Isopropenyl Acetoacetate and the Reaction of Diketene with Acetone[1a]

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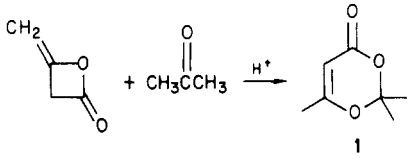
Received June 4, 1984

The acid-catalyzed reaction of diketene with acetone to form 2,2,6-trimethyl-4*H*-1,3-dioxin-4-one, when conducted by using acetone-d_6, yields a product with a high degree of deuterium scrambling. This scrambling is inconsistent with the intermediacy of either acetylketene or a 1,4-dipolar form of diketene in the reaction. Pathways involving isopropenyl acetoacetate or its protonated form are judged more compatible with the labeling results. Authentic isopropenyl acetoacetate was synthesized by using a retro-Diels–Alder route and was found to be converted to the title dioxinone under the diketene–acetone reaction conditions.

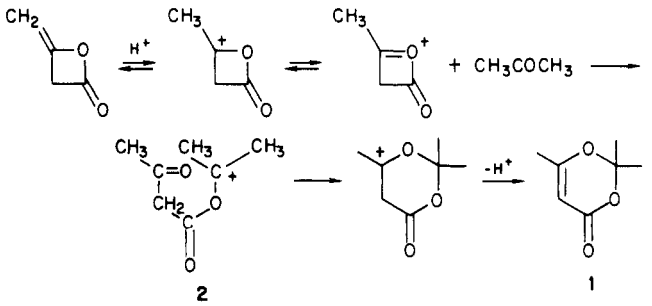
The acid-catalyzed reaction of diketene with acetone to form 2,2,6-trimethyl-4*H*-1,3-dioxin-4-one (**1**, "diketene–acetone adduct") was described by Carroll and Bader in the early 1950s.[1-3] After being largely ignored for over 2



1

decades, compound **1** is currently of considerable interest and has been shown to be a useful intermediate in synthesis.[4-12] In view of the increased activity in this field, we present some new information on the mechanism of the reaction of diketene with acetone.

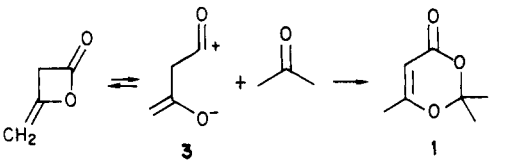
Carroll and Bader[2] pictured this process as proceeding via initial protonation of diketene followed by attack of the protonated diketene on the carbonyl goup of acetone; the resulting cation **2** would afford **1** after cyclization and proton loss.



2 **1**

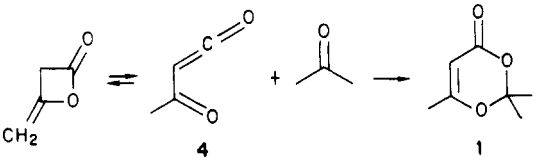
More recently Kato[13] has discussed this reaction in terms of a 1,4-addition of dipole **3** to the ketone carbonyl group.

A third mechanistic possibility involves the intermediacy of acetylketene **4** (proposed by Maujean and Chuche[14] in



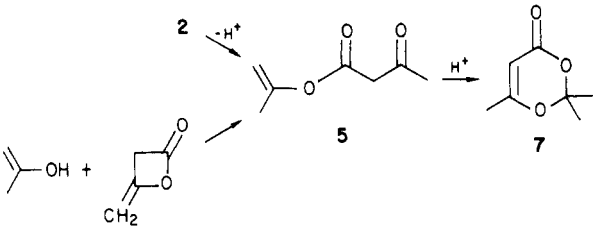
3 **1**

some base-catalyzed diketene reactions); ketene **4** could lead to **1** by a [4 + 2]-cycloaddition reaction.



4 **1**

Finally, we considered the discrete intermediacy of isopropenyl acetoacetate (**5**) the reaction. Produced either

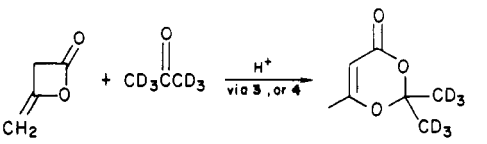


5 **7**

by proton loss from Bader's proposed cation **2** or by direct reaction of enolized acetone with diketene, **5** could easily cyclize to **1** under acidic conditions. However, isopropenyl acetoacetate has never been observed in acetone–diketene reactions.[2,15,16]

Results and Discussion

We considered that study of the reaction of diketene with acetone-d_6 might give useful mechanistic information. A cycloaddition reaction involving either dipole **3** or ketene **4** would result in a product with deuterium residing on the 2,2-dimethyl groups.



1-d_6

However, a reaction proceeding via cation **2** or isopropenyl acetoacetate (**5**) should incorporate some deuterium into the 6-methyl group. If we assume that there

(1) (a) Paper 19 in the series from these laboratories on "Ketenes". Preceding paper: Raynolds, P. W.; DeLoach, J. A. *J. Am. Chem. Soc.* **1984**, *106*, 4566. (b) Carroll, M. F.; Bader, A. R. *J. Am. Chem. Soc.* **1952**, *74*, 6305.

(2) Carroll, M. F.; Bader, A. R. *J. Am. Chem. Soc.* **1953**, *75*, 5400.

(3) Bader, A. R., Gutowsky, H. S.; Heesche, J. P., *J. Org. Chem.* **1956**, *21*, 821.

(4) Sato, M.; Ogasawara, H., Yoshizumi, E.; Kato, T. *Heterocycles* **1982**, *17*, 297.

(5) Sato, M.; Ogasawara, H.; Yoshizumi, E.; Kato, T. *Chem. Pharm. Bull.* **1983**, *31*, 1902.

(6) Sato, M.; Kanuma, N., Kato, T. *Chem. Pharm. Bull.* **1982**, *30*, 4359.

(7) Sato, M.; Kanuma, N.; Kato, T. *Chem. Pharm. Bull.* **1982**, *30*, 1315.

(8) Baldwin, S. W.; Wilkinson, J. M. *J. Am. Chem. Soc.* **1980**, *102*, 3634.

(9) Smith, A. B., III; Levenberg, P. A.; Jerris, P. J.; Scarborough, R. M.; Wovkulich, P. M. *J. Am. Chem. Soc.* **1981**, *103*, 1501.

(10) Boeckman, R. K., Jr.; Thomas, A. J. *J. Org. Chem.* **1982**, *47*, 2823.

(11) Jäger, G. *Chem. Ber.* **1972**, *105*, 137.

(12) Jäger, G.; Wenzelburger, J. *Liebigs Ann. Chem.* **1976**, 1689.

(13) Kato, T. *Acc. Chem. Res.* **1974**, *7*, 265.

(14) Maujean, A.; Chuche, J. *Tetrahedron Lett.* **1976**, 2905.

(15) Bal'yan and Shtangeev[16] reported formation of **5** from acetone and diketene in the presence of zinc chloride. The structure of their product was not rigorously established, and their procedure, in the present author's hands leads to formation of **1**.

(16) Bal'yan, K.; Shtangeev, A. *Zh. Obshch. Khim.* **1954**, *24*, 238.

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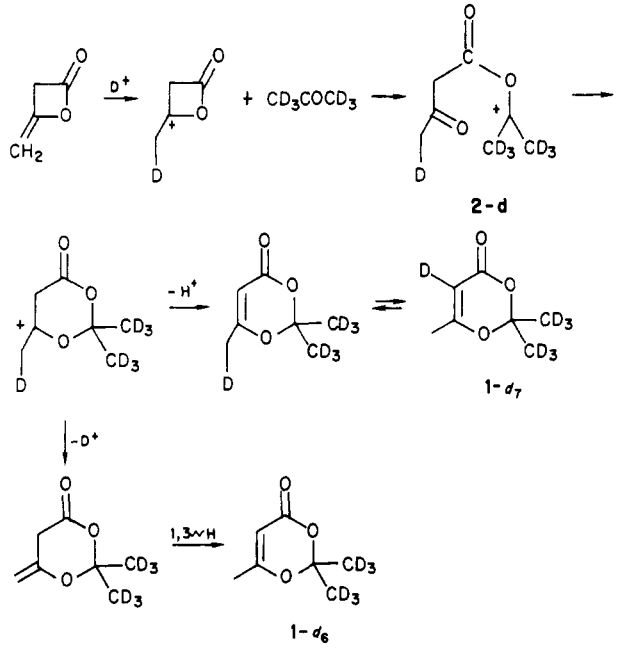
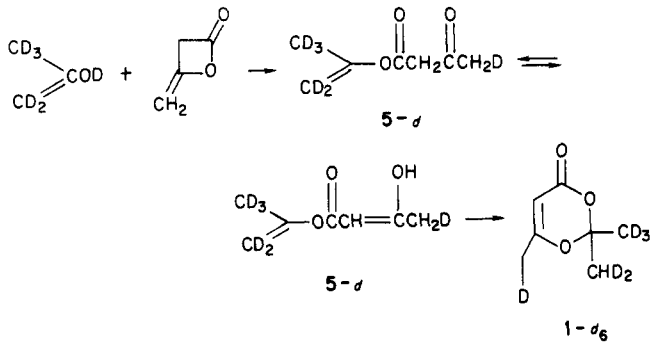
Scheme I



Scheme II



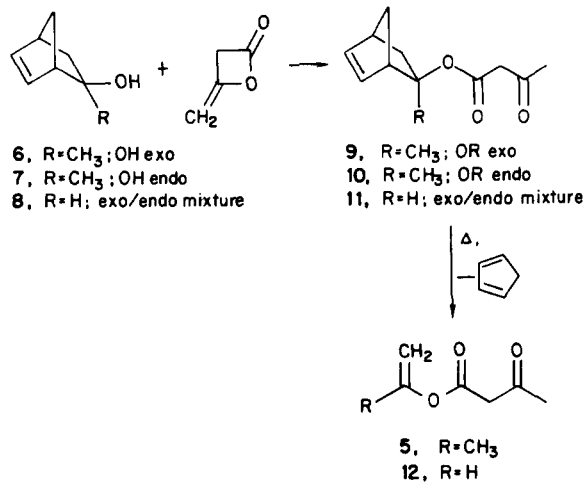
is rapid deuterium transfer between excess acetone-d_6 and *p*-toluenesulfonic acid catalyst, then the mechanism involving cation **2** leads to the prediction of considerable heptadeuterio product with the structure shown in Scheme I.

The reaction proceeding via intermediate **5** is shown in Scheme II. Johnson and Shiner[17] showed that the reaction of diketene with methanol-*d* gives, as the primary product, methyl acetoacetate-4-*d*; by analogy, acetone-d_6 enol and diketene should give isopropenyl acetoacetate, labeled as shown in the scheme. Intramolecular cyclization of labeled isopropenyl acetoacetate (**5**-*d*) would give diketene–acetone adduct bearing five deuteriums on the 2,2-dimethyls and one on the 6-methyl. Of course, the direct intermediacy of **5** would allow further intermolecular deuterium-scrambling reactions, and exchange processes with acetone-d_6 could lead to the formation of some d_7 product. But even these rather superficial mechanistic analyses leave one point clear: intermediacy of cation **2** or isopropenyl acetoacetate (**5**) should lead to a product carrying considerable deuterium on the 6-methyl group, whereas reaction of 1,4-dipole **3** and acetylketene (**4**) should not give such a product.

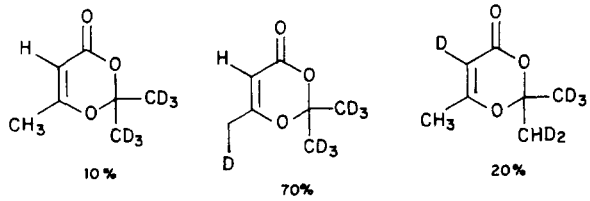
We have reacted diketene with acetone-d_6 in the presence of a trace of *p*-TsOH to provide labeled adduct **1**. Mass spectral analysis showed that the product was approximately 1% d_5, 80% d_6, 18% d_7, and 1% d_8.[18] Proton

(17) Johnson, J.; Shiner, V. *J. Am. Chem. Soc.* **1953**, *75*, 1350.

Scheme III



NMR analysis is consistent with the following distribution of d_6 products (ignoring d_5, d_7, and d_8 products).



Control experiments showed that deuterium scrambling did not occur before the reaction—i.e., diketene recovered from incomplete reactions was unlabeled. Scrambling also did not occur after the final step; i.e., unlabeled **1** did not undergo exchange with acetone-d_6/*p*-TsOH at reflux for 1 h and the NMR spectrum of labeled **1** did not change with extended reaction time.

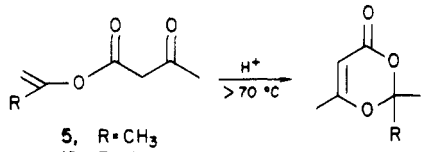
This result is clearly incompatible with pathways involving dipole **3** or ketene **4** and appears consistent with either Scheme I or II. The relatively low level of d_7 product and the preponderance of a product labeled on the 6-methyl supports Scheme II. We thought it worthwhile to futher test the plausibility of this route by independent synthesis and study of the chemistry of isopropenyl acetoacetate (**5**) under acidic conditions.

No examples of the acetoacetate esters of enols appear to have been reported previously. The retro-Diels–Alder route of Scheme III allowed preparation of isopropenyl acetoacetate (**5**) and vinyl acetoacetate (**12**). The known norbornenols **6**–**8** reacted with diketene to provide acetoacetates **9**–**11** which were subjected to vapor-phase pyrolysis in a quartz-packed tube at 575–625 °C (0.1 to 1.0 mmHg). Exit traps maintained at −20 °C and −78 °C collected the enol acetoacetate and cyclopentadiene, respectively. Vinyl acetoacetate (**12**) was obtained in 61% yield after redistillation. Isopropenyl acetoacetate (**5**) was produced in 48% yield from precursor **10**; the exo ester **9** gave a lower yield. The generally lower yields of isopropenyl acetoacetate (relative to vinyl acetoacetate) were not due to instability of the isopropenyl compound under the pyrolysis conditions; a competitive elimination to methyl norbornadiene, acetone, and CO_2 is the probable cause.[19] Acetone was identified in the −78 °C trap condensate.

(18) Probably because of the thermal lability of **1**, we have been unable to use EI mass spectrometry to observe useful fragmentations. The CI technique used gives only molecular ion peaks (see Experimental Section).

(19) Frissel, C.; Lawesson, S. *Arkiv. Khemi* **1961**, *17*, 401.

When isopropenyl acetoacetate (5) was heated to 70–79 °C in toluene containing a trace of *p*-TsOH, transformation



5, R = CH_3
12, R = H

1, R = CH_3
13, R = H

to acetone–diketene adduct (1) was rapid and essentially quantitative. This isomerization did not occur in the absence of acid catalyst nor was it seen in refluxing acetone–*p*-TsOH (bp 56 °C). If the usual 1:1 volume ratio of acetone and diketene is used, the temperature of a reacting acetone–diketene mixture rises from 70 °C initially to about 100 °C at the end of the reaction. To show that isopropenyl acetoacetate (5) could serve as a precursor to acetone–diketene adduct (1) under these conditions, a 1:1 molar mixture of 5 and diketene in excess acetone containing catalytic *p*-TsOH was heated under reflux and examined periodically by NMR. We observed that 1 was the sole product formed and that 5 was consumed about an order of magnitude faster than was diketene ($\tau_{1/2} \simeq$ 5 min vs. $\tau_{1/2} \simeq$ 45 min). The possibility that isopropenyl acetoacetate was not converted to acetone–diketene adduct (1) under these circumstances, but was instead decomposed to unobserved volatile products and acetone, was judged remote on the basis of the following experiments: When vinyl acetoacetate (12) was heated in toluene/*p*-TsOH (70–90 °C), dimethyldioxinone 13 was produced rapidly and cleanly. Like the isopropenyl ester 5, vinyl acetoacetate (12) did not cyclize in acetone–*p*-TsOH when refluxed. But when a mixture of vinyl acetoacetate and diketene in acetone–*p*-TsOH was refluxed, the starting materials were consumed and a mixture of dioxinones 1 and 13 was produced. Since vinyl acetoacetate cyclized under these conditions, it is reasonable that isopropenyl acetoacetate also cyclized when it was consumed in reacting acetone/diketene/*p*-TsOH.

Conclusions

The results presented above show that diketene and acetone-d_6 react under acid catalysis to produce acetone–diketene adduct (1) having a degree of deuterium scrambling inconsistent with the sole intermediacy of dipole 3 or ketene 4. The observed incorporation of protons into the *gem*-dimethyl group and of deuterons into the vinyl and methyl groups of adduct 1 can be accommodated by involving intermediate cation 2 or isopropenyl acetoacetate (5). Authentic isopropenyl acetoacetate, when subjected to the reaction conditions for synthesis of adduct 1, is converted to 1 at a rate much greater than that with which diketene and acetone are converted to 1. Thus isopropenyl acetoacetate and its protonated form 2 are credible intermediates in the reaction of diketene with acetone. Finally, Carroll and Bader reported that benzophenone did not react with diketene under acid catalysis to form a dioxinone.[2] This is, of course, consistent with the present results, since benzophenone cannot form an enol acetate.[20,21]

(20) Dehmlow and Shamout have used quanternary ammonium salts to catalyze diketene–ketone reactions and have prepared 2,2-diphenyl-6-methyl-4*H*-1,3-dioxin-4-one from benzophenone. However, the mechanism proposed for this salt-catalyzed process is quite different from those considered here.[21]

(21) Dehmlow, E.; Shamout, A. *Liebigs Ann. Chem.* **1982**, 1753.

Experimental Section

General Methods. Melting and boiling points are uncorrected. IR spectra were taken of neat samples on salt plates on a Perkin-Elmer Model 137 instrument. ^1H NMR spectra were obtained with Varian EM-360 and JEOLCO GX-400 spectrometers and are reported in ppm (δ) with tetramethylsilane as the internal standard. Mass spectra were recorded with a VG ZAB mass spectrometer in the field desorption (FD) or chemical ionization (CI, NH_3 atmosphere) modes.

2-Norbornen-5-yl Acetoacetate (11). A solution of 47.0 g of 2-norbornen-5-ol (exo/endo mixture) in 50 mL of toluene containing 0.3 g of pyridine was stirred at 20 °C and treated dropwise with 36.0 g of diketene. The mixture was stirred for 2 h after the initial exotherm subsided, the toluene was evaporated at reduced pressure, and the residue was distilled in vacuo to give 86.1 g (91%) of 11 as a colorless liquid: bp 92–97 °C (2 mm); IR 5.77, 5.85, 8.00 (br), 8.70, 8.99, 9.67, 13.85 μm; NMR ($CDCl_3$) δ 6.45 (m, 1 H), 6.04 (m, 1 H), 5.49 (m, 1 H), 3.45 (s, 2 H), 3.31–2.95 (br s, 2 H), 2.29 (s, 3 H), 2.2–0.75 (m, 4 H); mass spectrum (FD), *m/e* 194. Anal. Calcd: C, 68.0; H, 7.26; Found: C, 68.1; H, 7.21.

2-Methyl-5-norbornen-2-yl *exo*-Acetoacetate (9). A solution of 40.0 g of 2-methyl-5-norbornen-2-*exo*-ol[22] and 1.0 g of pyridine in 50 mL of toluene was stirred at 20 °C and treated dropwise with 27.1 g of diketene (exotherm to 50 °C). The mixture stood for 3 days at room temperature and then was distilled in vacuo to give 41.0 g (62%) of 9: bp 102–104 °C (2.7 mm); IR 5.78, 5.86, 9.07, 9.41, 10.61, 13.70 μm; NMR ($CDCl_3$) δ 6.22 (symmetrical m, 2 H), 3.46 (s, 2 H), 3.14 (br s, 1 H), 2.92 (br s, 1 H), 2.34 (s, 3 H), 1.61 (s, 3 H), 2.1–1.1 (m, 4 H); mass spectrum (FD), *m/e* 208. Anal. Calcd: C, 69.2; H, 7.75. Found: C, 69.2; H, 7.65.

2-Methyl-5-norbornen-2-yl *endo*-Acetoacetate (10). Reaction of 2-methyl-5-norbornen-*endo*-2-ol[22] with diketene as described above for the preparation of 11 produced an 84.6% yield of 10: bp 110–115 °C (2.5 mm); IR 5.85 (br), 8.00 (br), 9.00, 9.39, 13.85 (br) μm; NMR ($CDCl_3$) δ 6.10 (symmetrical, m, 2 H), 3.31 (s, 2 H), 3.25 (br s, 1 H), 2.83 (br s, 1 H), 2.22 (s, 3 H), 1.75 (s, 3 H), 2.0–1.4 (m, 4 H); mass spectrum (FD), *m/e* 208. Anal. Calcd: C, 69.2; H, 7.75. Found: C, 69.5; H, 7.88.

Isopropenyl Acetoacetate (5). An 18-in. quartz tube was packed with quartz chips and placed in a vertical electric furnance heated to 600 ± 20 °C. A pressure of 0.1–1.0 mm was maintained in the system and ester 9 or 10 (24 g) was added dropwise (1 h addition time) to the top of the tube. The tube exited to a vacuum system via two traps. The first was cooled to ca. −20 °C (CCl_4–dry ice), the second was at −78 °C (acetone–dry ice). The −20 °C trap collected 8.4 g of crude 5 as a dark liquid of ca. 90% purity (NMR); the second trap contained largely cyclopentadiene and acetone. Distillation of the crude product gave 8.0 g (48%) of 5 as a colorless liquid: bp 47–53 °C (1.5 mm); IR 5.67, 5.84, 6.02, 7.10, 7.39, 7.64, 8.22, 8.80, 9.70, 11.40 μm; NMR ($CDCl_3$) δ 4.80 (s, 2 H), 3.61 (s, 2 H), 2.33 (s, 3 H), 2.01 (s, 3 H); mass spectrum (FD), *m/e* 142. Anal. Calcd: C, 59.1; H, 7.09. Found: C, 59.1; H, 6.75.

Vinyl Acetoacetate (12). The procedure was that described for 5 above. Pyrolysis of 32.5 g of ester 11 gave, after distillation, 13.1 g (61%) of pure 12: bp 45–50 °C (1.00 mm); IR 5.65, 5.72, 6.01, 7.08, 7.31, 7.60, 8.70, 10.45, 11.27 μm; NMR ($CDCl_3$) δ 7.30 (four lines, apparent J = 7.5, 1 H), 5.10 (two lines, apparent J = 2, 1 H), 4.70 (six lines, apparent J = 2, 7.5, 1 H), 3.58 (s, 2 H), 2.33 (s, 3 H). Anal. Calcd: C, 56.24; H, 6.29. Found: C, 56.01; H, 6.24.

Reaction of Diketene with Acetone-d_6. A mixture of 10 mL of diketene, 10 mL of acetone-d_6 (99.8%), and 0.05 g of *p*-TsOH was stirred under reflux for 3 h.[2] The mixture was relieved of excess acetone on a rotary evaporator, and the residual labeled 1 was purified by Kugelrohr distillation; 50–75 °C (1.0 mm): IR 4.31, 5.80, 6.15, 7.21, 7.43, 8.42, 9.33, 10.62 μm; mass spectrum (chemical ionization, NH_3 vapor) (relative intensity) [(M + 1) peaks are observed under these conditions, unlabeled 1 gave *m/e* 143], 148 (d_5, 1), 149 (d_6, 80), 150 (d_7, 15), 151 (d_8, 1); NMR ($CDCl_3$) δ 5.21 (s, vinyl H, 0.83 H), 2.02 (s, allyl CH_3, 2.27 H), 1.74 (br s, *gem*-dimethyl, 0.90 H).

Cyclization of Isopropenyl Acetoacetate to 1. A. In Toluene-d_8. A solution of 0.15 g of isopropenyl acetoacetate (5)

(22) Brown, H. C.; Peters, E. *J. Am. Chem. Soc.* **1975**, *97*, 7442.

in 3 mL of toluene-d_8 was treated with a trace (ca. 0.005 g) of *p*-TsOH and heated to 70–90 °C (steam bath) for 1 h. NMR analysis showed loss of **5** and formation of **1** to be complete. Evaporation of solvent and IR analysis confirmed the product structure as **1**.

B. Under Acetone–Diketene Reaction Conditions. A mixture of 3.0 g of acetone, 1.30 g of diketene, 2.15 g of isopropenyl acetoacetate (**5**), and 0.05 g of *p*-TsOH was heated under reflux and monitored by NMR (aliquots were added to $CDCl_3$ containing benzene as internal standard). Compound **5** disappeared with $t_{1/2}$ = 5 min; dioxinone **1** was the only product observed. After 45 min, conversion of **5** to **1** was complete, and conversion of diketene to **1** was about half complete. After 4 h, **1** and acetone were the only components observable in the reaction mixture.

Cyclization of Vinyl Acetoacetate 12 to Dioxinone 13. A. In Toluene. To a solution of 0.01 g of *p*-TsOH in 50 mL of dry toluene was added 1 g of vinyl acetoacetate (**12**). After 10 min at reflux, NMR analysis showed about 75% conversion to **13**. The mixture was refluxed for another 15 min, let stand at 22 °C overnight, stripped of solvent at reduced pressure, and distilled to give 0.73 g (73%) of 2,6-dimethyl-4*H*-1,3-dioxin-4-one (**13**): bp 60–65 °C (2 mm); IR 5.75, 6.10, 7.20, 7.42, 8.10, 8.61, 9.00, 10.4 (br), 11.45, 12.20 μm; NMR ($CDCl_3$) δ 5.70 (q, *J* = 5, 1 H), 5.34 (s, 1 H), 2.07 (s, 3 H), 1.70 (d, *J* = 5, 3 H); mass spectrum (EI), *m/e* (relative intensity) 128, 85, 43 (100). Anal. Calcd: C, 56.2; H, 6.29. Found: C, 56.4; H, 6.45.

B. Under Acetone–Diketene Reaction Conditions. A mixture of 3 g of acetone, 3 g of diketene, 1.5 g of vinyl ester **12**, and 0.01 g of *p*-TsOH was heated under reflux for 2 h. NMR analysis showed complete consumption of diketene and **12**; dioxinones **13** and **1** and acetone were the only components detectable.

Registry No. **1**, 5394-63-8; **1**-d_6, 93304-62-2; **5**, 93304-66-6; **6**, 3212-13-3; **7**, 3212-14-4; *exo*-**8**, 2890-98-4; *endo*-**8**, 694-97-3; **9**, 93304-64-4; **10**, 93304-65-5; *exo*-**11**, 93304-63-3; *endo*-**11**, 93304-67-7; **12**, 2424-97-7; **13**, 49586-51-8; acetone, 67-64-1; diketene, 674-82-8; acetone-d_6, 666-52-4.

Thermal Decomposition of 2,2,6-Trimethyl-4*H*-1,3-dioxin-4-one and 1-Ethoxybutyn-3-one. Acetylketene[1a]

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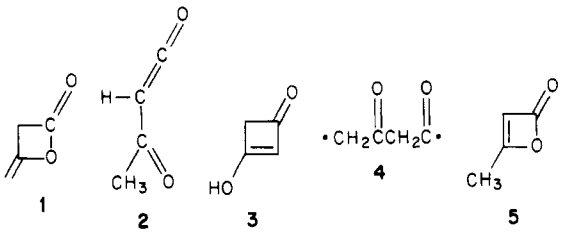
Received June 4, 1984

Acetylketene was first mentioned in the literature in 1907, but only in recent years has evidence for the existence of this species appeared. Previous work has indicated that acetylketene may be generated by pyrolysis of the title dioxinone, and we now present further chemical evidence in support of its presence. In particular, ethoxyacetylenes are known to generate ketenes upon pyrolysis. When the title alkyne was heated, it provided an intermediate that in six different trapping experiments gave the same products as those obtained via pyrolysis of the dioxinone. Acetylketene chemistry is predominated by [4 + 2]-cycloaddition reactions; no evidence for conversion to β-crotonolactone or diketene was seen.

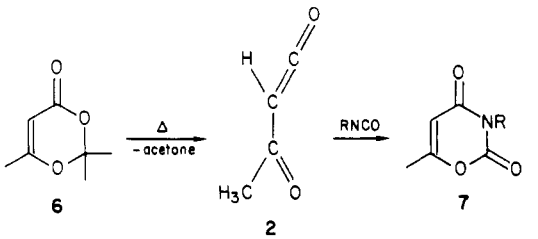
The dimer of ketene (diketene, **1**) has an unusual history. This four-carbon compound, which has been known for more than 40 years, was widely used in both laboratory research and in industrial production before its structure was unequivocally established and accepted by the scientific community.

After isolating diketene in 1907, Wilsmore observed that it reacted with nucleophiles to give derivatives of acetoacetic acid; he concluded that the acetylketene structure (**2**) was consistent with the reactivity observed for diketene.[1,2] In the decades that followed, other workers proposed that diketene was enolized 1,3-cyclobutanedione (**3**),[3] diradical **4**,[4] and β-crotonolactone (**5**).[5] The currently accepted 3-methylene-2-oxetanone structure (**1**) was proposed in 1940,[6] but it was not generally accepted until 1950.[7]



The acetylketene structure for the ketene dimer was still used in the 1940s,[8] but after the close of the diketene structure controversy, this interesting acylketene was not investigated for several decades.

In 1976 Jäger and Wenzelburger[9] reported the formation of 1,3-oxazine derivatives (e.g., **7**) from reaction of 2,2,6-trimethyl-4*H*-1,3-dioxin-4-one ("diketene–acetone adduct", **6**)[10] with cyanates, cyanamides, and isocyanates. It was



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