imine. Since **8** does not transfer an electron to cyclooctatetraene and does do so to SO_2 we tentatively assign EA(**8**) = 0.8 ± 0.3 eV.[54] Allyl anion[55] has EA = 0.357 eV; therefore, as expected, the nitrogen atom in **8** stabilizes the anion more than it stabilizes the radical. It would be interesting to know the EA more precisely and we hope to do this in the future.

Conclusion

In summary, we have shown that the methanimine anion (**2**) can readily be generated from (trimethylsilyl)methyl azide in the gas phase presumably through the azidomethide ion. Ion **2** was found to have an acidity of 388 ± 5 kcal/mol and an electron affinity of approximately 0.5 ± 0.1 eV, both of which are in accord with a recent calculation. The methanimine anion was also found to react with a variety of reagents. In particular, it is a reasonably efficient hydride donor, undergoes sulfur atom transfer with CS_2 or OCS to produce a resonance stabilized thiooxime anion, and reacts with ethylene oxide to produce the novel 2-azallyl anion. Furthermore, in the study of these reactions it was found that the azide ion is not completely inert and that it reacts with CS_2 to generate the thiocyanate ion.

The 2-azallyl anion was briefly examined and found to have ΔH_{acid} = 385 ± 5 kcal/mol and EA = 0.8 ± 0.3 eV. It thus has a slightly larger proton and electron affinity than the allyl anion.

Acknowledgment. We thank G. B. Ellison, J. Filley, and V. Bierbaum for several helpful discussions as well as aid in preparing this paper. We also thank B. Damrauer for supplying us with (trimethylsilyl)methyl azide. This work was supported by the U.S. Army Research office [Contract No. DAAG29-82-K-0025]. S.K. was also supported by the Army Research office [Contract No. DAAG29-81-K-0169].

Registry No. **2**, 28892-56-0; **3**, 87576-94-1; **7**, 96761-35-2; **8**, 73859-26-4; NH_2^-, 17655-31-1; N_3^-, 14343-69-2; N_2O, 10024-97-2; CO_2, 124-38-9; CS_2, 75-15-0; OCS, 463-58-1; O_2, 7782-44-7; $\overline{CH_2CH_2O}$, 75-21-8; HN_2O^-, 66833-68-9; HCO_2^-, 71-47-6; HCS_2^-, 37619-02-6; $HC(O)S^-$, 37619-01-5; NCO^-, 661-20-1; $CH_2{=}NCH_2CO_2^-$, 96761-36-3; $CH_2{=}NCH_2N_2O^-$, 96761-37-4; N_2S, 56400-02-3; NCS^-, 302-04-5; $CD_2{=}NCD_2^-$, 96761-38-5; D_2O, 7789-20-0.

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[54] The electron affinity of SO_2 is 1.1 eV. Celotta, R. J.; Bennett, R. A.; Hall, J. L. *J. Chem. Phys.* **1974**, *60*, 1740.

[55] Oakes, J. M.; Ellison, G. B. *J. Am. Chem. Soc.*, in press.

Mechanism of Fragmentation of Alkylidene-Meldrum's Acids. Carboxyketene, Vinylketene, and Methyleneketene Intermediates from 5-Cyclopentylidene-2,2-dimethyl-1,3-dioxane-4,6-dione

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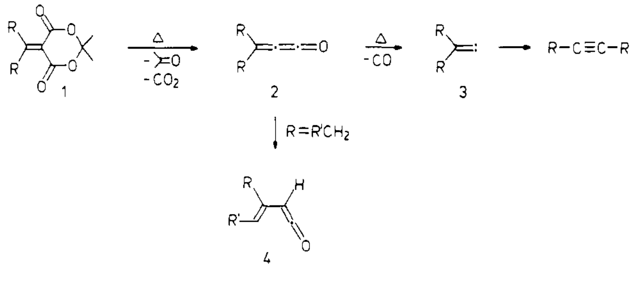
Three ketenes were successively observed on flash vacuum pyrolysis of 5-cyclopentylidene-2,2-dimethyl-1,3-dioxane-4,6-dione (**5**), viz., carboxycyclopentenylketene (**11**, 2126 cm^{-1}), cyclopentylideneketene (**12**, 2087 cm^{-1}), and cyclopentenylketene (**13**, 2110 cm^{-1}). **11** was thermally converted to **13** and probably also to **12**. **12** itself rearranged thermally to **13**. The three ketenes were trapped with methanol to give the esters **14**, **15**, and **16**. **14** was thermally unstable, rearranging at room temperature to methyl cyclopentylidenemalonate (**14a**) and decarboxylating at 150 °C, predominantly to **16**. A dimer of **12**, 2,4-bis(cyclopentylidene)cyclobutane-1,3-dione (**17**), was also isolated. 1-Cyclopentenyldiazomethane (**18**) was prepared and pyrolyzed to 1,3-cyclohexadiene and benzene. No evidence for the formation of cyclohexyne (**17**) was obtained in any of these experiments.

The thermal decomposition of 5-alkylidene-2,2-dimethyl-1,3-dioxane-4,6-diones (Meldrum's acid derivatives) **1** has been the subject of much investigation,[2] but little is known about the mechanism. It is generally believed that methyleneketenes **2** are the first-formed intermediates, and that these eliminate CO to give vinylidenes **3** and thence acetylenes, particularly when R = aryl,[2] or else isomerize to vinylketenes **4** when R = alkyl.[3]



We now wish to show that this sequence of events is not always followed, that the first step can lead to a vinylcarboxyketene, that this in a second step decarboxylates to a vinylketene, that a methyleneketene is also formed, and that at higher temperatures the methyleneketene also isomerizes to the vinylketene.

We chose the cyclopentylidene-Meldrum's acid **5** as a subject for a detailed investigation because the gas-phase pyrolysis of this compound had been previously reported to yield 1,3-cyclohexadiene (**9**) and benzene in a combined yield of 92%.[4] This was believed to occur via the vinylidene **6**, possibly in equilibrium with cyclohexyne (**7**) and the bicyclohexene **8**. Although the authors rightly point out that there was no evidence for the existence of cyclohexyne, the homologue cyclooctyne was isolated from the analogous pyrolysis of cycloheptylidene-Meldrum's acid.[4] It therefore appeared worthwhile to attempt the low-temperature isolation of **7** from the pyrolysis of **5**. As it turned

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[1] Address correspondence to this author at the University of Queensland.

[2] Brown, R. F. C. "Pyrolytic Methods in Organic Chemistry"; Academic Press: New York, 1980.

[3] Mohmand, S.; Hirabayashi, T.; Bock, H. *Chem. Ber.* **1981**, *114*, 2609.

[4] Baxter, G. J.; Brown, R. F. C. *Aust. J. Chem.* **1978**, *31*, 327.

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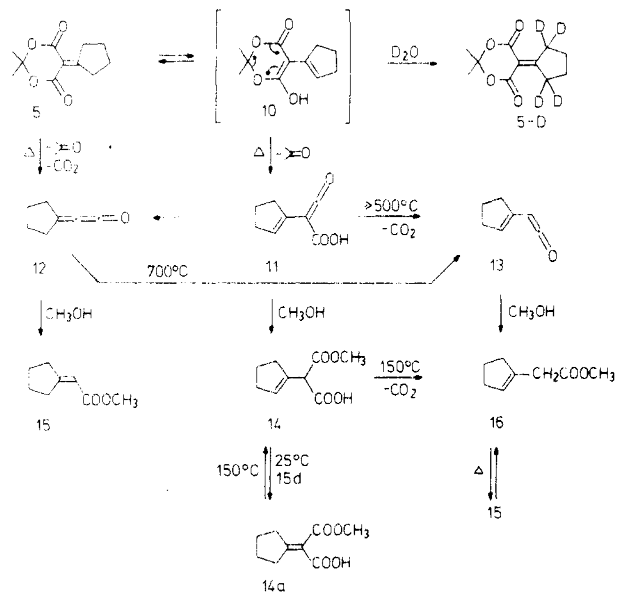
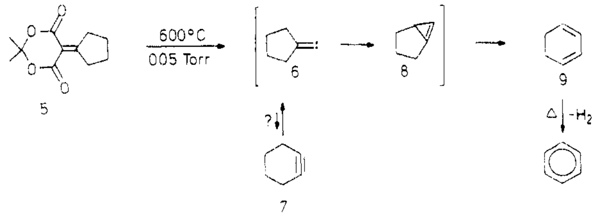
Scheme I



out, no trace of **7** was found, and **7** is not implicated in the formation of **9**. Instead, three different ketenes were observed.



Results and Discussion

The flash vacuum pyrolysis of **5** was monitored by low temperature (-196 °C) IR spectroscopy with an apparatus previously described.[5] The disappearance of the starting material as a function of temperature was monitored by observation of a strong band at 1600 cm^{-1}, and the appearance of CO_2 and acetone by observation at 2340 and 1705 cm^{-1}, respectively. A ketene absorption ascribed to cyclopentenylcarboxyketene **11** started appearing at 2126 cm^{-1} at a pyrolysis temperature as low as 380 °C. At this temperature, most of the starting material remained unchanged; acetone was formed, but CO_2 was not. The 2126 cm^{-1} band could be observed up to a pyrolysis temperature of 600 °C, the optimum being 450–500 °C. At 500 °C the starting material had completely disappeared, acetone was formed, but only a trace of CO_2 was present. In addition, a second ketene, absorbing weakly at 2087 cm^{-1} and ascribed to **12** as elaborated below, had started appearing.

The acid ketene **11** exhibited strong, broad absorptions at 2500–3400 cm^{-1}, typical of carboxylic acids, in addition to ketene, carbonyl, and C=C absorptions at 2126, 1670, and 1630 cm^{-1}, respectively. The latter three absorptions disappeared simultaneously on warming the sample from -196 °C to -50 °C. The fact that acetone but not CO_2 was formed supports the contention that the 2126 cm^{-1} species belongs to **11**, formed via tautomerization[6] of **5** to the enol **10**; a cycloreversion of **10** gives acetone and **11** (Scheme I).

Although the enol **10** was not directly detected, evidence for the tautomeric equilibrium **5** $\rightleftarrows$ **10** in the liquid phase is given by the complete formation of the $\alpha,\alpha,\alpha,\alpha$-tetradeuterio derivative **5-D** in the course of 4 months in $(CD_3)_2SO/D_2O$ solution at room temperature. As could be expected, the exchange was dramatically catalyzed by base.

For further proof of the identity of **11**, the pyrolysis product was mixed with methanol vapor at the exit of the pyrolysis tube. The resulting methanol solution was isolated at -196 °C, methanol was evaporated in high vacuum at -40 °C, and a ^1H NMR spectrum recorded at 25 °C clearly demonstrated the presence of methyl cyclopentenylmalonate **14** as the main product (84%). In addition, smaller amounts of the isomeric ester **14a** (5%), the decarboxylated ester **16** (0.4%), and methyl cyclopentylideneacetate **15** (10%) were present. The presence of **15** is due to trapping of the second ketene **12**, absorbing at 2087 cm^{-1}, which will be further described below. The presence of **14a** is due to the fact that **14** is thermodynamically less stable and isomerizes to **14a**. The isomerization **14** → **14a** was complete after 15 days in $CDCl_3$ solution at room temperature. Both **14** and **14a** decarboxylated to give **16** (and not **15**) on injection onto a gas chromatograph at 200 °C. **14a** also decarboxylated in solution ($CDCl_3$) at 150 °C ($t_{1/2}$ = 50 min). In all likelihood the decarboxylation of **14a** is not direct but proceeds via tautomerization back to **14**, since only **14** can give **16** via a six-membered cyclic transition state. Indeed, the formation of **14** can be observed by NMR during the decarboxylation of **14a**. After heating **14a** for 10 min at 150 °C in $CDCl_3$ solution, a 4:1 ratio of **14a** and **14** was present, and this ratio remained constant as decarboxlation proceeded. Under these conditions, the decarboxylation gave both **15** and **16** because these two acetates also interconvert thermally, with an equilibrium ratio of 1:3.7 at 150 °C (1:2.2 at 200 °C). Control experiments demonstrated that **15** and **16** do *not* interconvert under gas chromatography conditions. The two esters were reisolated from the gas chromatograph and their identities established by ^1H NMR. Accordingly, only gas chromatography gives a true picture of the initial products of decarboxylation of **14** and **14a**. There is much precedent for the decarboxylation of cyclopentylidene- and cyclohexylidenemalonic acid derivatives to cyclopentenyl- and cyclohexenylacetic acid derivatives in the older literature.[7]

As mentioned above, a second ketene, absorbing at 2087 cm^{-1}, started appearing at a pyrolysis temperature of 500 °C. The intensity of the 2087 cm^{-1} signal increased with increasing temperature till 700 °C. At the same time, the first ketene (2126 cm^{-1}) disappeared completely (at 650 °C), and a third ketene started appearing (2110 cm^{-1}) at 600 °C. The 2087 cm^{-1} band disappeared again above 700 °C, but the 2110 band remained strong up to 800 °C. Thus, the 2087 cm^{-1} species cannot be observed alone, but the other two can. Trapping experiments with methanol as described above allow the firm conclusion that the third ketene (2110 cm^{-1}) is cyclopentenylketene (**13**), which on trapping gives **16**. The second ketene (2087 cm^{-1}) is cyclopentylideneketene (**12**), which on trapping gives **15**. Furthermore, a preparative pyrolysis (see Experimental Section) of **5** at the optimum temperature for the formation of **12** (600 °C) allowed the isolation of the dimer **17**

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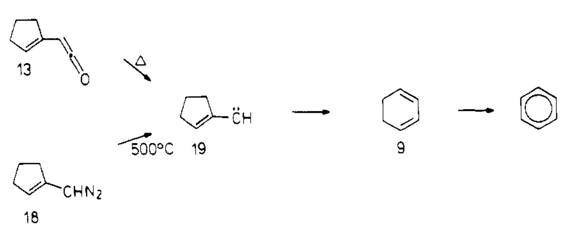
(5) Briehl, H.; Luckosch, A.; Wentrup, C. *J. Org. Chem.* **1984**, *49*, 2772.

(6) (a) A related tautomerism of 4-alkylideneisoxazol-5(4*H*)-ones was described previously: (b) Wollweber, H.-J.; Wentrup, C. *J. Org. Chem.* **1985**, *50*, 2041.

(7) Harding, V. J.; Haworth, W. N. *J. Chem. Soc.* **1910**, *97*, 486. Dickins, A. H.; Hugh, W. E.; Kon, G. A. R. *Ibid.* **1929**, 572. Kandiah, A.; Linstead, R. P. *Ibid.* **1929**, 2139. For equilibration of diethyl cyclopentylidene- and cyclopentenylmalonate, see: Cope, A. C.; Hardy, E. M. *J. Am. Chem. Soc.* **1940**, *62*, 3319. For equilibration of cyclohexylidenean cyclohexenylacetic acids, see: Linstead, R. P. *J. Chem. Soc.* **1930**, 1603.

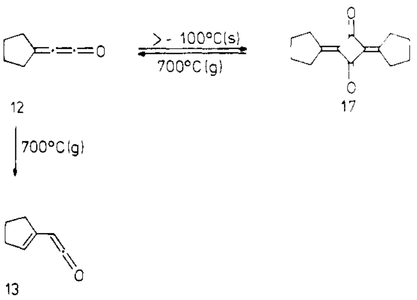
Scheme II



as yellow crystals in 30% yield. This compound was completely characterized spectroscopically and analytically. Moreover, the conversion of **12** to **17** was directly monitored by IR spectroscopy of the product of a 600 °C pyrolysis, isolated at −196 °C. The 2087 cm^{-1} absorption disappeared at −100 °C concomitantly with the appearance of a new ketene absorption at 1685 cm^{-1} due to the dimer **17**.

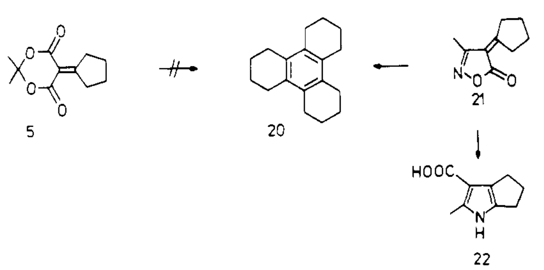
We now need to establish the interconvertibility of the three ketenes. This was performed by using dual pyrolysis tubes, each of the same length (5 cm) as the single pyrolysis tube used in the previous experiments. The products were isolated at −196 °C and examined by IR spectroscopy as above. When dual pyrolysis tubes each at 500 °C were used, strong signals for **11** and **13** were observed together with a weak signal for **12**. Since the single tube at 500 °C produces **11** (s) and **12** (w), but no **13**, the secondary thermal conversion **11** → **13** is implied. When dual tubes were used with the first at 500 °C and the second at 600 °C, **12** (m) and **13** (s) were obtained, implying that also **11** → **12**. With the first tube at 600 °C, the second at 700 °C, **12** (w) and **13** (s) were obtained, implying **12** → **13**. It cannot be excluded, however, that there is an independent route **5** → **12** entering in competition with the main pathways delienated in Scheme I at high temperatures.

For further proof of the methyleneketene–vinylketene rearrangement **12** → **13**, an independent source of **12** was sought. The dimer **17** was useful in this regard. Although the pyrolysis of **17** was inefficient below 700 °C, a weak 2087 cm^{-1} band (**12**) was observed on pyrolysis at 550 °C. At 700 °C **12** (w) and **13** (s) were observed, and at 800 °C only the rearranged ketene **13** (2110 cm^{-1}) was detectable.



The high temperature isomerization **12** → **13**, previously believed to be the only isomerization on this energy surface,[3] is only a minor part of the interrelationship (Scheme I) and contrary to previous beliefs it is not easily effected. Vinylcarboxyketenes ought to have been observable in the photoelectron spectroscopic study[3] also. We have shown elsewhere that the interrelationships of Scheme I apply to simple ethylidene and 2-propylidene derivatives of Meldrum's acid also.[8]

Scheme III



Since **13** is the only compound surviving at the highest temperatures, it is logical to propose that this is the source of the final products, cyclohexadiene (**9**) and benzene, a proposal also at variance with previous beliefs stated in the Introduction. The decarbonylation of **13** takes place at 800 °C and above, giving **9** and benzene as detected by gas chromatography. Presumably, the ketene **13** first decarbonylates to cyclopentenylcarbene (**19**) (Scheme II). Independent evidence that this carbene will indeed give cyclohexadiene and benzene was secured by preparing and pyrolyzing the diazo compound **18** which, at 500 °C/10^{-3} torr, gave **9** (40%) and benzene (10%). Benzene is, as already reported,[4] a secondary pyrolysis product of **9**.

The above experiments leave no room for cyclohexyne (**7**) as an isolable intermediate. Even if **7** could not be detected by IR spectroscopy, it would be expected, if formed, to trimerize to dodecahydrotriphenylene (**20**). No trace of **20** could be detected by meticulous capillary column gas chromatography of the pyrolyzates of **5**, obtained between 600 and 850 °C. An authentic sample of **20** was available for comparison.

In contrast, a *trace* of **20** was detected by GC of the pyrolyzate of 4-cyclopentylidene-3-methylisoxazol-5-(4*H*)-one (**21**) at 800 °C/10^{-3} torr (Scheme III). Isoxazolones of the type **21** are known to furnish pyrroles (**22**) as the major products,[6b] and vinylidene and hence acetylene formation is at most a minor pathway.

In conclusion, alkylidene-Meldrum's acids decompose thermally via vinylcarboxyketenes (**11**). These decarboxylate to vinylketenes (**13**) and, probably less efficiently, to alkylideneketenes (**12**). Furthermore, **12** isomerizes to **13** at elevated temperatures. Some alkylideneketene (**12**) may be formed directly from the starting material (**5**), and this becomes the exclusive pathway in nontautomerizable Meldrum's acids (**1**, R = aryl).

Experimental Section

General Methods. General features of the pyrolysis equipment have been described.[5,9] The analytical pyrolysis apparatus employed a 10 × 0.8 cm (i.d.) quartz tube, of which the first 5-cm length was a sublimation zone, the last 5 cm the actual pyrolysis zone. In dual pyrolysis experiments, both zones were used as pyrolysis zones. The products were collected on KBr disks mounted on Air Products liquid nitrogen cryostats. IR spectra were recorded on a Perkin-Elmer 281 instrument with a resolution of 2 cm^{-1}. The preparative pyrolysis apparatus employed a 20 × 2 cm quartz tube. Both systems were pumped to 10^{-3}–10^{-5} torr. The analytical pyrolyses are fully described above. The following pyrolyses pertain to the preparative apparatus only.[10]

5-(2,2,5,5-Tetradeuteriocyclopentylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione (5-D). 5-Cyclopentylidene-2,2-dimethyl-1,3-dioxane-4,6-dione (**5**)[11] (10 mg) was dissolved in

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[8] (a) The pyrolysis of alkylidene-Meldrum's acids **1** (**a**, R, R = H,CH$_3$; **b**, R,R = CH$_3$,CH$_3$) has been examined by tandem mass spectrometry and low temperature IR spectroscopy and the presence of vinylcarboxyketenes, methyleneketenes, and vinylketenes was observed.[8b] (b) Maquestiau, A.; Pauwels, P.; Flammang, R.; Lorenčak, P.; Wentrup, C. *Org. Mass Spectrom.*, submitted for publication.

[9] Wentrup, C.; Damerius, A.; Reichen, W. *J. Org. Chem.* **1978**, *43*, 2037.

[10] Due to the different designs, different temperatures are required to bring about the same chemistry in the two pyrolysis apparatuses. A 100° lower temperature may be required in the preparative apparatus.

$(CD_3)_2SO$ (0.5 mL) and D_2O (0.2 mL): ^{1}H NMR δ 1.60 (s, 6 H, $(CH_3)_2$), 1.69 (s, 4 H, β-CH_2), 3.72 (s, 4 H, α-CH_2). The sample was kept at room temperature and the ^{1}H NMR spectrum, recorded every few weaks, demonstrated a gradual decrease of the α-CH_2:β-CH_2 ratio. After 4 months the signals due to the α-CH_2 groups had completely disappeared, while the rest of the spectrum remained unchanged except that the peak due to H_2O had increased and integrated for 4 H. The solvent was evaporated in vacuo, the solid residue sublimed, and a 70-eV electron ionization mass spectrum recorded and compared with that of **5**.

5: m/z 195([$M^{+\cdot}$ − CH_3], 7.3), 152 ([$M^{+\cdot}$ − CH_3COCH_3], 100), 124 ([$M^{+\cdot}$ − CH_3COCH_3 − CO], 42.4), 108 ([$M^{+\cdot}$ − CH_3COCH_3 − CO_2], 20.6), 79 (31.3), 43 (36.8). The $M^{+\cdot}$ peak (m/z 210) was observed with field desorption only.

5-D: m/z 199 (3.8), 156 (100), 128 (34.6), 112 (19.7), 83 (11.6), 43 (41.6).

The experiment was repeated adding one drop of concentrated NaOD solution. The exchange of the α-protons was complete in one day.

2,4-Dicyclopentylidenecyclobutane-1,3-dione (17). 5-Cyclopentylidene-2,2-dimethyl-1,3-dioxane-4,6-dione (**5**)[11] (300 mg, 1.4 mmol) was pyrolyzed at 600 °C (sublimation temperature 40 °C) and 10^{-4} torr. A yellow pyrolyzate was condensed at −196 °C. On warming to room temperature, this first liquefied, then solidified, and turned red. The red material was dissolved in 1,2-dichloroethane and recrystallized from the same solvent to give 47 mg (31%) of yellow crystals: mp 174–175 °C dec; IR (KBr) ν 2970 (m), 2880 (m), 1685 (s), 1640 (s), 1455 (m), 1400 (m), 1320 (m), 1290 (m), 1270 (m), 1190 (m), 830 (m), 730 (m), 700 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.77–1.81 (m, 8 H), 2.77–2.81 (m, 8 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 25.6 (β-CH_2), 33.8 (α-CH_2), 147.2 (C-2, C-4), 167.9 (C-1, C-3), 188.9 (C-1′, cyclopentylidene); mass spectrum, m/z 217 ($[M + 1]^+$, 14), 216 ($[M]^+$, 100), 188 ($[M - CO]^+$, 30), 160 ($[M - 2CO]^+$, 6), 117 (11), 109 (81), 108 ($[M]^+/2$ or $[M]^{2+}$, 23), 91 (15), 81 (14), 79 (34), 67 (17), 57 (13). Anal. Calcd for $C_{14}H_{16}O_2$: C, 77.75; H, 7.46. Found: C, 77.53; H, 7.56.

Pyrolysis of 5 at 800 °C. **5** (300 mg, 1.4 mmol) was pyrolyzed at 800 °C/10^{-4} torr. The volatile product was examined by ^{1}H NMR and GC–MS and found to consist of 1,3-cyclohexadiene, benzene, and acetone as previously reported.[4] The dimer **17** was not detectable by ^{1}N NMR spectroscopy of the largely polymeric, solid residue.

Methyl 2-(1-Cyclopentenyl)malonate (14). **5** (300 mg, 1.4 mmol) was pyrolyzed at 400 °C[9] by using the preparative apparatus fitted with a methanol vapor inlet tube inside the pyrolysis tube and ending 5 cm before the end of the pyrolysis zone. Methanol vapor was introduced through a needle valve at such a rate that the initial pressure of 10^{-4} torr increased $6 \cdot 10^{-2}$–$8 \cdot 10^{-2}$ torr during the pyrolysis. The products were isolated together with methanol on a cold finger (−196 °C). After the pyrolysis was completed, the apparatus was flushed with N_2 and the cold finger allowed to warm up, causing the methanol solution to drip into a round-bottomed flask equipped with a magnetic stirring bar and cooled to −40 °C. After evaporating the methanol in high vacuum with stirring at −40 °C, and toward the end at room temperature, the remaining material was dissolved in $CDCl_3$ and a ^{1}H NMR spectrum recorded at room temperature: ^{1}H NMR (90 MHz) δ 9.29 (s, 1 H, COOH), 5.71 (br s, 1 H, vinyl), 4.25 (s, 1 H, *H*C(COOH)COOMe), 3.71 (s, 3 H, CH_3), 2.4–1.5 (m, 6 H, CH_2); IR (film) ν 3500–2500 (br s, COOH), 1740–1710 (s, CO) cm^{-} The sample contained 10.4% of **15**, 0.4% of **16**, and 5.6% of **14a** as determined by ^{1}H NMR, gas chromatography, and GC–MS.

Injection on a gas chromatograph at 200 °C (column Apiezon M at 150 °C) caused complete decomposition into **16**. The area of the peak due to **15** remained unchanged. **15** and **16** were isolated and their identities established by ^{1}H NMR spectroscopy.

Methyl Cyclopentylidenemalonate (14a). A sample containing **14** (83.6%), **14a** (5.6%), **15** (10.4%), and **16** (0.4%) was kept in $CDCl_3$ solution at room temperature for 15 days, after which time **14** had completely isomerized to **14a**. Spectral subtraction allowed the extraction of the spectra of **14a**: ^{1}H NMR ($CDCl_3$, 90 MHz) δ 10.22 (s, 1 H, COOH), 3.70 (s, 3 H, CH_3), 2.87–2.50 (m, 4 H, α-CH_2), 1.76–1.52 (m, 4 H, β-CH_2); ^{13}C NMR ($CDCl_3$, 25 MHz) δ 25.6, 25.7 (β-CH_2), 35.2, 35.4 (α-CH_2), 51.9 (CH_3), 118.5 (c-quart), 166.9, 168.6 (CO), 175.2 (C-1′, cyclopentylidene).

Injection of **14a** onto a gas chromatograph at 200 °C (column Apiezon M at 120 °C) caused almost quantitative (>95%) decarboxylation to methyl cyclopentenylacetate (**16**) as verified by isolation and ^{1}H NMR spectroscopy of the material. Decarboxylation of **14a** was also carried out in $CDCl_3$ solution and monitored by ^{1}H NMR spectroscopy. At 100 °C the decarboxylation half-life was ca. 205 min, at 150 °C 50 min. At 150 °C **14a** partly tautomerized to **14** again, giving a ratio **14a**:**14** $\simeq$ 4 throughout the decarboxylation process. The equilibrium ratio **16**:**15** of the products of decarboxylation was 3.7 at 150 °C and 2.2 at 200 °C as established in separate experiments with pure **15** or **16**. The identities of **15** and **16** were established by ^{1}H NMR and gas chromatographic comparison with the authentic samples, prepared as described below.

Methyl Cyclopentylideneacetate (15) and Methyl Cyclopentenylacetate (16). Methyl cyclopentenylacetate (**16**) was prepared from cyclopentanone and methyl bromoacetate according to Wallach.[12] The Reformatsky reaction between these two components gave directly **16** and not methyl 2-(1-hydroxypentyl)acetate as described by Wallach. Treatment of 5 g (0.036 mol) of **16** with 10 g (0.074 mol) of $KHSO_4$ for 2 h at 160 °C gave a 1:1 mixture of **15** and **16** in quantitative yield. The two esters were separated on a Varian Aerograph A 90 (Apiezon M, He carrier gas 150 mL/min, 120 °C isothermal). **15**: retention time 12.9 s; ^{1}H NMR ($CDCl_3$, 90 MHz) δ 5.72 (pentuplet, 1 H, vinyl), 3.59 (s, 3 H, CH_3), 2.52–2.26 (m, 2 H, α-CH_2), 2.16–1.92 (m, 2 H, α-CH_2), 1.46–1.11 (m, 4 H, β-CH_2); ^{13}C NMR ($CDCl_3$, 25 MHz) δ 25.4, 26.3 (β-CH_2), 32.5, 35.8 (α-CH_2), 50.6 (CH_3), 111.1 (CH), 167.0 (C=O), 169.2 (C-quart).

16: retention time 7.7 s; ^{1}H NMR ($CDCl_3$, 90 MHz) δ 5.48 (br s, 1 H, CH), 3.62 (s, 3 H, CH_3), 3.07 (s, 2 H, CH_2), 2.74–2.13 (m, 4 H, $C_3{}'$ and $C_5{}'$), 2.03–1.72 (m, 2 H, $C_4{}'$); ^{13}C NMR ($CDCl_3$, 25 MHz) δ 23.4 ($C_4{}'$), 32.4 ($C_3{}'$), 35.0 ($C_5{}'$), 36.7 (CH_2), 51.6 (CH_3), 128.2 ($C_2{}'$), 136.4 ($C_1{}'$), 171.7 (C=O).

Trapping of the Ketenes 12 and 13 with Methanol. Pyrolyses of **5** were carried out at various temperatures with methanol as trapping agent as described above. The products were examined by analytical gas chromatography (Perkin-Elmer F-30 equipped with a Spectra Physics Autolab integrator with a SE 52 column at 80 °C initial temperature, initial time 8 min, programmed at 12 °C/min, final temperature 250 °C), GC–MS (Varian Aerograph 2700 with an SE 52 column coupled to a Varian MAT 711 mass spectrometer), and NMR spectroscopy (Bruker WH 90 and WH 400 instruments). Products were identified by comparison of retention times with authentic specimens, by peak enhancement method, and by ^{1}H NMR spectroscopy. The results of the three methods agreed within a 5% experimental error. At a pyrolysis temperature[9] of 600 °C there was obtained 29% **15** and 36% **16**. At 800 °C there was obtained 4% **15** and 34% **16** together with 1,3-cyclohexadiene (20%) and benzene (7%).

Cyclopentene-1-carboxaldehyde *p*-Toluenesulfonylhydrazone. Cyclopentene-1-carboxaldehyde (5.55 g, 59.09 mmol) was added to a solution of *p*-toluenesulfonylhydrazine (10.0 g, 63.3 mmol) in 200 mL of toluene. The hydrazone precipitated from the clear solution after 30 min at room temperature. After adding 20 mL of petroleum ether (bp 40–60 °C) the product was filtered and dried to give 13.78 g (95%) of colorless crystals: mp 164 °C; ^{1}H NMR ($(CH_3)_2SO$-d_6, 400 MHz) δ 1.8 (pentuplet, 2 H), 2.36 (s, 3 H), 2.5 (m, 4 H), 6.1 (m, 1 H, H–C(2)), 7.4 (d, 2 H, H-meta), 7.68 (d, 2 H, H-ortho), 7.72 (s, 1 H, CH=N), 11.1 (s, 1 H, NH); ^{13}C NMR ($(CH_3)_2SO$-d_6, 25.16 MHz) δ 20.9, 22.5, 30.1, 32.8, 127.1, 129.4, 136.2, 138.2, 140.4, 143.2, 145.2. Anal. Calcd for $C_{13}H_{16}N_2$: C, 59.07; H, 6.10; N, 10.60. Found: C, 58.88; H, 6.00; N, 10.63.

Formation and Pyrolysis of 1-Cyclopentenyldiazomethane (18). (i) The aforementioned *p*-toluenesulfonylhydrazone (0.5 g, 18.9 mmol) was dissolved in 500 mL of absolute EtOH. Sodium hydride (0.45 g, 18.75 mmol) was added with stirring. After stirring for 24 h the precipitated sodium salt was filtered under N_2 and

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dried in high vacuum at 50 °C for 10 h. 100 mg of salt was decomposed at 80 °C/10^{-4} torr and the resulting 1-cyclopentenyldiazomethane (**18**) condensed with Ar on the cold end of a vacuum cryostat at 14 K. **18** was identified by its UV (λ_{max} 478 nm) and IR (2040, 1620, 1390, 1365, 1285 cm^{-1}) spectra.

(ii) One gram of the sodium salt was decomposed by slowly increasing the temperature from 80 °C to 180 °C in the course of 4 h. The diazo compound so produced was led directly into the pyrolysis tube maintained at 500 °C/10^{-4} torr. The product, condensed in a liquid N_2 trap, was found by ^1H NMR spectroscopy to consists of 1,3-cyclohexadiene (40%) and benzene (10%).

Pyrolysis of 4-Cyclopentylidene-3-methylisoxazol-5-(4*H*)-one (21). **21**[6b] (200 mg, 1.21 mmol) was pyrolyzed at 800 °C/10^{-3} torr (sublimation temperature 85 °C). Analysis of the product by GC on two columns (SE 52 and SE 30) revealed the presence of a trace of dodecahydrotriphenylene (**20**). An authentic sample of **20** was available for comparison.

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Registry No. **5**, 3968-30-7; **5-D**, 96913-83-6; **11**, 96913-89-2; **12**, 96913-90-5; **13**, 96913-91-6; **14**, 96913-85-8; **14a**, 96913-86-9; **15**, 40203-73-4; **16**, 21622-07-1; **17**, 96913-84-7; **18**, 96913-88-1; **20**, 1610-39-5; **21**, 17975-64-3; cyclopentene-1-carboxaldehyde, 6140-65-4; tosylhydrazine, 1576-35-8; cyclopentene-1-carboxaldehyde *p*-toluenesulfonylhydrazone, 78632-40-3; cyclopentene-1-carboxaldehyde *p*-toluenesulfonylhydrazone sodium salt, 96913-87-0.

Adiabatic Photodehydroxylation of 9-Phenylxanthen-9-ol. Observation of Carbocation Fluorescence in Neutral Aqueous Solution

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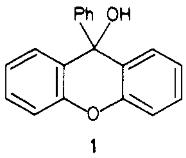
The photobehavior of the title compound (1) has been studied in aqueous solution and organic solvents. Evidence is presented that shows that 1 undergoes adiabatic photodehydroxylation in aqueous solution—it being the first example of a new class of adiabatic photochemical reactions. The reaction is not observed in CH_3CN and 95% EtOH. The photogenerated carbocation can be trapped by methanol in aqueous methanol solution. The photobehavior of 1 is interpreted as being due to the enhanced basicity (as measured by the ionization constant pK_{R^+}) of the molecule in S_1 relative to that of the ground state (S_0). It is postulated that the enhanced electron-donating effect of the ortho oxygen of 1 in the excited singlet state is responsible for this effect.

Previous studies from our laboratories[3-5] have demonstrated that certain carbocations may be readily photogenerated via protonation of excited-state aromatic alkenes, alkynes, and allenes in aqueous sulfuric acid, as shown in eq 1 for aromatic alkynes. A recent work[6] has also demonstrated that photochemical intramolecular proton transfer from a phenolic proton to aromatic alkyne can be a rapid process, leading to efficient hydration of the aromatic alkyne moiety. A review of these reactions summarizing the present understanding of these photoprotonation processes to carbon is now available.[7]

$$\mathrm{ArC{\equiv}CH} \xrightarrow[\mathrm{H^+}]{h\nu} \mathrm{Ar\overset{+}{C}{=}CH_2} \xrightarrow{\mathrm{H_2O}} \mathrm{ArC(OH){=}CH_2} \rightleftharpoons \mathrm{ArC({=}O){-}CH_3} \quad (1)$$

Not addressed in these studies is the question of adiabaticity of the photoprotonation (primary) step, i.e., whether the carbocation so generated is on the S_1 surface (adiabatic process) or is funneled down to the ground-state surface (diabatic process).[8] Since fluorescence emissions from carbocations were not observed under steady-state photolysis conditions at room temperature in these photoprotonation reactions, no direct evidence was available to suggest an adiabatic process. A number of excited-state prototropic reactions are known to be adiabatic.[9] However, these involve proton transfer to or from heteroatoms, usually resulting in no overall chemical change. Since the carbocations generated via photoprotonation of simple aromatic alkenes, alkynes, and allenes would be expected to be very short-lived in both S_0 and S_1, we decided to study a system where the corresponding cation would be at least structurally rigid enough to permit fluorescence emission to compete with other nonradiative modes. The xanthene structure provides such a rigid molecular backbone, and molecules possessing this backbone are known to be highly fluorescent, as exemplified by fluorescein (Φ_f = 0.9) and rhodamine B ($\Phi_f > 0.9$). We report here our study of a model system: the adiabatic photodehydroxylation of 9-phenylxanthen-9-ol (1), to generate



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a discrete triaryl carbocation intermediate in S_1. This system was chosen to test for the possibility of adiabatic carbocation formation in aqueous solution under neutral pH conditions. Although the triaryl carbocation so generated from 1 cannot be obtained via photoprotonation of any alkene, these results greatly extend our knowledge of the dynamics of photochemically generated carbocations in aqueous solution by uncovering a new class of adiabatic

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