrile rearrangement to such an extent that 34c is no longer detectable. This has also been confirmed in the present study: the pyrolyses of 32c at 400–500 °C gave only 35c, identified by comparison with the material previously prepared.⁵ A preparative pyrolysis of 32c gave an 83% yield of diphenylcyanamide (35c).

6. Fulminates from Oxime Esters. The oxime 38²⁶ was converted to the silver salt and alkylated with methyl or ethyl iodide to give the *O*-alkyl oximes 39a,b. Arylation with diaryliodonium salts gave the *O*-phenyl and *O*-*p*-tolyl derivatives 39c–e. Several pyrolyses of the free oxime 38 were performed, but, in stark contrast to the corresponding isoxazalone 41 (R = H) which gives a quantitative yield of fulminic acid (HCNO),⁶ only traces of this product were obtained from 38. This, presumably, is due to the tautomerizable nature of 38 as well as the iminoketene derived therefrom (cf. section 2).

The problem of tautomerism does not pertain to the esters 39a–e which thermolyze to the fulminates 40a–e just as described⁷ for the isoxazolones 41a–c (Scheme IX). For example, 39a at 580 °C gave 40a (2160 cm⁻¹; stable below -120 °C) together with HCN (2090 cm⁻¹) and formaldehyde. 39b at 580 °C gave 40b (2160 cm⁻¹; stable below -100 °C) together with ethylene and fulminic acid. 39c at 585 °C gave phenyl fulminate (40c; 2120, 2140 cm⁻¹; stable below -105 °C) together with phenyl cyanate (42) and benzisoxazole (43), the latter two identified by GC–MS analytic comparison with authentic samples.

Moreover, an Ar matrix photolysis of 39c at 12 K gave, after 30 min irradiation at 254 nm, IR signals due to CO₂, acetone, and phenyl fulminate (40c; 2108, 2134 cm⁻¹), the spectrum of the latter being identical with that obtained by irradiation of 41c under the same conditions.⁷ We can thus confirm that both peaks at 2108 and 2134 cm⁻¹ belong to phenyl fulminate. Upon further photolysis at 12 K and 254 nm a new, complex band due to phenyl cyanate (42) developed at 2235–2280 cm⁻¹ in the course of 6 h.

Pyrolyses of the *O*-aryl oximes 39d,e at 405 °C and 610 °C, respectively, gave rise to IR absorptions at 2125 cm⁻¹,

ascribed to the fulminates 40d,e and disappearing on warming to -100 °C and -75 °C, respectively. This last observation is important since it suggests that it may be possible to stabilize aryl fulminates by substitution.

7. Conclusion. Amine-substituted methyleneketenes of the types 13 and 19 are generally obtained and observable on flash vacuum pyrolysis of Meldrum's acid derivatives 12, but they easily tautomerize to isomeric imidoalkynes (e.g., 14 and 20)²⁹ which undergo further reactions. Imidoalkynes are also selectively obtained from pyrrole-2,3-diones 16. As a consequence of tautomerization, the methyleneketenes do not eliminate CO to give vinylidenes and hence aminoacetylenes and thereby differ drastically from the corresponding isoxazolones 1 (Z = RNHCH) which do form aminoacetylenes in high yields.

The iminoketene intermediates (e.g., 33) formed by expulsion of acetone and CO₂ from the hydrazone and oxime derivatives 32 and 39 are however, extremely unstable, being imines of the unknown molecule O=C=C=O.³⁰ Therefore, they decarbonylate very readily to isocyanamines 34 and fulminates 40, viz., the same products as obtained from the isoxazolones 36 and 41. The diverse and often disparate reactivities of isoxazolones and Meldrum's acid derivatives therefore allow the syntheses of a large number of interesting molecules, and it is now possible to predict the initial thermal reactions of both types of precursors (1 and 2) with a high degree of confidence.

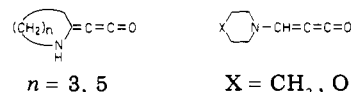
Experimental Section

General Methods. The preparative pyrolysis apparatus was as previously described (Apparatus A).³¹ The apparatus used for low-temperature IR spectroscopy consisted of a 10-cm quartz pyrolysis tube (i.d. 8 mm); the products were condensed on KBr or BaF₂ disks at -196 °C by using an Air Products cold-end and vacuum shroud. The flight distance between the exit of the pyrolysis tube and the cold disk was 1–2 cm. A turbomolecular pump kept the system under a vacuum of 10⁻⁴–10⁻⁶ torr during pyrolysis; pressures reported were measured in the pyrolysis tube by using Penning gauges. IR spectra were recorded on a Perkin-Elmer 281, ¹H NMR spectra on a Bruker WH 400, and ¹³C NMR spectra on a Varian XL 100 (25.16 MHz) instrument, respectively. Mass spectra were recorded at 70 eV and with direct inlet on Varian-MAT CH 7a, or with field desorption on the 711 instruments. Elemental analyses were carried out in the micro-analytical laboratory in this department. Melting points are uncorrected.

5-(Aminomethylidene)-2,2-dimethyl-1,3-dioxane-4,6-diones 12. General details of preparation and analytical data are collected in Table I and ¹³C NMR data in Table II. Full IR, ¹H NMR, and mass spectral data are available as supplementary material (see paragraph at the end of paper). Further preparative details are illustrated in the examples given below.

12b: 6.4 g (44 mmol) of Meldrum's acid was added to a solution of 9.5 g (89 mmol) of *p*-toluidine in 45 mL of triethyl orthoformate.

(29) We have extended this investigation to methyleneketenes of the types



which again are directly observable by IR spectroscopy although the former, possessing a tautomerizable NH function, readily isomerize to the corresponding imidoalkynes: Briehl, H.; Wentrup, C., unpublished results. Briehl, H. Dissertation, Marburg, 1984.

(30) Haddon, R. C. *Tetrahedron Lett.* 1972, 3897. Fleischauer, J.; Beckers, M.; Scharf, H.-D. *Ibid.* 1973, 4275. Raine, G. P.; Schaefer, H. F., III; Haddon, R. C. *J. Am. Chem. Soc.* 1983, 105, 194.

(31) Wentrup, C.; Damerius, A.; Reichen, W. *J. Org. Chem.* 1978, 43, 2037.

The mixture was stirred at 50 °C for 1 h. The yellow precipitate was filtered, washed twice with triethyl orthoformate, and recrystallized from petroleum ether-CCl₄ (1:1) to give 10.0 g (86%) of yellow-green crystals, mp 152–153 °C.

12c: The reaction mixture from 2.88 g (0.02 mol) of Meldrum's acid, 2.18 g (0.02 mol) of *p*-aminophenol, and 65 mL of triethyl orthoformate (Table I) was crystallized at 0 °C to give 1.1 g (21%) of yellow-green crystal, mp 207–209 °C dec.

12d: 3.65 g (50 mmol) of *n*-butylamine was added to a 5 °C cold solution of 7.2 g (50 mmol) of Meldrum's acid in 40 mL of triethyl orthoformate. After stirring for 15 min, the yellow precipitate was filtered, washed twice with petroleum ether, and recrystallized from ethanol to give colorless crystals.

12g: the reaction between 7.2 g (0.05 mol) Meldrum's acid, 5.65 g (0.05 mol) cycloheptylamine, and 50 mL of triethyl orthoformate at 0 °C gave a yellow, viscous precipitate. The mixture was heated at 80 °C till the precipitate had redissolved, and on cooling in ice a yellow crystalline product was obtained. This was recrystallized from ethanol and washed twice with petroleum ether to give pale yellow crystals.

12h: the white to pale yellow compound was recrystallized from ethanol.

12i: a viscous product was initially obtained as described for **12g** above. The mixture was then heated at 80 °C for 15 min, causing dissolution of the precipitate. The red-brown solution was concentrated in vacuo at room temperature, and the resulting oil was dissolved in ethanol and allowed to stand in the open flask. This product crystallized in the course of 3 h to an oily mass which was filtered, dried in vacuo, and recrystallized from ethanol to give colorless to light yellow crystals.

12j: the components were mixed at 0 °C and the mixture was stirred for 30 min, allowing it to warm to room temperature. The product was obtained as light yellow crystals from ethanol.

Preparative Flash Vacuum Pyrolysis of Compounds 12b–j. The starting materials were sublimed at the temperatures given at 10^{−4} torr and pyrolyzed at the temperatures given. The products were condensed on a cold finger cooled with liquid N₂. After the completion of the pyrolysis, the coolant was removed and the CO₂ and acetone formed were distilled in vacuo during warmup. The remaining product either distilled into a second recipient at room temperature (10^{−3} torr), or, if it was an involatile solid was taken up in CCl₄ or CHCl₃ and purified by recrystallization from these solvents or by sublimation in high vacuum.

4-Hydroxy-6-methylquinoline (15b). **12b** (200 mg, 0.77 mmol) was sublimed at 130 °C and pyrolyzed at 700 °C during 2.5 h: yield 80 mg (66%); mp 236–238 °C (lit.³² mp 234–235 °C; lit.²⁰ mp 237–239 °C).³³

4,6-Dihydroxyquinoline (15c). **12c** (200 mg, 0.76 mmol) was sublimed at 150 °C and pyrolyzed at 600 °C during 3 h: yield 70 mg (57%); yellow crystals, mp 298–300 °C (lit.³⁴ mp dec above 230 °C).³³

(Z)-3-Enaminoacroleins 22. ¹H and ¹³C NMR chemical shifts and coupling constants are tabulated in Table IV. IR and mass spectra are given as supplementary material (see paragraph at end of paper).

(Z)-3-((E)-1-Butenylamino)acrolein (22d). **12d** (0.5 g, 2.2 mmol) was sublimed at 95 °C and pyrolyzed at 500 °C during 2 h. The product, a yellow oil, 120 mg (44%), was taken up in acetone and distilled in high vacuum. For analytical purposes the compound was purified by gas chromatography (SE-30, 120 °C).

Anal. Calcd for C₇H₁₁NO: C, 67.17; H, 8.86; N, 11.19. Found: C, 67.40; H, 8.94; N, 11.25.

(Z)-3-(Cyclopenten-1-ylamino)acrolein (22e). **12e** (350 mg, 1.46 mmol) was sublimed at 100 °C and pyrolyzed at 500 °C in 3 h. The yellow substance formed was sublimed at 65–70 °C (10^{−1} torr): yield 180 mg (90%); mp 135–137 °C, storable below 0 °C.

Anal. Calcd for C₈H₁₁NO: C, 70.04; H, 8.08; N, 10.21. Found: C, 70.00; H, 8.16; N, 10.43.

2-Deuterio-(Z)-3-(cyclopenten-1-ylamino)acrolein (27). **12e** (1 g) was dissolved in a small amount of CH₃OD and 4 mL

D₂O was added. The solvent was removed in vacuo and the procedure was repeated. The pyrolysis of **23** so obtained was carried out as described for the preparation of **22e** above. The ¹H and ¹³C NMR spectra of **27** demonstrated that H_b and only H_b (see formula in Table IV) had been replaced by deuterium. The spectra are discussed in section 4.

(Z)-3-(Cyclohexen-1-ylamino)acrolein (22f). **12f** (240 mg, 0.95 mmol) was sublimed at 80–100 °C and pyrolyzed at 600 °C in 1.5 h. Light yellow crystals, 130 mg (91%), were obtained after recrystallization from CCl₄, mp 114–117 °C.

Anal. Calcd for C₉H₁₃NO: C, 71.49; H, 8.67; N, 9.26. Found: C, 70.52; H, 8.78; N, 9.48.

(Z)-3-(Cyclohepten-1-ylamino)acrolein (22g). **12g** (1.0 g, 3.75 mmol) was sublimed at 90 °C and pyrolyzed at 500 °C in 4 h. The product was sublimed at 60 °C (10^{−2} torr) to give 480 mg (78%) of white crystals, mp 88–90 °C.

Anal. Calcd for C₁₀H₁₅NO: C, 72.69; H, 9.15; N, 8.48. Found: C, 72.19; H, 9.11; N, 8.68.

(Z)-3-(Cycloocten-1-ylamino)acrolein (22h). **12h** (750 mg, 2.7 mmol) was sublimed at 120 °C and pyrolyzed at 500 °C in 3 h. The yellow pyrolysate was distilled in high vacuum whereupon the distillate crystallized at room temperature to give 450 mg (93%) of light yellow crystals, mp 84–86 °C.

Anal. Calcd for C₁₁H₁₇NO: C, 73.70; H, 9.56; N, 7.81. Found: C, 73.28; H, 9.49; N, 7.88.

(Z)-3-(3-Indenylamino)acrolein (22i). **12i** (80 mg, 0.28 mmol) was sublimed at 50–80 °C and pyrolyzed at 500 °C in 1.5 h. The resulting yellow-orange oil was taken up in CH₃OH, evaporated, and dried in vacuo, and the solid so obtained was recrystallized from CHCl₃ to give yellow-orange crystals: mp 146–147 °C; ¹H NMR (CD₃OD) δ 3.41 (s, 2 H), 4.61 (s, 1 H), 5.80 (t, 1 H), 6.06 (s, 1 H), 7.22–7.33 (m, 2 H), 7.45 (d, *J* = 7.5 Hz, 1 Ar H), 7.53 (d, *J* = 7.5 Hz, 1 Ar H), 9.12 (d, *J* = 8.8 Hz, 1 H).

(Z)-3-(2-Norbornen-2-ylamino)acrolein (22j). The pyrolysis of **12j** at 500 °C gave a viscous orange oil which decomposed at room temperature within a few minutes. This compound was not obtained pure, but the ¹H NMR spectrum (Table IV) was in agreement with the structure given.

2,2-Dimethyl-1,3-dioxane-4,5,6-trione 5-Dimethylhydrazone (32a).

A solution of 6 g (20 mmol) of 5,5-dibromo-2,2-dimethyl-1,3-dioxane-4,6-dione in 50 mL of ethanol was cooled to 0 °C in an ice/salt bath, and 2 mL (26 mmol) of 1,1-dimethylhydrazine was added at such a rate that the inner temperature did not exceed 5 °C. After the completion of the addition, the mixture was stirred at room temperature for 1 h during which time the product started crystallizing. After filtering and recrystallizing from ethanol, 2.25 g (57%) of yellow crystals, mp 170–172 °C was obtained.³⁵ ¹H NMR (CDCl₃) δ 1.73 (s, 6 H, C(CH₃)₂), 3.36 (s, 3 H, NCH₃), 3.76 (s, 3 H, NCH₃); ¹³C NMR; see Table II.

Anal. Calcd for C₈H₁₂N₂O₄: C, 47.99; H, 6.04; N, 13.99. Found: C, 48.10; H, 6.02; N, 13.82.

2,2-Dimethyl-1,3-dioxane-4,5,6-trione 5-Phenylhydrazone (32b).

This compound was obtained in the same manner as described for **32a** by using phenylhydrazine: yield 65%; mp 177–178 °C (lit.²⁶ mp 175 °C); ¹H NMR (CDCl₃) δ 1.80 (s, 6 H, (CH₃)₂), 7.26–7.54 (m, 5 H, Ar), 9.67 (s, br, 1 H, NH); ¹³C NMR, see Table II.

Anal. Calcd for C₁₂H₁₂N₂O₄: C, 58.07; H, 4.88; N, 11.29. Found: C, 57.87; H, 4.90; N, 11.20.

2,2-Dimethyl-1,3-dioxane-4,5,6-trione 5-Diphenylhydrazone (32c).

The product was obtained from diphenylhydrazine by using the procedure described for **32a** above: yield 76%; light yellow crystals; mp 180 °C dec;³⁵ ¹H NMR (CDCl₃) δ 1.71 (s, 6 H), 7.16–7.52 (m, 10 H, Ar); ¹³C NMR, see Table II.

Anal. Calcd for C₁₈H₁₆N₂O₄: C, 66.66; H, 4.97; N, 8.64. Found: C, 66.78; H, 4.94; N, 8.66.

Silver Salt of 2,2-Dimethyl-1,3-dioxane-4,5,6-trione 5-Oxime. The sodium salt of 2,2-dimethyl-1,3-dioxane-4,5,6-trione 5-oxime monohydrate²⁶ (6.9 g, 32 mmol) was dissolved in a mixture of 50 mL of H₂O and 50 mL of ethanol, and a concentrated equimolar solution of silver nitrate (3.5 g in 10 mL of H₂O) was added with stirring. After stirring for another 30 min, a violet

(32) Roberts, R. M. *J. Org. Chem.* 1949, 14, 277.

(33) IR, ¹H NMR, and mass spectra are given as supplementary material (see paragraph at end of paper).

(34) Hirsch, F. *Monatsh. Chem.* 1896, 17, 327.

(35) IR and mass spectra are given as supplementary material (see paragraph at end of paper).

precipitate was filtered, washed twice with H₂O and twice with ether, and dried, first over CaCl₂ and then at 70 °C (10⁻³ torr) for 3 h to give a dry violet powder: 6.3 g (70%); IR (KBr) 3000 (w), 1715 (s), 1650 (s), 1400 (s), 1385 (m), 1300 (s), 1265 (m), 1200 (s), 1155 (s), 1040 (m), 1000 (m), 930 (s), 785 (m), 710 (m), 630 (m) cm⁻¹; ¹H NMR (Me₂SO-*d*₆) δ 1.59 (s, (CH₃)₂).

Anal. Calcd for C₆H₆NO₅Ag: C, 25.74; H, 2.16; N, 5.00; Ag, 38.53. Found: C, 25.11; H, 1.90; N, 4.91; Ag, 38.74.

2,2-Dimethyl-1,3-dioxane-4,5,6-trione 5-*O*-Methyloxime (39a). The foregoing silver salt (1.36 g, 4.86 mmol) was suspended in 20 mL of dry acetone, and a solution of 0.7 g (4.92 mmol) of methyl iodide in 15 mL of dry acetone was added dropwise at room temperature, whereupon the mixture was heated to 50 °C. After an induction period of 10 min a rapid reaction set in and the previously wine-red suspension turned white-yellow. After being stirred for another hour at room temperature the mixture was filtered, the filtrate evaporated, and the resulting light brown oil dissolved in a small volume of ether and allowed to stand in a freezer overnight. This gave a black oily precipitate, from which was decanted, and after further cooling, a yellow solid crystallized from the solution. This was taken up in CCl₄ and reprecipitated with petroleum ether (bp 40–60 °C) to give 180 mg (20%) of pale yellow crystals; mp 78 °C;³⁵ ¹H NMR (CDCl₃) δ 1.79 (s, 6 H, C(CH₃)₂), 4.44 (s, 3 H, OCH₃); ¹³C NMR (CDCl₃), see Table II.

Anal. Calcd for C₇H₉NO₅: C, 44.93; H, 4.85; N, 7.48. Found: C, 44.72; H, 4.75; N, 7.49.

2,2-Dimethyl-1,3-dioxane-4,5,6-trione 5-*O*-Ethyloxime (39b). This compound was prepared from ethyl iodide in the same manner as described for 39a above: yield 180 mg (26%); from 1.4 g (5 mmol) of the silver salt) of orange crystals, mp 42–43 °C;³⁵ ¹H NMR (CDCl₃) δ 1.46 (t, 3 H, CH₃), 1.78 (s, 6 H, C(CH₃)₂), 4.68 (q, 2 H, CH₂); ¹³C NMR, see Table II.

Anal. Calcd for C₈H₁₁NO₅: C, 47.76; H, 5.51; N, 6.96. Found: C, 47.47; H, 5.44; N, 6.85.

2,2-Dimethyl-1,3-dioxane-4,5,6-trione 5-*O*-Phenyloxime (39c). A suspension of 5.6 g (20 mmol) of the silver salt of 38 in 250 mL of acetone was stirred and cooled to 0 °C and 6.13 g (20 mmol) of diphenyliodonium chloride was added in small portions in the course of 30 min. After stirring for 1 h at 0 °C the cooling was removed and stirring was continued for 1.5 h. During this time the violet color faded and a yellow mixture resulted. After filtering and evaporating the filtrate, a yellow oil was obtained that crystallized at 0 °C. This precipitate was recrystallized from ethanol to give 2.7 g (54%) of yellow crystals, mp 124 °C, sensitive to light (causing red coloration), for which reason this preparation should be carried out in the dark;³⁵ ¹H NMR (Me₂SO-*d*₆) δ 1.79 (s, 6 H, C(CH₃)₂), 7.28 (t, 1 H, *p*-phenyl), 7.36 (d, 2 H, *o*-phenyl), 7.49 (t, 2 H, *m*-phenyl); ¹³C NMR, see Table II.

Anal. Calcd for C₁₂H₁₁NO₅: C, 57.83; H, 4.45; N, 5.62. Found: C, 57.55; H, 4.46; N, 5.65.

2,2-Dimethyl-1,3-dioxane-4,5,6-trione 5-*O*-*p*-Tolyloxime (39d). This compound was prepared from di-*p*-tolyliodonium bromide as described for 39c above; 1.16 g (22%) of light yellow, light-sensitive crystals was obtained after recrystallizing twice from ethanol;³⁵ ¹H NMR (CDCl₃) δ 1.84 (s, 6 H, C(CH₃)₂), 2.35 (s, 3 H, CH₃), 7.18 (d, 2 H, Ar), 7.28 (d, 2 H, Ar); ¹³C NMR, see Table II.

Anal. Calcd for C₁₃H₁₃NO₅: C, 59.31; H, 4.98; N, 5.32. Found: C, 59.19; H, 4.88; N, 5.43.

2,2-Dimethyl-1,3-dioxane-4,5,6-trione 5-*O*-(3-Nitrophenyl)oxime (39e). This compound was prepared from 3,3'-dinitrodiphenyliodonium bromide as described for 39c above, except that the reaction mixture was stirred for 4 h at 0 °C and then for 16 h at room temperature. After filtering a red-brown solid and concentrating the filtrate, a red oil was obtained. Addition of ether gave a yellow-brown precipitate which was filtered and dried for 12 h at 60 °C (10⁻³ torr). Two recrystallizations from ethanol gave 0.4 g (24%; from 1.6 g (5.7 mmol) of the silver salt of 38): light orange crystals, mp 162 °C;³⁵ ¹H NMR (CDCl₃) δ 1.87 (s, 6 H, C(CH₃)₂), 7.61 (t, 1 H, Ar), 7.76 (d, 1 H, Ar), 8.11 (d, 1 H, Ar), 8.28 (s, 1 H, Ar); ¹³C NMR, see Table II.

Anal. Calcd for C₁₂H₁₀N₂O₇: C, 48.99; H, 3.43; N, 9.52. Found: C, 48.81; H, 3.39; N, 9.43.

Pyrolysis of Compounds 32 and 39. In these pyrolyses the products, dimethylisocyanamine, dimethylcyanamide, phenylcyanamide, diphenylcyanamide, indazole, HCN, fulminic acid, phenyl cyanate, and benzisoxazole were identified by direct IR and, except for HCN and fulminic acid, GC-MS comparison with authentic samples.

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Registry No. 11, 2033-24-1; 11 (dibromide), 66131-14-4; 12a, 15568-92-0; 12b, 25063-44-9; 12c, 90367-97-8; 12d, 90367-98-9; 12e, 90367-99-0; 12f, 15568-90-8; 12g, 90368-00-6; 12h, 90368-01-7; 12i, 90368-02-8; 12j, 90368-03-9; 13b, 90368-04-0; 14b, 90368-05-1; 15a, 611-36-9; 15b, 23432-40-8; 15c, 3517-61-1; 16a, 36684-30-7; 16b, 90368-06-2; 16c, 90368-07-3; 16d, 61350-44-5; 16e, 61350-69-4; 17a, 90368-08-4; 17b, 90368-09-5; 17c, 90368-10-8; 17d, 90368-11-9; 17e, 90368-12-0; 18, 61707-51-5; 19, 90368-13-1; 20, 90368-14-2; 21, 90368-15-3; 22d, 90368-16-4; 22e, 90368-17-5; 22f, 90368-18-6; 22g, 90368-19-7; 22h, 90368-20-0; 22i, 90368-21-1; 22j, 90368-22-2; 23, 90368-23-3; 24, 90368-24-4; 25, 90368-25-5; 26, 90368-26-6; 27, 90368-27-7; 32a, 90368-28-8; 32b, 75307-67-4; 32c, 90368-29-9; 34a, 3298-64-4; 34b, 61743-02-0; 35a, 1467-79-4; 35b, 622-34-4; 35c, 27779-01-7; 38, 81539-54-0; 39a, 90368-30-2; 39b, 90368-31-3; 39c, 90368-32-4; 39d, 90368-33-5; 39e, 90368-34-6; 40a, 67347-39-1; 40b, 76347-07-4; 40c, 67249-97-2; 40d, 90368-35-7; 40e, 90368-36-8; 41a, 90368-37-9; 41b, 90368-38-0; 41c, 90368-39-1; 41d, 90368-40-4; 41e, 90368-41-5; 42, 1122-85-6; 43, 271-95-4; HC(OEt)₃, 122-51-0; C₆H₅NH₂, 62-53-3; *p*-CH₃C₆H₄NH₂, 106-49-0; *p*-HOC₆H₄NH₂, 123-30-8; *n*-C₄H₉NH₂, 109-73-9; H₂NN(CH₃)₂, 57-14-7; H₂NNHPh, 100-63-0; H₂NNPh₂, 530-50-7; cyclopentylamine, 1003-03-8; cyclohexylamine, 108-91-8; cycloheptylamine, 5452-35-7; cyclooctylamine, 5452-37-9; 1-indanyllamine, 34698-41-4; *exo*-2-norbornylamine, 7242-92-4.

Supplementary Material Available: Full IR, ¹H NMR, and mass spectra for compounds 12b–e and 12g–j, IR, ¹H NMR, ¹³C NMR, and mass spectra for 15b–c, IR and mass spectra for 22d–h, and mass spectrum for 22i, IR and mass spectra for 32a, 32c, and 39a–e (5 pages). Ordering information is given on any current masthead page.