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.

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# 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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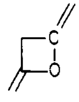
Acetylketene was first mentioned in the literature in 1907, but only in recent years has evidence for the existence of this species appeared. Previous work has indicated that acetylketene may be generated by pyrolysis of the title dioxinone, and we now present further chemical evidence in support of 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]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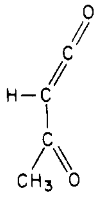
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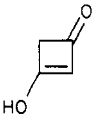
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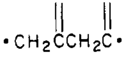
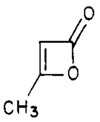
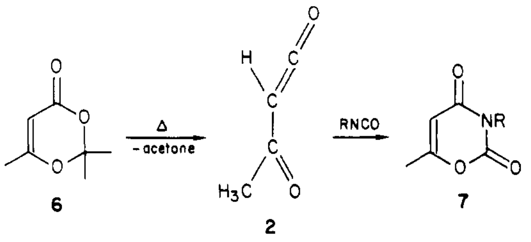

$$\cdot CH_2\overset{O}{\overset{\|}{C}}CH_2\overset{O}{\overset{\|}{C}}\cdot$$
4


5

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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[1] (a) Paper 20 in the series on "Ketenes" from this laboratory. Paper 19: Hyatt, J. A. *J. Org. Chem.*, preceding paper in this issue. (b) Stewart, A.; Wilsmore, N. *Nature London* **1907**, *75*, 510. (c) Wilsmore, N. *J. Chem. Soc.* **1907**, *91*, 1938. (d) Wilsmore, N. *Proc. Chem. Soc.* **1907**, *23*, 229.

[2] (a) Chick, F.; Wilsmore, N. *J. Chem. Soc.* **1908**, *93*, 946. (b) Chick, F.; Wilsmore, N. *Proc. Chem. Soc.* **1908**, *24*, 100.

[3] Staudinger, H.; Bereya, S. *Chem. Ber.* **1909**, *42*, 4908.

[4] (a) Chick, F.; Wilsmore, N. *Proc. Chem. Soc.* **1910**, *26*, 217. (b) Chick, F.; Wilsmore, N. *J. Chem. Soc.* **1910**, *97*, 1978.

[5] Hurd, C.; Williams, J. *J. Am. Chem. Soc.* **1936**, *58*, 962.

[6] Boese, A. *Ind. Eng. Chem.* **1940**, *32*, 16. Boese credits A. L. Wilson (Mellon Institute for Industrial Research) with first suggesting this structure for diketene.

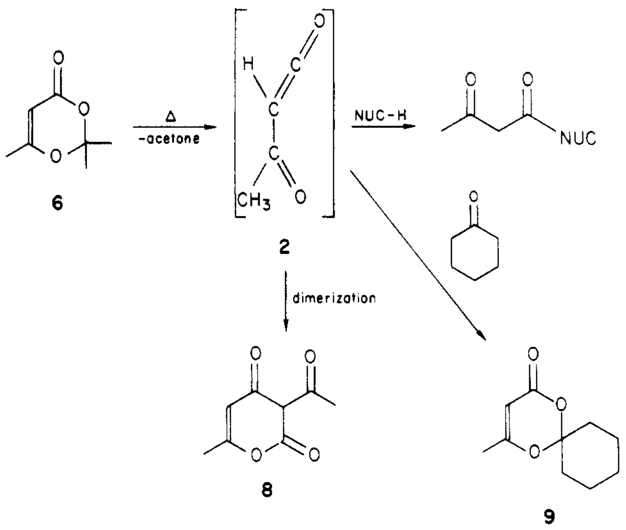
[7] Hurd, C.; Blanchard, C. *J. Am. Chem. Soc.* **1950**, *72*, 1461.

[8] (a) Hurd, C.; Kelso, C. *J. Am. Chem. Soc.* **1940**, *62*, 1548. (b) Calvin, M.; Magel, T.; Hurd, C. *J. Am. Chem. Soc.* **1941**, *63*, 2174.

[9] Jäger, G.; Wenzelburger, J. *Leibigs Ann. Chem.* **1976**, 1689.

0022-3263/84/1949-5105$01.50/0

Scheme I



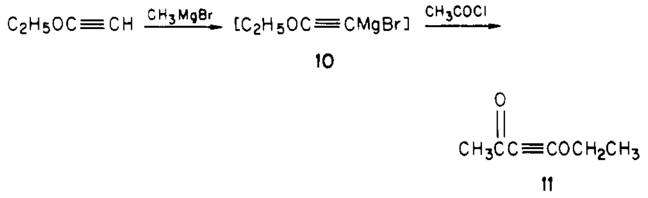
suggested that these reactions might proceed via acetylketene (2) generated by retro-Diels–Alder fragmentation of 6. In 1982 Kato et al.[11a] used diketene–acetone adduct (6) to prepare *N*-acylacetoacetamides, and in 1983 these workers reported the observation of a weak IR absorption band at 2150 cm$^{-1}$ during the gas-phase pyrolysis of adduct 6. This IR absorption was assigned to acetylketene (2).[11b] Other groups have recently implicated acetylketene in amine-catalyzed reactions of diketene[12] and in base-catalyzed decomposition of 6-methyl-4-oxo-2-thio-2,3-dihydro-4*H*-1,3-oxazine.[13] In view of the resurgence of interest in both acetylketene and diketene–acetone adduct (6),[14] we present here some new observations on the chemistry of these materials.

## Results and Discussion

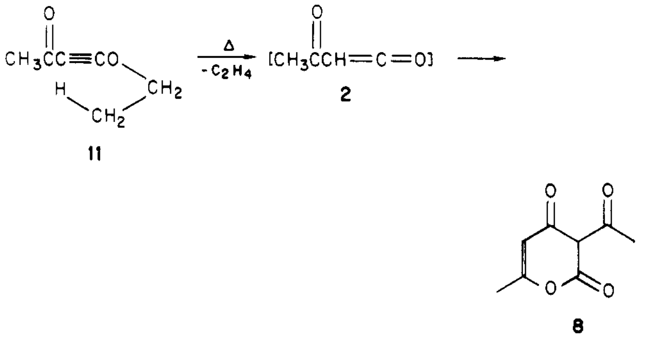
Carroll and Bader[10] described the formation of acetoacetate derivatives upon acid- or base-catalyzed reactions of 6 with nucleophiles. We obtained equally good or better product yields when the reactions were conducted in the absence of catalyst and at temperatures exceeding 100 °C.[15] Furthermore, we found that uncatalyzed pyrolysis of 6 gave dehydroacetic acid (8) in nearly quantitative yield;[16] this product can be viewed as a Diels–Alder dimer of acetylketene (2). Also, the spiro compound 9 was formed when 6 was heated with cyclohexanone (Scheme I). These observations, like those of Jäger, can be rationalized in terms of acetylketene (2) as an intermediate, and we endeavored to directly observe the formation of acetylketene from 6.

Dioxinone 6 was subjected to flash vacuum pyrolysis[17] at temperatures above 200 °C and the pyrolysate was trapped at −78 °C. Examination of the pyrolysate by IR and NMR failed to indicate the presence of a ketene; nor were diketene, β-crotonolactone, propyne, or allene seen. Acetone and dimer 8 (70–80% yield after crystallization),

Scheme II



Scheme III



along with a trace of 2,6-dimethyl-4-pyrone (1–5% yield), were the only products found.[18] Similarly, when 6 was heated above 100 °C in toluene-$d_8$ in a sealed NMR tube, loss of 6 and appearance of acetone and 8 were observed, but no absorptions attributable to 2 appeared. Attempts to observe 2 by using Fourier transform infrared analyses of decomposing 6 in the gas, solution, and neat liquid phases also failed. We were thus unable to reproduce the observation of the 2150-cm$^{-1}$ IR band reported by Kato and co-workers[11] for decomposing gas-phase 6. It appeared from these studies that ketene 2 either is not formed in large amounts from 6 or has an extremely short lifetime under our experimental conditions.

After failing to observe acetylketene (2) by spectroscopic means, we sought further chemical evidence which could imply or deny its intermediacy in reactions of 6.[19] An alternative, unambiguous synthesis of 2 and comparison of its reactivity with that of 6 seemed desirable. To avoid the possible effects of acidic or basic catalysts in subsequent reactions of acetylketene,[20] we applied Arens' procedure for the thermal fragmentation of ethoxyacetylenes[21] to the preparation of 2. Ethoxyacetylene was converted to the Grignard reagent 10 by reaction with methylmagnesium bromide in tetrahydrofuran. Reagent 10 was cooled to −78 °C and added to a slight excess of acetyl chloride; workup gave 1-ethoxybutyn-3-one (11) in 32% yield (Scheme II).

Compound 11 was an unstable lachrymatory oil that could be stored for several weeks at 0 °C. When a solution of 11 in $CCl_4$ was heated at 90 °C in a sealed NMR tube, the formation of ethylene and dehydroacetic acid (8) was

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

(11) (a) Sato, M.; Kanuwa, N.; Kato, T. *Chem. Pharm. Bull.* **1982**, *30*, 1315. (b) Sato, M.; Ogasawa, H.; Yoshizumi, E.; Kato, T. *Chem. Pharm. Bull.* **1983**, *31*, 1902.

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

(13) Sasaki, T.; Ito, E.; Asai, K. *Heterocycles* **1983**, *20*, 1089.

(14) Hyatt, J. *J. Org. Chem.*, preceding paper in this issue and references cited therein.

(15) For a detailed survey of the uncatalyzed chemistry of 6 see: Clemens, R.; Hyatt, J. *J. Org. Chem.*, submitted for publication.

(16) Clemens, R. J. U.S. Pat. Appl. 487396 (1983).

(17) Wiersum, U. *Recl. Trav. Chim. Pays-Bas* **1982**, *101*, 317.

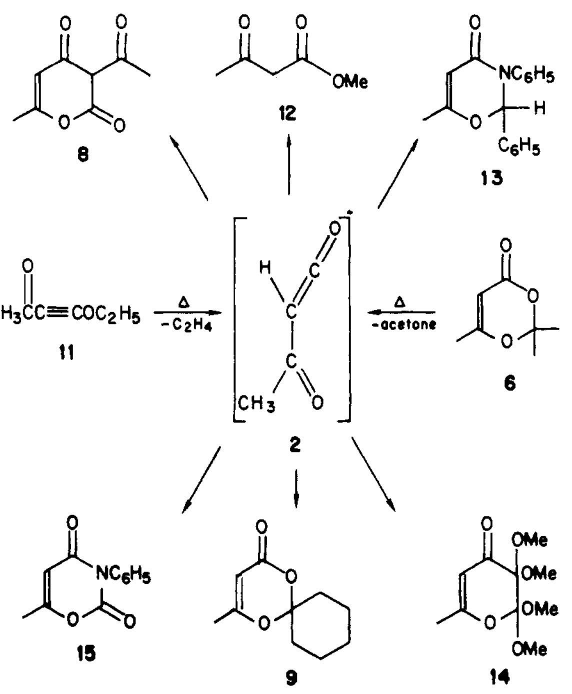
(18) The mechanism by which this pyrone is formed has not been established. One possible route would involve isomerization of 2 to 5, followed by scission to $CO_2$ and propyne; cycloaddition of 2 with propyne could give the pyrone. However, we failed to detect 5 or propyne and furthermore found that 6 did not react with 1-octyne in refluxing xylene. Thus we regard this route unlikely. An alternate process involving cycloaddition of 2 to enolized acetone, followed by dehydration, seems possible.

(19) Kato et al.[11] reacted acetoacetyl chloride with triethylamine to generate 2. When conducted in the presence of benzylidinepropylamine, this reaction gave product ratios and byproduct structures different from those obtained from 6 and benzylidinepropylamine. This result may be due to catalysis by triethylamine or triethylammonium chloride.

(20) Luche, J. L.; Kagan, H. *Bull. Soc. Chim. Fr.* **1968**, 2450.

(21) (a) Nieuwenhuis, J.; Arens, J. *Recl. Trav. Chim. Pays-Bas* **1958**, *77*, 761. (b) Ward, R. S. In "The Chemistry of Ketenes, Allenes, and Related Compounds"; Patai, S., Ed.; Wiley: London, 1980; p 237.

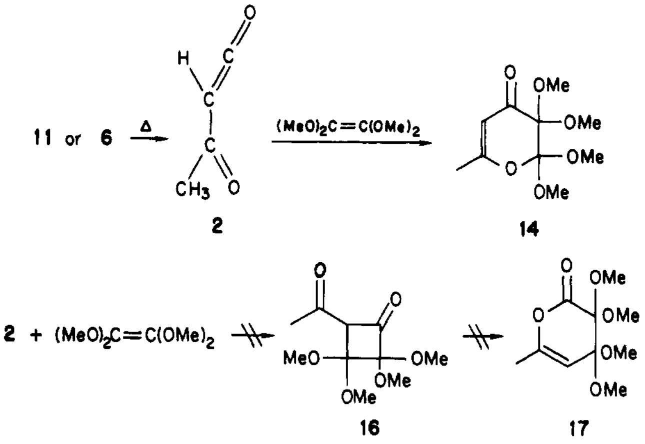
Scheme IV



observed (Scheme III). As with dioxinone **6**, no direct observation of acetylketene was made by NMR or IR methods during pyrolysis of ethoxyacetylene **11**. However, the formation of ethylene and dehydroacetic acid (**8**) from **11** was strongly indicative that the fragmentation of **11** was occurring as expected to give acetylketene. Also, the acetylketene generated from **11** showed reactivity similar to that of the reactive intermediate generated from pyrolysis of dioxinone **6**.

We next examined the thermal decomposition of acetylene **11** in the presence of several trapping agents. When **11** was heated to 90 °C in the presence of methyl alcohol, methyl acetoacetate (**12**) was formed, whereas in the presence of *N*-benzylidineaniline, oxazine **13** was formed. When **11** was heated with tetramethoxyethylene, pyrone **14** was obtained (vide infra). Cyclohexanone and phenyl isocyanate reacted with **11** to give heterocycles **9** and **15**, respectively. Products **8**, **12**, **13**, **9**, and **15** were previously known; the structure of **14** rests on spectroscopic data. Yields ranged from 14% to 77%; dehydroacetic acid (**8**) was often a byproduct and some polymerization of **11** usually occurred. When dioxinone **6** was reacted instead of acetylene **11** (a slightly higher temperature was required to give convenient reaction rates), *the same products were obtained in every case.* Yields were generally higher in the reactions that started with diketene–acetone adduct (**6**), as **6** did not have the same propensity as **11** toward polymerization, but in no case was a difference in product structure observed (Scheme IV).

The formation of pyrone **14** deserves comment. Reaction of either dioxinone **6** or alkyne **11** with tetramethoxyethylene gave as the major isolable product a liquid with the formula $C_{10}H_{16}O_6$. The cyclobutanone structure **16** was ruled out by both IR and NMR evidence (see Experimental Section), which were more consistent with the structure **14**. The $^{13}C$ NMR spectrum was in general agreement with compound **14**, but the lowest field resonance at $\delta$ 169.0 was higher than expected for the ketone carbonyl C-4 of **14**. We therefore considered the alternative structure **17** for the tetramethoxyethylene product; compound **17** could have arisen through ring expansion of cyclobutanone **16**. However, the UV spectrum of compound **14** had $\lambda_{max}^{EtOH}$ 240 nm ($\epsilon$ 10 000). This value is consistent with the presence of a $\beta$-alkoxy enone chromophore, such as in compound **6** ($\lambda_{max}^{EtOH}$ 247 nm ($\epsilon$ 8300)) or 2,6-dimethyl-2,3-dihydro-pyranone ($\lambda_{max}^{EtOH}$ 263 nm ($\epsilon$ 7000)), but not with the presence of enol lactone formulation **17** (compare with isopropenyl acetate, $\lambda_{max}^{EtOH}$ 208 nm ($\epsilon$ 800), or $\alpha$-angelicalactone, $\lambda_{max}^{EtOH}$ 217 nm ($\epsilon$ 370)). Furthermore, the EI mass spectrum of **14** showed a fragmentation to give *m/e* 142 (M − 90), which corresponds to a loss of dimethyl carbonate inconsistent with structure **17**.



The consistent formation of identical products from such disparate starting materials as **6** and **11** suggests a high probability that a common intermediate is involved, and the well-established generation of ketenes from ethoxyacetylene pyrolysis[21,22] makes the intermediacy of acetylketene (**2**) very plausible. Our results therefore support Jäger's original mechanistic suggestion[9] and point out some interesting properties of **2**. The failure to directly observe **2** in the flash vacuum pyrolysis experiments indicates that **2** is highly reactive and can dimerize to dehydroacetic acid (**8**) even at a low temperature. Furthermore, the rarity of cyclobutanone products in the chemistry of **2** is surprising. [2 + 2]-Cycloaddition to form cyclobutanones is a characteristic reaction of ketenes,[23] but this tendency is apparently overridden by the availability of [4 + 2]-cycloaddition pathways for **2**.[24,25] We have seen no evidence that **2** either isomerizes to the as-yet-unreported $\beta$-crotonolactone (**5**) or reverts to diketene **1**. And although Wilsmore's 1907 postulate of structure **2** for diketene was erroneous, it is interesting to note that the most facile route to **2** proceeds via diketene and its acetone adduct **6**. Further studies on the chemistry of these substances are under way, and results will be reported.

## Experimental Section

**General Methods.** Melting points were obtained with a Thomas-Hoover apparatus and are uncorrected. Infrared spectra were recorded from Perkin-Elmer Model 137 and Digilab FTS-14 B/D instruments. $^1H$ NMR spectra were recorded by using Varian EM-360 and JEOLCO GX-400 spectrometers; $^{13}C$ NMR spectra were recorded from Varian CFT-20 and JEOLCO GX-400 in-

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(22) For further examples of ketene generation from ethoxyacetylenes, see: (a) VanLeusen, A.; Arens, J. *Recl. Trav. Chim. Pays-Bas* **1959**, *78*, 551. (b) Shchukouskaya, L.; Pal'chik, R. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1964**, 2228. (c) Ruden, R. *J. Org. Chem.* **1974**, *39*, 3607. (d) Mazerolles, P.; Laporterie, A.; Lesbre, M. *Compt. Rend. C* **1969**, *268*, 361.

(23) Brady, W. T. In "The Chemistry of Ketenes, Allenes, and Related Compounds"; Patai, S., Ed.; Wiley: London, 1980; pp 279–297.

(24) Kato et al.[11] obtained an azetidinone in 4% yield from a reaction of **6** with *N*-benzylidine-*tert*-butylamine, but it seems possible that this material arose by rearrangement of an oxazine primary product.

(25) Some examples of non-[2 + 2]-cycloadditions have been reported for vinyl ketenes: Danheiser, R.; Sard, H. *J. Org. Chem.* **1980**, *45*, 4812.

struments. Mass spectra were recorded with a VG ZAB mass spectrometer in the field desorption and electron impact modes.

**1-Ethoxybutyn-3-one (11).** A solution of 26 mL of 2.85 M methyl magnesium bromide (0.077 mol) in dry tetrahydrofuran (25 mL) was added under argon to a 0 °C solution of 4.0 g (0.057 mol) of ethoxyacetylene in 25 mL of dry tetrahydrofuran. After the mixture was stirred for 1 h at 0 °C, it was allowed to warm to 20 °C for 4 h and then was cooled to −78 °C. This Grignard solution was then added via cannula to a −78 °C solution of 11.85 g (0.148 mol) of acetyl chloride in 100 mL of tetrahydrofuran. The red-brown reaction mixture was allowed to warm to 25 °C over 2 h and was then poured into 300 mL of saturated aqueous $NaHCO_3$. The dark organic phase was removed and the aqueous phase was extracted with ether (4 × 50 mL). The combined organic phases were dried ($Na_2SO_4$) and stripped of solvent in vacuo. The residue was distilled in vacuo and crude product was obtained at 52–62 °C (2.0 mmHg). The yellow product was twice distilled to give 2.04 g (32%) of 11: bp 54–56 °C (2.2 mmHg); IR (neat) 2227, 1664, 1095, 965, 823, 806 $cm^{-1}$; NMR ($CCl_4$) $\delta$ 4.41 (q, $J = 7$, 2 H), 2.34 (s, 3 H), 1.44 (t, $J = 7$, 3 H). Satisfactory combustion analysis was not obtained for this unstable material. The EI mass spectrum showed $m/e$ (relative intensity) 112.0515 (12; calcd for $C_6H_8O_2$ 112.0522), 97 (55), 84 (20), 69 (60), 43 (100).

**Dehydroacetic Acid (8).** A solution of 0.345 g (3.08 mmol) of alkyne 11 in ~0.5 mL of $CCl_4$ was sealed in an NMR tube and heated at 90–95 °C. After 1 h, NMR analysis showed loss of 11 and formation of ethylene ($\delta$ 5.39) and 8 as the major products. The tube was cooled and opened, and the contents were extracted with saturated aqueous $Na_2CO_3$. The organic phase was dried and evaporated to leave 0.06 g of neutral material, which was not investigated. The aqueous phase was acidified (10% HCl) and extracted with ether. The extract was dried and the solvent was removed in vacuo to give crude 8, which was recrystallized from alcohol: yield 0.21 g (77%); mp, IR and NMR spectra were identical with those of a commercial sample.

Compound 8 was also obtained when acetone–diketone adduct (6, 14.2 g, 0.1 mol) was heated for 45 min in 20 mL of refluxing xylene while acetone was being removed. The mixture was poured into 50 mL of ethanol and cooled, and the resulting precipitate was collected by filtration to afford a 93% yield of dehydroacetic acid.

**Methyl Acetoacetate (12).** A mixture of 0.14 g (1.25 mmol) of alkyne 11, 0.11 g (3.4 mmol) of methanol, and 0.5 mL of $CCl_4$ was heated in a sealed NMR tube at 90 °C for 2 h. NMR analysis disclosed the presence of methyl acetoacetate (yield, ca. 60%) and ethylene in addition to some 8 and residual 11. The reaction mixture was subjected to preparative TLC (SiGel, 1:1 ether:hexane elution); 0.020 g (14%) of 12 was obtained and identified by IR and NMR. (The low isolated yield of 12 is probably due to losses during TLC isolation.) Compound 12 was also obtained in 72% yield from 6 and methanol at 110–120 °C; the product was isolated by distillation.

**3,4-Dihydro-6-methyl-2,3-diphenyl-2*H*-1,3-oxazin-4-one (13).** A mixture of 0.123 g of 11 (1.1 mmol), 0.20 g (1.1 mmol) of *N*-benzylidineaniline, and 1.5 mL of $CCl_4$ was heated at 90–95 °C for 1.5 h. The crude reaction mixture was subjected to preparative TLC (6:4 ether:hexane) to give a product (0.067 g, 24%) identical (IR, NMR, TLC) with authentic **13** prepared from **6** and *N*-benzylidineaniline (refluxing xylene, 34% yield).[11]

**4-Methyl-1,5-dioxaspiro[5.5]undec-3-en-2-one (9).** A solution of 14.2 g (0.1 mol) of acetone–diketene adduct (**6**) and 10.8 g (0.1 mmol) of cyclohexanone in 10 mL of xylene was heated at 130 °C for 1 h and volatiles were allowed to distill out.[26] The crude product was distilled (0.2 torr, bp 107–110 °C) to afford 18.1 g (94%) of a pale yellow liquid identical (IR, NMR, TLC) with sample prepared by the method of Dehmlow and Shamout.[27] Compound **9** was also obtained from alkyne **11** and cyclohexanone ($CCl_4$, 90–100 °C, 4 h, TLC workup, 51% yield).

**3-Phenyl-3,4-dihydro-6-methyl-2*H*-1,3-oxazine-2,4-dione (15).** A mixture of 0.21 g of acetylene **11** (1.9 mmol), 0.41 g of phenyl isocyanate (3.4 mmol), and 1.0 mL of $CCl_4$ was heated in a sealed tube at 90–95 °C for 2 h. The tube was cooled and opened, and the reaction mixture was diluted with ether. After the mixture stood overnight in a −10 °C freezer, crystals of **15** were deposited. Filtration gave 0.16 g (41%) of **15** as a tan solid identical by IR, NMR, and TLC with a sample prepared from **6** (56%) by the method of Jäger.[9] A sample of **15** recrystallized from $CHCl_3$ had a melting point of 161–161.5 °C (lit.[9] mp 169–170 °C). Our sample of **15** prepared according to ref 9 also had a melting point of 161–161.5 °C. Anal. Calcd for $C_{11}H_9NO_3$: C, 65.0; H, 4.46; N, 6.89. Found: C, 64.9; H, 4.40; N, 6.74.

**2,3-Dihydro-2,2,3,3-tetramethoxy-6-methyl-4*H*-pyran-4-one (14).** A mixture of 2.0 g of tetramethoxyethylene[28] (0.014 mol), 2.15 g of **6** (0.015 mol), and 15 mL of xylene was heated to reflux for 40 min, the solvent was removed in vacuo, and the residue was subjected to flash-column chromatography (SiGel, 10% acetone in hexane elution). A colorless liquid **14** was obtained (1.18 g, 38%): IR (film) 1709, 1656, 1439, 1389, 1261, 1087, 909, 775 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 4.41 (q, $J = 1.5$, 1 H), 3.81 (s, 3 H), 3.60 (s, 3 H), 3.54 (s, 3 H), 3.48 (s, 3 H), 2.35 (t, $J = 1.5$, 3 H); $^{13}C$ NMR ($CDCl_3$) $\delta$ 169.0, 165.2, 121.5, 105.4, 83.1, 57.6, 52.7, 51.0, 49.8, 14.4; mass spectrum, $m/e$ (relative intensity) 232 ($M^+$, 22), 201 ($M - OCH_3$, 100), 185 ($M - OCH_3 - O$, 14), 142 ($M - (CH_3O-)_2 - CO$, 74), 127 (40), 75 (55), 43 (25); UV spectrum $\lambda_{max}^{EtOH}$ 240 ($\epsilon$ 10000). Anal. Calcd for $C_{10}H_{16}O_6$: C, 51.7; H, 6.94. Found: C, 51.7; H, 7.07. Compound **14** was also formed (24% yield) from **11** and tetramethoxyethylene in $CCl_4$ at 90–95 °C. In both preparations of **14**, considerable **8** and polymeric material were produced.

**Registry No.** **2**, 691-45-2; **6**, 5394-63-8; **8**, 520-45-6; **9**, 4412-03-7; **11**, 93279-40-4; **12**, 105-45-3; **13**, 61369-33-3; **14**, 93279-41-5; **15**, 34132-56-4; EtOC≡CMgBr, 36678-63-4; methylmagnesium bromide, 75-16-1; ethoxyacetylene, 927-80-0; acetyl chloride, 75-36-5; methanol, 67-56-1; *N*-benzylidineaniline, 538-51-2; cyclohexanone, 108-94-1; phenyl isocyanate, 103-71-9; tetramethoxyethylene, 1069-12-1.

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(26) Failure to remove acetone from this reaction resulted in an incomplete reaction, accompanied by the formation of dehydroacetic acid.

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

(28) Brady, W.; Watts, R. *J. Org. Chem.* **1980**, *45*, 3525.