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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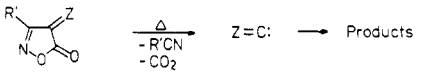
Received January 10, 1984

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 imidoylketenes are directly observed and their transformation into product 22 monitored by low-temperature IR spectroscopy. Imidoylketenes are also formed and observed upon thermal CO extrusion from pyrrole-2,3-diones 16. Isocyanoamines 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.

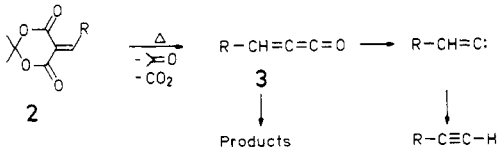
The thermal decomposition of isoxazolones of the general formula 1 under flash vacuum pyrolysis conditions allows the preparation of a large number of interesting molecules, viz., acetylenes (Z = RCH),[1] aminoacetylenes



1

(Z = RNHCH or R_2NCH),[2] isocyanides (Z = RN),[3] isocyanoamines (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]

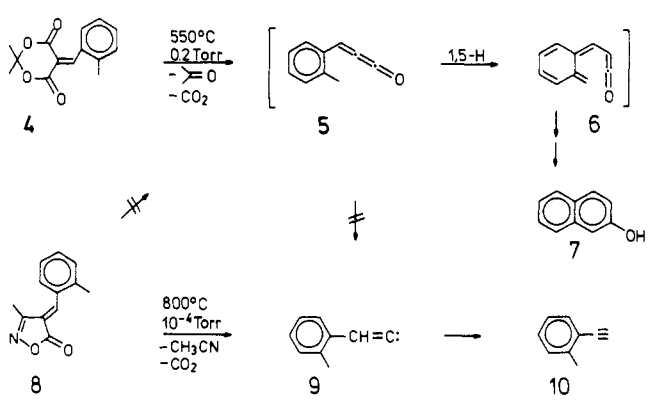
Concurrently with these investigations, the pyrolysis of derivatives of Meldrum's acid (2) has been shown to lead



2

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]

Scheme I



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

(1) Wentrup, C.; Reichen, W. *Helv. Chim. Acta* **1976**, *59*, 2615. Wentrup, C.; Winter, H.-W. *Angew. Chem.* **1978**, *90*, 643; *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 609.
(2) Winter, H.-W.; Wentrup, C. *Angew. Chem.* **1980**, *92*, 743; *Angew. Cchem., Int. Ed. Engl.* **1980**, *19*, 720.
(3) Wentrup, C.; Stutz, U.; Wollweber, H.-J. *Angew. Chem.* **1978**, *90*, 731; *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 688.
(4) Reichen, W.; Wentrup, C. *Helv. Chim. Acta* **1976**, *59*, 2618.
(5) Wentrup, C.; Winter, H.-W. *J. Org. Chem.* **1981**, *46*, 1045.
(6) Wentrup, C.; Gerecht, B.; Briehl, H. *Angew. Chem.* **1979**, *91*, 503; *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 467.
(7) Wentrup, C.; Gerecht, B.; Laqua, D.; Briehl, H.; Winter, H.-W.; Reisenauer, H. P.; Winnewisser, M. *J. Org. Chem.* **1981**, *46*, 1046, 5459.
(8) Ramsay, D. A.; Winnewisser, M. *Chem. Phys. Lett.* submitted for publication.
(9) Wentrup, C. *Adv. Heterocycl. Chem.* **1981**, *28*, 231-361, p 251.
(10) Brown, R. F. C.; Eastwood, F. W. In "The Chemistry of Ketenes, Allenes and Related Compounds"; Patai, S., Ed.; Wiley-Interscience: Chichester, England, 1980; p 757 ff.
(11) Brown, R. F. C.; McMullen, G. L. *Aust. J. Chem.* **1974**, *27*, 2385.

0022-3263/84/1949-2772$01.50/0

Scheme II

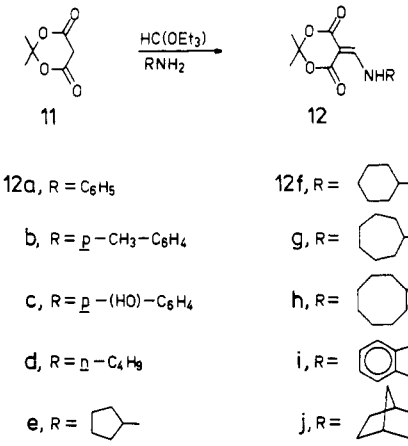


Table I. 5-(Aminomethylidene)-Meldrum's Acids 12[a]

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	$C_{13}H_{13}NO_5$
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	$C_{15}H_{23}NO_4$
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.

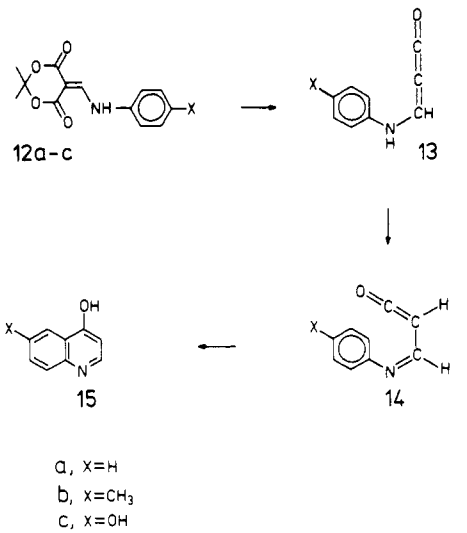
I).[12] Accordingly, in all cases where the intermediate methyleneketene can tautomerize, disparate products may be expected from Meldrum's acids and isoxazolones. Several further examples have been published.[13] Moreover, other cases are known in which acetylenes are obtained from Meldrum's acid derivatives 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 coworkers[17] in Meldrum's acid chemistry, and has been thoroughly studied by Wolfbeis for other systems.[18] The same procedure can be applied to prepare 4-(aminomethylidene)isoxazol-5(4*H*)-ones (**1**, Z = RR'NCH)[2] and 3-(aminomethylidene)furan-2(3*H*)-ones.[18,19] Reaction conditons 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 ^{13}C NMR chemical shifts and coupling constants are collected in Table II.

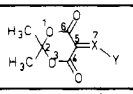
Scheme III



2. 4-Hydroxyquinolines/4-Quinolones 15 from 12a–c. It is known[20] 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 BaF_2 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, CO_2 (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

(12) Winter, H.-W., Ph.D. Dissertation, University of Marburg, 1980.
(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.
(15) Wentrup, C.; Wollweber, H.-J.; Gross, G.; Berstermann, H.-M. papers in preparation.
(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.; Knierzinger, A.; Wolfbeis; O. S. *Z. Naturforsch.* **1978**, *33b*, 1550. For antiallergic activity of related derivatives, see: Lesher, G. Y.; Singh, B.; Mielens, Z. E. *J. Med. Chem.* **1982**, *25*, 837.
(17) Bihlmayer, G. A.; Derflinger, G.; Derkosch, J.; Polansky, O. E. *Monatsh. Chem.* **1967**, *98*, 564.
(18) Wolfbeis, O. S. *Monatsh. Chem.* **1981**, *112*, 369 and references therein.
(19) Berstermann, H.-M., Ph.D. Dissertation, University of Marburg, 1984.
(20) Sterling Drug Inc. Brit. 1 147 760; *Chem. Abstr.* **1969**, *71*, 49967a.
(21) Gordon, H. J.; Martin, J. C.; McNab, H. *J. Chem. Soc., Chem. Commun.* **1983**, 957.
(22) Brown, R. F. C.; Eastwood, F. W.; Harrington, K. J. *Aust. J. Chem.* **1974**, *27*, 2373.

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



cmpd	CH_3	C-2	C-4 ($^3J_{CH}$)	C-6 ($^3J_{CH}$)	C-5	C-7 ($^1J_{CH}$)	other carbons[b]
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 = CH, Y = 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 $(CD_3)_2SO$.

Table III. IR Absorptions of Imidoylketenes 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).

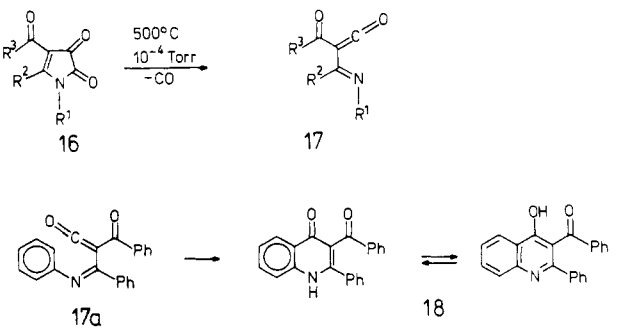
order to confirm the assignment of the 2123 cm^{-1} peak to the imidoylketene **14b**, we have generated such ketenes in a different manner, as described in the following section, and found that they absorb generally in the range 2122–2140 cm^{-1} and also cyclize to quinolones in the gas-phase.

3. Imidoylketenes 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 imidoylketenes **17** are observed by IR spectroscopy (Scheme IV and Table III). These absorptions, at 2122–2140 cm^{-1}, disappeared on warming between −105 and −70 °C.

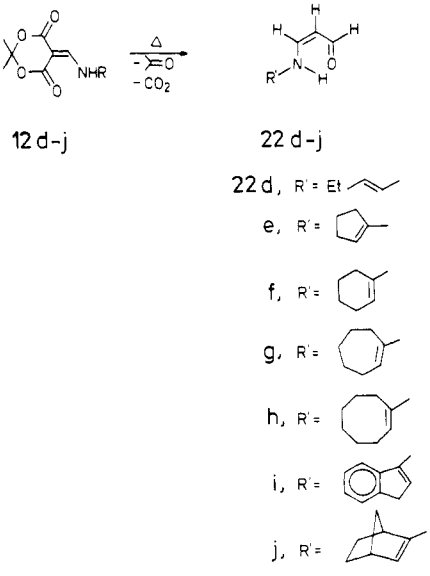
In the case of **17a**, the ketene absorption was absent at pyrolysis temperatures above 600°C, and isolation of the product confirmed its identity with the quinolone–4-hydroxyquinoline tautomeric pair **18** previously isolated from a solution thermolysis of **16a**.[24] This result implies a gas-phase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

A few other imidoylketenes have been matrix isolated by other workers and found to absorb at 2130–2140 cm^{-1}.[25]

Scheme IV



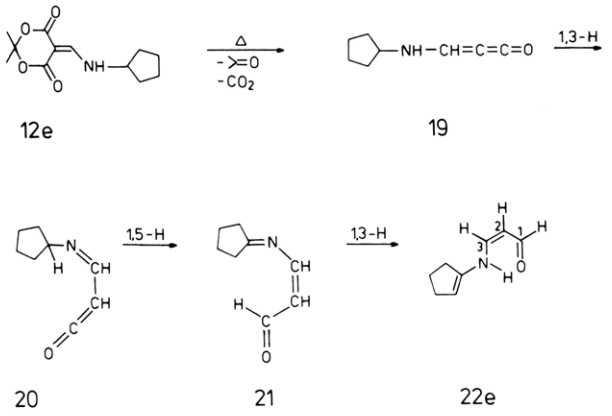
Scheme V



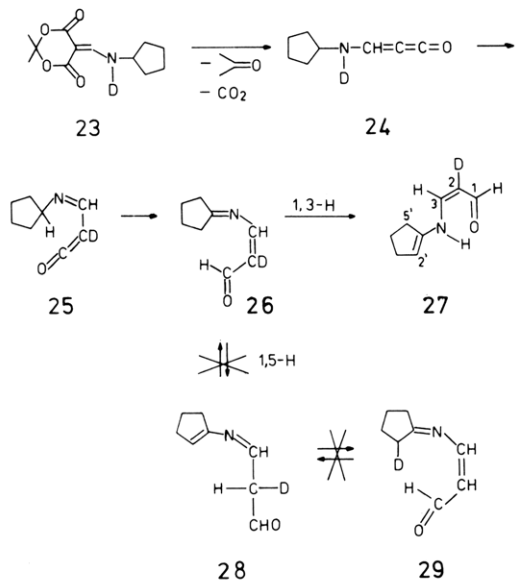
4. Enaminoacroleins from 12d–j. The preparative pyrolyses of the Meldrum's acid derivatives **12d–j** at 500–600 °C gave results entirely different from those described for **12a–c** in Section 2: no cyclization products were formed, but instead, enaminoacroleins **22d–j** (Scheme V) were isolated in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

(23) Ott, W. *Synthesis* **1976**, 478.
(24) Kollenz, G.; Igel, H.; Ziegler, E. *Monatsh. Chem.* **1972**, 103, 450. Kollenz, G.; Penn, G.; Ott, W.; Peters, K.; Peters, E.-M.; Schnering, H.-G. von, *Chem. Ber.*, in press.
(25) Krantz, A.; Hoppe, B. *J. Am. Chem. Soc.* **1975**, *97*, 6590. Maier, G.; Schäfer, U. *Tetrahedron Lett.* **1977**, 1053.

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 imidoylketene **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** → **22e** must occur between −90 °C and +25 °C. Under preparative conditions involving longer contact times, the whole sequence **12e** → **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, $^3J_{H1,H2} = 2.1$ Hz, and with H-3, $^3J_{H2,H3} = 7.3$ 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 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.

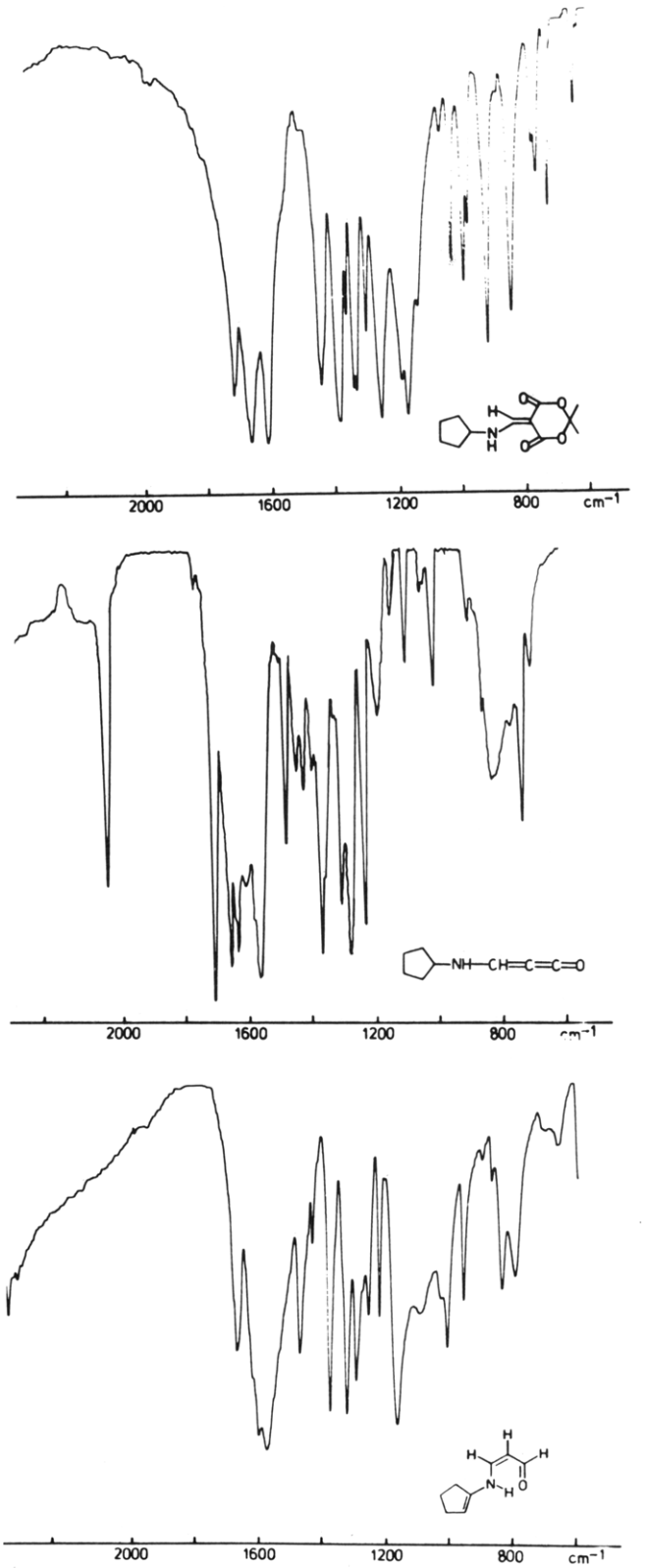
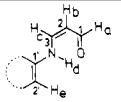


Figure 1. Infrared spectra of **12e** (KBr) (top), **19** (−196 °C) (center), and **22e** (KBr, 25 °C) (bottom).

The sequence **24** → **25** → **26** → **27** therefore constitutes a necessary and sufficient number of steps. This is in contrast to a recent communication by McNab and coworkers,[21] who in a study of the analogous formation of

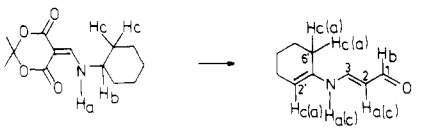
Table IV. Proton and Carbon-13 NMR Chemical Shifts and Coupling Constants for (*Z*)-3-Enaminoacroleins 22[a]



cmpd		H_a C_1	H_b C_2	H_c C_3	H_d C'_1	H_e C'2	other Hs other Cs	J_{ab} $^1J_{C_1H}$	J_{ac} $^2J_{C_1H}$	J_{bc} $^1J_{C_2H}$	J_{cd} $^2J_{C_2H}$	$^1J_{C_3H}$	$^1J_{C'_2H}$
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		
	δ^{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		
	δ^{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		
	δ^{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		
	δ^{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		
	δ^{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 ^{1}H 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**:



30 31

To explain this, a series of hydrogen shifts corresponding to **26** ⇌ **28** ⇌ **29** (Scheme VII) was proposed. From the ^{1}H and ^{13}C NMR data described for **27** above, we can *exclude* the occurrance 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** → **27** is faster than the 1,5-shift **26** → **28** also indicates that the 1,3-shift is auto- or wall-catalyzed.

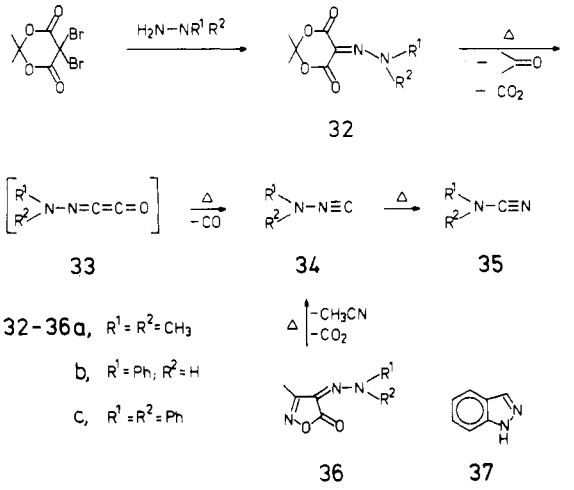
The pyrolyses of **12d** and **12f–j** to give **22d** and **22f–j** proceeded as described above for **12e**. Only in the case of **22j** was the product so unstable that a complete characterization including elemental analysis was not possible.

The ^{1}H 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. Isocyanoamines 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 dimethylisocyanoamine (**34a**) (IR neat) 2080 cm^{-1}) which had the chemical properties previously described for the compound prepared in a different

Scheme VIII



32 33 34 35

32-36a, $R^1 = R^2 = CH_3$

b, $R^1 = Ph$; $R^2 = H$

c, $R^1 = R^2 = Ph$

36 37

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.

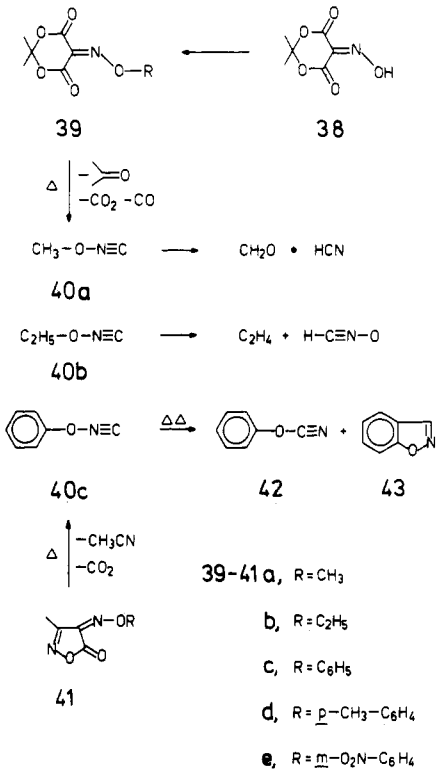
The phenylhydrazone **32b** gave, at 400 °C, strong IR signals for the isocyanide **34b** (2120, 2155 cm^{-1}) and phenylcyanamide (**35b**) (2220 cm^{-1}). Most importantly, the doublet assigned to *N*-isocyanoaniline (**34b**) was exactly identical with that previously observed for the compound generated 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 observed[5] 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) Bredereck, H.; Föhlisch, 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 **38**[26] 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 isoxazolone **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 described[7] 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 CO_2, 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 imidoylketenes (e.g., **14** and **20**)[29] which undergo further reactions. Imidoylketenes 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 CO_2 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 isocyanoamines **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.

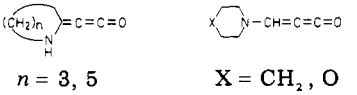
Experimental Section

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 BaF_2 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 ^{13}C 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 microanalytical 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 ^{13}C 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



$n = 3, 5$ $X = CH_2, O$

which again are directly observable by IR spectroscopy although the former, possessing a tautomerizable NH function, readily isomerize to the corresponding imidoylketenes: 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–CCl_4 (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 N_2. After the completion of the pyrolysis, the coolant was removed and the CO_2 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 CCl_4 or $CHCl_3$ 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 ^{13}C 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 $C_7H_{11}NO$: 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 $C_8H_{11}NO$: 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 CH_3OD and 4 mL D_2O 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 ^{13}C 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 CCl_4, mp 114–117 °C.

Anal. Calcd for $C_9H_{13}NO$: 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 $C_{10}H_{15}NO$: 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 $C_{11}H_{17}NO$: 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 CH_3OH, evaporated, and dried in vacuo, and the solid so obtained was recrystallized from $CHCl_3$ to give yellow-orange crystals: mp 146–147 °C; ^1H NMR (CD_3OD) 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*)-(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 ($CDCl_3$) δ 1.73 (s, 6 H, $C(CH_3)_2$), 3.36 (s, 3 H, NCH_3), 3.76 (s, 3 H, NCH_3); ^{13}C NMR; see Table II.

Anal. Calcd for $C_8H_{12}N_2O_4$: 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 ($CDCl_3$) δ 1.80 (s, 6 H, $(CH_3)_2$), 7.26–7.54 (m, 5 H, Ar), 9.67 (s, br, 1 H, NH); ^{13}C NMR, see Table II.

Anal. Calcd for $C_{12}H_{12}N_2O_4$: 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 ($CDCl_3$) δ 1.71 (s, 6 H), 7.16–7.52 (m, 10 H, Ar); ^{13}C NMR, see Table II.

Anal. Calcd for $C_{18}H_{16}N_2O_4$: 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 monohydrate[28] (6.9 g, 32 mmol) was dissolved in a mixture of 50 mL of H_2O and 50 mL of ethanol, and a concentrated equimolar solution of silver nitrate (3.5 g in 10 mL of H_2O) 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 H_2O and twice with ether, and dried, first over $CaCl_2$ 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 (Me_2SO-d_6) δ 1.59 (s, $(CH_3)_2$).

Anal. Calcd for $C_6H_6NO_5Ag$: 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 CCl_4 and reprecipitated with petroleum ether (bp 40–60 °C) to give 180 mg (20%) of pale yellow crystals; mp 78 °C,[35] ^1H NMR ($CDCl_3$) δ 1.79 (s, 6 H, $C(CH_3)_2$), 4.44 (s, 3 H, OCH_3); ^{13}C NMR ($CDCl_3$), see Table II.

Anal. Calcd for $C_7H_9NO_5$: 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 ($CDCl_3$) δ 1.46 (t, 3 H, CH_3), 1.78 (s, 6 H, $C(CH_3)_2$), 4.68 (q, 2 H, CH_2); ^{13}C NMR, see Table II.

Anal. Calcd for $C_8H_{11}NO_5$: 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 (Me_2SO-d_6) δ 1.79 (s, 6 H, $C(CH_3)_2$), 7.28 (t, 1 H, *p*-phenyl), 7.36 (d, 2 H, *o*-phenyl), 7.49 (t, 2 H, *m*-phenyl); ^{13}C NMR, see Table II.

Anal. Calcd for $C_{12}H_{11}NO_5$: 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 ($CDCl_3$) δ 1.84 (s, 6 H, $C(CH_3)_2$), 2.35 (s, 3 H, CH_3), 7.18 (d, 2 H, Ar), 7.28 (d, 2 H, Ar); ^{13}C NMR, see Table II.

Anal. Calcd for $C_{13}H_{13}NO_5$: 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 ($CDCl_3$) δ 1.87 (s, 6 H, $C(CH_3)_2$), 7.61 (t, 1 H, Ar), 7.76 (d, 1 H, Ar), 8.11 (d, 1 H, Ar), 8.28 (s, 1 H, Ar); ^{13}C NMR; see Table II.

Anal. Calcd for $C_{12}H_{10}N_2O_7$: 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, dimethylisocyanoamine, 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.

Acknowledgment. This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie. We thank Dr. H.-W. Winter for some low-temperature IR measurements and Dr. W. Ott (Graz) for supplying samples of pyrrolediones. H. Briehl thanks the University of Marburg for a teaching assistantship which made this doctoral work possible.

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; $C_6H_5NH_2$, 62-53-3; p-$CH_3C_6H_4NH_2$, 106-49-0; p-$HOC_6H_4NH_2$, 123-30-8; n-$C_4H_9NH_2$, 109-73-9; $H_2NN(CH_3)_2$, 57-14-7; H_2NNHPh, 100-63-0; H_2NNPh_2, 530-50-7; cyclopentylamine, 1003-03-8; cyclohexylamine, 108-91-8; cycloheptylamine, 5452-35-7; cyclooctylamine, 5452-37-9; 1-indanylamine, 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, ^{13}C 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.