with 1 drop of H_2O and 25 mg of $NaBH_4$. Stirring was continued for a total of 18 h, at which time the reaction mixture was poured into H_2O and extracted three times with ether. The combined ether extracts were dried over $MgSO_4$, filtered, concentrated, and chromatographed on silica gel. Elution with 1:2 ether–hexanes yielded 41 mg (70%) of the diol **24** as a solid melting at 139–140 °C: R_f 0.41 (1:1 ether–hexanes); IR ($CHCl_3$) 3590, 3360, 2950, 2928, 2860, 1720, 1460, 1400, 1380, 1360, 1250, 1134, 1104, 1089, 1057, 1004, 881, 860, 834 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 4.86 (dd, 1 H, J = 10.27, 4.74 Hz), 4.07 (m, 1 H), 3.90 (dd, 1 H, J = 11.73, 3.99 Hz), 3.38 (dd, 1 H, J = 11.76, 3.85 Hz), 2.40 (d, 1 H, J = 4.66), 2.07–1.50 (m, 14 H), 1.26 (s, 3 H), 1.11 (s, 3 H), 0.88 (s, 9 H), 0.05 (s, 6 H); MS (5 eV) base peak 189.

(1*S,2*S**,5*R**,9*S**,12*S**)-4-(*tert*-Butyldimethylsiloxy)-13,13-dimethyl-7-oxatetracyclo[7.5.0.0.^{1,5}.0^{2,12}]tetradecan-8-one (25).** A suspension of 35 mg (0.097 mmol) of diol **24** and 540 mg (5 equiv) of Fetizon's reagent (Ag_2CO_3 on Celite) in 10.6 mL of benzene was heated at reflux for 40 min. The suspension, initially a light green color, rapidly turned black. After filtration through a pad of Celite, the clear liquid was concentrated and chromatographed (silica gel, 1:5 ether–hexanes) to give 16 mg each of the two regioisomeric lactones **25** and **26** with a total yield of 92%. Both compounds were solids with **25** melting at 139–140 °C and **26** melting at 76–78 °C. Data for **25**: R_f 0.55 (1:1 ether–hexanes); IR ($CHCl_3$) 3030, 2960, 2933, 2900, 2861, 1740, 1470, 1460, 1383, 1359, 1345, 1335, 1320, 1302, 1292, 1275, 1255, 1188, 1157, 1133, 1113, 1081, 1070, 1058, 1042, 1005, 968, 957, 939, 908, 879, 869, 850, 835 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 4.23 (br s, 2 H), 4.04 (m, 1 H), 2.54 (d, 1 H, J = 6.94 Hz), 2.22 (dd, 1 H, J = 13.48, 6.13 Hz), 2.06–1.50 (m, 10 H), 1.25 (s, 3 H), 1.12 (s, 3 H), 0.88 (s, 9 H), 0.06 (s, 6 H); ^{13}C NMR ($CDCl_3$) δ 175.08, 77.85, 67.18, 54.21, 53,31, 52.89, 51.20, 48.69, 46.39, 39.42, 38.92, 35.06, 28.02, 26.83, 25.86, 18.71, 18.00, –4.38, –4.68; MS (18 eV) parent 364, base peak 307. Data for **26**: R_f 0.44 (1:1 ether–hexanes); IR ($CHCl_3$) 2980, 2959, 2931, 2910, 2860, 1730, 1471, 1461, 1390, 1371, 1361, 1330, 1308, 1295, 1264, 1228, 1181, 1170, 1136, 1103, 1077, 1063, 1055 1045 1030, 1005, 980, 962, 938, 920, 895, 861, 838, 700 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 4.31 (t, 1 H, J = 11.99 Hz), 4.21 (m, 1 H), 4.09 (dd, 1 H, J = 11.21, 4.69 Hz), 2.71 (d, 1 H, J = 6.09 Hz), 2.11–1.69 (m, 11 H), 1.26 (s, 3 H), 1.12 (s, 3 H), 0.89 (s, 9 H), 0.10 (s, 3 H), 0.06 (s, 3 H).

(1*S,2*S**,5*R**,9*S**,12*S**)-13,13-Dimethyl-7-oxatetracyclo[7.5.0.0^{1,5}.0^{2,12}]tetradecane-4,8-dione. (±)-Quadrone (1).** To a solution of 16 mg (0.044 mmol) of the lactone **25** in 1.5 mL of acetone at 0 °C was added 50 μL of 2.67 M Jones reagent. The stirred mixture was allowed to warm to room temperature over a period of 1 h and was then treated with 3 drops of isopropyl alcohol. The green suspension was poured into saturated $NaHCO_3$ and extracted three times with ether. The combined ether extracts were dried over $MgSO_4$, filtered, concetrated, and chromatographed on silica gel. Elution with 1:1 ether–hexanes yielded 10.8 mg (100%) of (±)-quadrone (**1**) as a white solid, mp 139–141 °C (lit.[3a] 140–142 °C): R_f 0.62 (ether); IR ($CHCl_3$) 3014, 2997, 2980, 2958, 2930, 2902, 2895, 2873, 1742, 1700, 1495, 1488, 1469, 1450, 1438, 1411, 1385, 1371, 1353, 1346, 1320, 1298, 1285, 1270, 1252, 1208, 1190, 1178, 1166, 1141, 1129, 1113, 1091, 1074, 1062, 1044, 1021, 1002, 958, 910, 897, 870, 857, 845, 831, 718, 660, 625 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 4.63 (d, 1 H, J = 11.75 Hz), 4.20 (dd, 1 H, J = 11.75, 5.52 Hz), 2.73 (d, 1 H, J = 6.84 Hz), 2.66 (dd, 1 H, J = 17.28, 14.26), 2.39 (, 3 H), 2.09–1.61 (m, 7 H), 1.27 (s, 3 H), 1.21 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 216.57, 173.98, 65.26, 52.47, 52.18, (2C), 49.83, 48.66, 45.92, 43.17, 40.42, 34.79, 28.04, 26.87, 19.28; MS (15 eV) parent 248, base peak 248. An analytical sample was prepared by recrystallization from hexanes.

Anal. Calcd for $C_{15}H_{20}O_3$: C, 72.55; H, 8.12. Found: C, 72.29; H, 8.11.

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Ketenes. 18.[1] Evidence for an Intermediate in the Reaction of Ketenes with Silyl Enol Ethers

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Abstract: The reactions of diethylketene and diphenylketene with various silyl enol ethers and the chemistry of some of the reaction products have been investigated. The formation of a rearranged adduct, in addition to the normally expected cyclobutanone, was taken as an indication that the reaction proceeds by an ionic mechanism. The same rearranged product arose from the thermolysis of a 3-silyloxycyclobutanone and a 2-silyloxyoxetane, which suggests that a zwitterionic intermediate occurs in all three reactions.

One tool with which to distinguish between concerted and stepwise [2 + 2] cycloadditions is the use of reactants that should give "abnormal" products if a zwitterionic or diradical intermediate is formed. Nishida has used the propensity of cyclopropylcarbinyl carbonium ions and radicals to rearrange to differentiate concerted, diradical, and zwitterionic mechanisms in [2 + 2] cycloadditions to olefins.[2] For instance, extensive rearrangement occurred and none of the normal [2 + 2] cycloadduct was formed when 1,1-diphenyl-2-vinylcyclopropane was reacted with tetracyanoethylene (TCNE). Since 1,1-diphenyl-2-vinylcyclopropane gave a normal Diels–Alder adduct, its rearrangement with TCNE was taken as an indication that the reaction was not concerted and that it proceeded via an intermediate.[2b] The same concept can be applied to the addition of ketenes to enol ethers, a reaction generally thought to be concerted.[3]

Many useful synthetic methods rely on the rearrangement of α-silyloxy carbonium ions to carbonyl compounds. Catalyzed aldol-type condensations of silyl enol ethers and acetals are known,[4]

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(1) Paper 17 in this series: Martin, J. C.; Gott, P. G.; Meen, R. H.; Raynolds, P. W. *J. Org. Chem.* **1981**, *46*, 3911–3.

(2) (a) Shimizu, N.; Nishida, S. *J. Chem. Soc., Chem. Commun.* **1972**, 389–390. (b) Shimizu, N.; Fujioka, T.; Ishizuka, S.; Tsuji, T.; Nishida, S. *J. Am. Chem. Soc.* **1977**, *99*, 5972–5977. (c) Shimizu, N.; Nishida, S. *Ibid.* **1974**, *96*, 6451–6462. (d) Shimizu, N.; Ishizuka, S.; Tsuji, T.; Nishida, S. *Chem. Lett.* **1975**, 751–756. (e) Nishida, S. *Angew Chem., Int. Ed. Engl.* **1972**, *11*, 328. (f) Reetz, M. T. *Angew. Chem.* **1982**, *94*, 97–109.

(3) (a) Ghosez, L.; O'Donnell, M. J. *Pericyclic React.* **1977**, *2*. (b) Huisgen, R.; Feiler, L. A.; Binsch, G. *Chem. Ber.* **1969**, *102*, 3460–3474. (c) Swieton, G.; von Jouanne, J.; Kelm, H.; Huisgen, R. *J. Chem. Soc., Perkin Trans. 2* **1983**, 37–43. (d) Huisgen, R.; Feiler, L. A.; Otto, P. *Tetrahedron Lett.* **1968**, 4485–4490.

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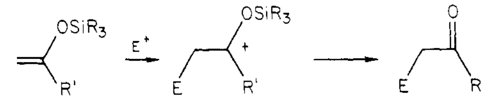
Table I. Product Yields from the Reaction of Ketenes with Silyl Enol Ethers

reactants	products	yield,[a] %
1a, **2a**	**3a**	86
1a, **2b**	**3b**	56
1b, **2a**	**4c**	99
1b, **2b**	**3d**, **4d**	50, 30
1c, **2a**	**4e**	79
1c, **2b**	**3f**, **4f**	77[b]
1d, **2a**	**4g**	96
1d, **2b**	**3h**, **4h**	76[c]
1e, **2a**	**4i**, **5**	41, 45

[a] Isolated yield after chromatography. [b] A mixture of **3f** and **4f**. [c] A 1:1 mixture of **3h** and **4h**.

and Murai has shown that sufficiently active electrophiles like phenylsulfenyl chloride and trichloroacetyl chloride react with silyl enol ethers without a catalyst.[5]

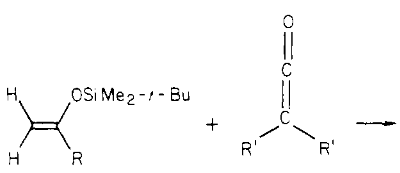


On the other hand, the ability of silyl enol ethers to survive the concerted Diels–Alder cycloaddition is without question, since the reaction of silyloxybutadienes has been used to advantage in synthesis.[6] Thus, determination of the products of the reaction of silyl enol ethers with ketenes should enable a distinction to be made between a concerted and a stepwise mechanism. If a zwitterionic intermediate like **7** is formed, it is possible that a rearranged product, **4**, might be obtained in place of, or in addition to, the "normal" cyclobutanone, **3**.

Although both product types, **3** and **4**, were observed by Hassner, his results with dichloroketene led him to the conclusion that there was not sufficient evidence to support the intermediacy of a structure like **7** and that **4** was formed only from **3** by another route.[7a] Brady and Lloyd reached similar conclusions from their investigation of the reaction of chloroketenes with various cyclic, linear, and conjugated silyl enol ethers.[7b–d] Brady and Watts concluded that the addition of chloroketenes to O-silylated ketene acetals proceeded through a zwitterionic intermediate when they observed rearranged products like **4**, and they speculated that all ketene reactions with electron-rich olefins occur by a stepwise mechanism.[8] We have already made a similar observation regarding the dimerization of monoalkylketenes[9] and report here an investigation of the reaction of silyl enol ethers with diethylketene and diphenylketene. It will be shown that **4** can be generated by a route that does not involve **3**, that **7** is a reasonable intermediate for the reaction of ketenes with silyl enol ethers, and that cyclobutanones like **3** and the oxetane **5** revert to ketene and olefin by a stepwise mechanism.

Results

Diphenylketene (**2a**) reacted exothermically with *tert*-butyldimethylsilyl vinyl ether (**1a**) at room temperature to give **3a**, while diethylketene (**2b**) and **1a** required heating at 135 °C for 2 h to give **3b**. Both **3a** and **3b** were stable at 135 °C for 12 h, and in neither case were byproducts—other than the ketene dimers—indicated by the NMR spectra of the crude product mixture. When heated with **2b** at 135 °C, the aromatic compounds **1b**, **1c**, and **1d** initially yielded **3** and the rearranged product, **4**. As

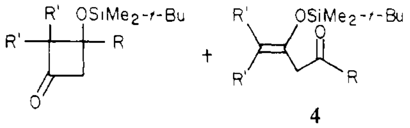


1

2

a, $R = H$
b, $R = p\text{-}C_6H_4Cl$
c, $R = C_6H_5$
d, $R = p\text{-}C_6H_4OCH_3$
e, $R = t\text{-}C_4H_9$

a, $R' = C_6H_5$
b, $R' = CH_2CH_3$



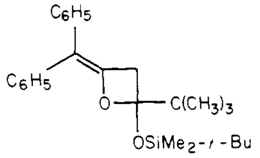
3

4

a, $R = H; R' = C_6H_5$
b, $R = H; R' = C_2H_5$
c, $R = p\text{-}C_6H_4Cl; R' = C_6H_5$
d, $R = p\text{-}C_6H_4Cl; R' = C_2H_5$
e, $R = C_6H_5; R' = C_6H_5$
f, $R = C_6H_5; R' = C_2H_5$
g, $R = p\text{-}C_6H_5OCH_3; R' = C_6H_5$
h, $R = p\text{-}C_6H_5OCH_3; R' = C_2H_5$
i, $R = t\text{-}C_4H_9; R' = C_6H_5$

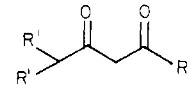
heating was continued for 2 h to complete the reaction, it was obvious from the NMR spectra that the proportion of **4** had increased, and after 24 h, all of **3** had disappeared. It was not possible to accurately measure the ratio of **4**:**3** because compounds **3d**, **3f**, and **3h** did not survive GLC conditions, but it was apparent from the NMR spectrum that **4** was present, even at very low conversion.

It was shown that the changing ratio of **4**:**3** was due to the slow conversion of **3** to **4** at 135 °C. At 96 °C the conversion of **3** to **4** was almost completely suppressed, and the time-independent **4d**:**3d** = 0.25 at this temperature established that **4d** was being formed directly from **1b** and **2b** without the intermediacy of **3d**. The more reactive diphenylketene (**2a**) yielded only **4c**, **4e**, and **4g** when reacted with **1b**, **1c**, and **1d** at room temperature, although peaks that could be assigned to **3c** and **3e** were observed in the NMR spectrum at short reaction times. The silyl enol ether of pinacolone (**1e**) afforded a mixture of **4i** and **5** when reacted with



5

2a. There was no indication in the IR spectrum that any **3i** had been formed. A similar adduct has been reported from **2a** and tetramethoxyethene.[10] The structures of **3**, **4**, and **5** were deduced from their spectral properties, as well as by the hydrolysis of **4** and **5** to the corresponding diketones, **6**. The results are summarized in Table I.



6

A 5% solution of **3d** in toluene heated in a sealed tube at 137 °C for 22 h gave diethylketene dimer, **1b**, and **4d** in yields of 28%, 39%, and 41%.

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(6) (a) Danishefsky, S.; Kitahara, T. *J. Am. Chem. Soc.* **1974**, *96*, 7807–7808. (b) Danishefsky, S. *Acc. Chem. Res.* **1981**, *14*, 400–406.

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(8) Brady, W. T.; Watts, R. D. *J. Org. Chem.* **1981**, *46*, 4047–4050.

(9) Raynolds, P. W. "Abstracts of Papers", 184th National Meeting of the American Chemical Society, Kansas City, MO, 1982; American Chemical Society: Washington, D.C., 1982 ORGN 021.

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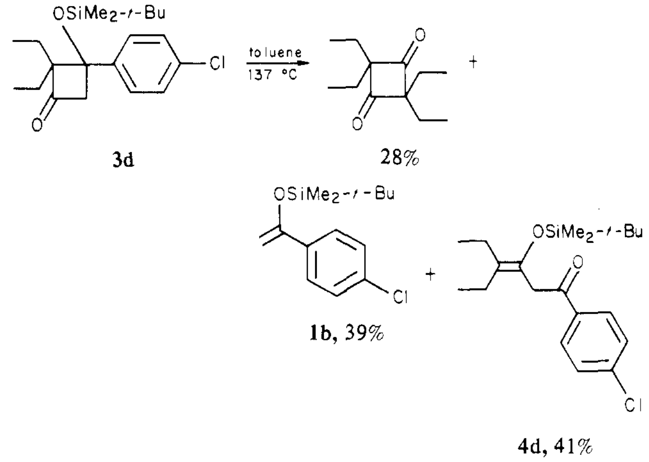


3d

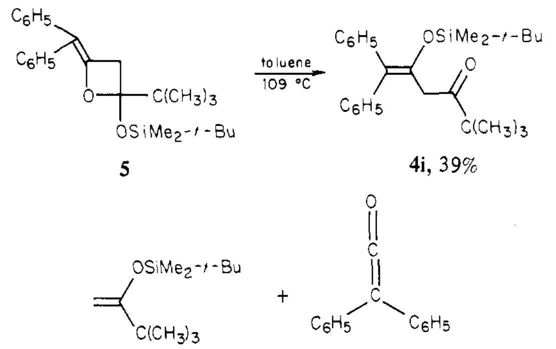
28%

1b, 39%

4d, 41%

Unidentified minor products were observed by GLC in amounts that decreased as the solution was made more dilute. Although some of the **4d** was certainly due to the recombination of **1b** and **2b**, a trapping experiment showed that about half of the observed **4d** was due to a process that did not involve free diethylketene. A competitive experiment established that **1a** reacted at least twice as rapidly with **2b** as **1b** did with **2b**. When **3d** was heated as a 5% solution in **1a** at 137 °C for 20 h, a 19% absolute GLC yield of **4d** was obtained. The formation of this much **4d** in the presence of a large excess of an efficient trapping agent demonstrated that some **4d** was formed directly from **3d** without the intermediacy of diethylketene, **2b**.

The yellow color characteristic of diphenylketene was observed within a few minutes when **5**, as a 5% solution in toluene, was heated at 109 °C. As heating was continued, the yellow color faded, and after 88 h **4i** was the major product in an absolute GLC yield of 79%. When a toluene solution of **5** was pyrolyzed in the injector port of a GLC, **4i**, **1e**, and **2a** were observed in yields of 23%, 55%, and 52%, respectively, whereas when the toluene solution was heated at 109 °C for 45 min before GLC analysis, the same compounds were observed in yields of 39%, 46%, and 41%. These results indicated that the **1e** and **2a** produced in the initial pyrolysis recombined under the reaction conditions, to drive the system to **4i** at long reaction times. A 22% yield of **4i** was obtained when **5** was heated as a 4% solution in **1a**. As before, the formation of rearranged product, **4i**, in the presence of a large excess of an efficient diphenylketene trap demonstrates that some **4i** was produced directly from **5** by a route that did not involve free diphenylketene. It was shown that **1a** reacted faster with diphenylketene than did **1e** and that **4i**, **1e**, and **3a** were unchanged by the conditions used. The yields of products from both **3d** and **5** were determined by GLC with octadecane as the internal standard. Corrections were made for differing detector response factors.



5

4i, 39%

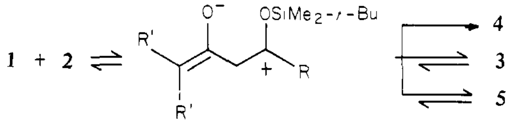
1e, 46%

2a, 41%

Discussion

Proofs of the concertedness of ketene–olefin cycloadditions have relied heavily on arguments that a zwitterionic intermediate was inconsistent with experimentally determined solvent effects, stereospecificity, and activation parameters. Ketene–vinyl ether cycloadditions are thought to be concerted because of the solvent dependence on the rate of reaction of diphenylketene with butyl vinyl ether, $k(\mathrm{CH_3CN})/k(\text{cyclohexane}) = 160$ at 31.4 °C,[3d] and the retention of configuration to the extent of 96.2% and 97.5% for the reaction of *trans*- and *cis*-propenylpropyl ethers, respectively, with diphenylketene.[3b] We remain unconvinced by the lengthy arguments asserting that these results are consistent only with a concerted mechanism. It appears to us that many of the assumptions of how a zwitterionic intermediate should behave were not based on appropriate model compounds. For instance, stereospecificity is often cited as a reliable indication of concertedness,[3a] with the apparent belief that all zwitterions are free to rotate. England and Krespan have shown, however, that the reaction of bis(trifluoromethyl)ketene with enol ethers, which is regarded as a good model for a stepwise cycloaddition with a zwitterionic intermediate,[12] is stereospecific in solvents of low polarity.[13] On the other hand, the loss of configuration in the addition of *trans*-butene to dimethylketene has never been rationalized in terms of a concerted mechanism.[14] Thus it would appear that examples exist of stepwise stereospecific and concerted nonstereospecific cycloadditions. Gompper, in his review of cycloadditions with polar intermediates, pointed out that other criteria—such as a small solvent effect on the rate of reaction or a large, negative entropy of activation—cannot be relied on to distinguish between a concerted and a stepwise mechanism. The opinion was expressed that in most cases useful information can be obtained only by isolation or interception of the intermediate.[15]

The rationale of this work was to intercept the hypothesized intermediate by a well-precedented rearrangement process, and our results are consistent with a stepwise mechanism. It is proposed that the ketene **2** reacts with the silyl enol ether **1** to afford an intermediate, probably a zwitterion, **7**, which partitions among four processes—reversal, rearrangement, and the two modes of ring closure—in response to steric and electronic factors. Compound **4** is a reasonable, expected product of **7**.[11] A concerted reaction of **1** and **2** to give **4** would be without precedent and would have to accommodate our observation,[16] as well as those by others,[7] that trimethylsilyl enol ethers and the much more bulky *tert*-butyldimethylsilyl enol ethers differ little in their reactivity toward ketenes. Formation of **4** exclusively from **3**, as proposed by Hassner,[7] is inconsistent with the ratio [**4d**]:[**3d**] = 0.25. We conclude that the formation of **4** is indicative of an intermediate like **7**. Compounds **3** and **5** are reasonable and expected ring-closure products of **7**, although these experiments do not rule out their generation by other routes. The formation of **5**, probably as a consequence of the steric bulk of the *tert*-butyl group, is especially gratifying, since Ghosez and O'Donnell have argued that the absence of oxetane products implies the absence of a zwitterionic intermediate in ketene–olefin cycloadditions.[12]



7

Further support for the proposed mechanism would be forthcoming if the reactive intermediate, **7**, could be generated by an independent route, preferably in the absence of interfering reagents. Traditionally, this has been accomplished by the expulsion of molecular nitrogen from a suitably designed diazo

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(11) Pinnavia and McClarin (Pinnavaia, T. J.; McClarin, J. A. *J. Am. Chem. Soc.* **1974**, *96*, 3012) have observed that acyclic silyl enol ethers undergo rapid 1,5-silyl group migration between two oxygen centers.

(12) Ghosez, L.; O'Donnell, M. J. *Pericyclic React.* **1977**, *2*, 96.

(13) England, D. C.; Krespan, C. G. *J. Org. Chem.* **1970**, *35*, 3312–3322.

(14) Frey, H. M.; Issacs, N. S. *J. Chem. Soc. B* **1970**, 830–832.

(15) Gompper, R. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 312–327.

(16) Trimethylsilyl enol ethers were used in the initial studies until problems with product isolation caused us to change to *tert*-butyldimethylsilyl enol ethers. Qualitatively similar results were obtained with both ethers, although more rearrangement was observed with the trimethylsilyl enol ethers.

compound, but here, the appropriate structures were judged to be difficult to synthesize. Another technique, used to generate both radicals and carbonium ions, is to thermally decompose a molecule with a particularly weak bond. Both **3d** (which was the cyclobutanone most readily isolated in pure form) and **5** were expected to be suitable precursors for the intermediate, **7**, because of the driving force provided by relief of ring strain and the high degree of charge stabilization. Both compounds decomposed readily in dilute solution at moderate temperatures, and the intermediacy of **7** is implied by the formation of **4** by a route that does not involve a kinetically free ketene molecule. Compounds **1b** *and* **2b**, *probably formed by cleavage of* **7**, *were also observed.* Thus the hypothesized intermediate **7** does everything required of it: it forms when it is expected to form, in three different systems, and behaves chemically as such a structure is expected to behave in the four possible modes of decomposition—reversion, rearrangement, and ring closure to afford cyclobutanone or oxetane. Whether the proposed mechanism can be considered to be proven, in a rigorous sense, or not, it certainly can be used to predict the course of ketene–silyl enol ether reactions.

Summary

The formation of an "abnormal" product, **4**, in the reaction of ketenes with silyl enol ethers has been observed in isolated cases, and it has been regarded as a secondary product derived from a cyclobutanone.[7a] This study, which is the first systematic investigation of this reaction with purified ketenes in a salt-free medium, has shown that **4** is a primary product of the reaction of diethylketene with **1b**, as well as of the thermolysis of **3d** and **5**. It is difficult to understand how rearrangement could have occurred in these three different systems if not via an intermediate like **7**, and we conclude that these reactions are not concerted. Although we have not ruled out the possibility that **3** and **5** were formed in separate, concerted processes, we believe that the simultaneous occurrence of two transition states of similar structure, one with charge separation and one without, in the reaction of so many combinations of ketenes and olefins of vastly differing electronic and steric character is highly unlikely.

Experimental Section

General. Melting points were determined on a Thomas-Hoover melting point apparatus and are uncorrected. IR spectra were recorded on a Perkin-Elmer 137 spectrometer. IR values are given in wavenumbers. Proton spectra were recorded on a Varian EM-360 spectrometer with tetramethylsilane (δ 0) as an internal standard. Coupling constants (J) are given in hertz. Preparative chromatographic separations were performed on a 2.5 × 17 cm column containing 0.040–0.063-mm silica gel by eluting with heptane containing 0–4% ethyl acetate. Analytical GLC analysis was performed on a HP 5750 chromatograph with a 2-m SE-30 column. Integrations were done with a HP 3380-A recording integrator, and absolute yields were determined by using octadecane as an internal standard. Silyl enol ether **1a** was prepared by the method of Jung,[18] while the other ethers were prepared by the method of Cazeau.[19] Diphenylketene was prepared by Taylor's method,[20] and diethylketene was prepared by passing 2-ethylbutyric anhydride at 5 torr through a 2.5 × 25 cm column packed with quartz chips and heated to 550 °C. Acid and uncoverted anhydride were trapped at +5 °C, while the diethylketene was collected in a dry ice cooled trap and redistilled.

Preparation of 3a. A mixture of 0.87 g of **1a** (5.5 mmol) and 1.0 g of **2a** (5.15 mmol) was let stand for 3 days. Chromatography afforded 1.56 g (86%) of the crystalline adduct **3a**, mp 69–71 °C: NMR ($CDCl_3$) δ 7.6–7.1 (m, 10 H), 5.21 (t, J = 6, 1 H), 3.40 (d of d, J = 6, 17, 1 H), 2.95 (d of d, J = 6, 17; 1 H), 0.78 (s, 9 H), 0.02 (s, 6 H); IR (KBr) 5.65, 6.25, 8.00, 8.40, 8.72, 11.90, 12.80, 14.30; MS, m/e 352; ^{13}C NMR ($CDCl_3$) δ 206.2, 139.3, 137.3, 128.6, 127.7, 126.9, 126.8, 126.6, 79.7, 66.8, 54.1, 25.4, 17.7, −4.8, −5.1. Anal. Calcd for $C_{22}H_{28}O_2Si$: C, 74.95 H, 8.00. Found: C, 75.15 H, 8.09.

Preparation of 3b. A mixture of 3.2 g (20 mmol) of **1a**, 1.96 g (20 mmol) of diethylketene (**2b**), and 8 mL of toluene was refluxed under nitrogen for 18 h. Toluene and excess diethylketene were removed under vacuum, yielding 4.36 g of **3b** contaminated with ca. 8% diethylketene dimer and 4% of an unknown by GLC. Chromatography failed to cleanly separate dimer and **3b**, but a small quantity of pure **3b** was obtained as an oil: NMR ($CDCl_3$) δ 4.27 (t, J = 6, 1 H), 3.24 (d of d, J = 6, 18; 1 H), 2.87 (d of d, J = 6, 18; 1 H), 2.1–1.4 (m, 4 H), 1.2–0.7 (m, 15 H), 0.11 (s, 6 H); IR (film) 5.62, 6.85, 7.99, 8.39, 11.90, 12.85; MS, m/e 214 (loss of C_2H_2O (ketene); molecular ion not observed). Anal. Calcd for $C_{14}H_{28}O_2Si$: C, 65.56; H, 11.00. Found: C, 65.82; H, 11.05.

Reaction of 1e with 2a. A mixture of 3.0 g (15.5 mmol) of diphenylketene and 2.6 g (12.1 mmol) of **1e** was heated without solvent at 64 °C for 1 h. The progress of the reaction was monitored by IR, and no peaks that could be attributed to a cyclobutanone were observed. NMR analysis indicated a mixture of **1e**, **5**, and **4i** in the ratio 1:10:8. Chromatography afforded 2.22 g (45%) of **5** as an oil which was crystallized from methanol, mp 54–56 °C: NMR ($CDCl_3$) δ 7.6–7.1 (m, 10 H), 3.40 (A of an AB, J = 16, 1 H), 2.87 (B of an AB, J = 16, 1 H), 1.01 (s, 9 H), 0.90 (s, 9 H), 0.24 (s, 3 H), 0.20 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 149.4, 138.3, 137.4, 129.9, 128.3, 127.9, 126.2, 125.2, 111.3, 110.4, 39.8, 38.5, 25.7, 23.5, 17.8, −3.0, −4.0; IR (KBr) 5.95, 6.22, 8.00, 8.45, 10.75, 11.71; UV (CH_3OH) λ_{max} 269 nm (ϵ 16773); MS, m/e 408.2489. Calcd for $C_{26}H_{36}O_2Si$: 408.2483. Anal. Calcd for $C_{26}H_{36}O_2Si$: C, 76.41; H, 8.88. Found: C, 76.38; H, 9.02.

Further elution yielded **4i** as an oil (2.0 g, 41%). Crystallization from methanol gave 1.37 g, mp 50–52 °C: NMR ($CDCl_3$) δ 7.4–7.1 (m, 10 H), 3.43 (s, 2 H), 1.01 (s, 9 H), 0.80 (s, 9 H), −0.10 (s, 6 H); IR (KBr) 5.82, 6.12, 7.99, 10.15, 12.03, 12.78, 14.29; UV (CH_3OH): λ_{max} 256 nm (ϵ 11580); MS, m/e 408. Anal. Calcd for $C_{26}H_{36}O_2Si$: C, 76.41; H, 8.88. Found: C, 76.43; H, 8.98.

Hydrolysis of 4i and 5. Hydrolysis of **4i** and **5** in aqueous acetone with HCl yielded **6i**, mp 84.5–86 °C from methanol: NMR ($CDCl_3$, 87:13 enol–keto mixture) δ 7.35 (s, 10 H), 5.66 (s, 1 H, enol), 5.37 (s, 1 H, keto), 5.00 (s, 1 H, enol), 3.71 (s, 2 H, keto), 1.12 (s, 9 H); IR (KBr) 6.30 (s, br), 6.70, 6.90, 8.80, 12.55, 13.06, 13.41, 14.10; FDMS, m/e 294. Anal. Calcd for $C_{20}H_{22}O_2$: C, 81.60; H, 7.53. Found: C, 81.78; H, 7.54.

Reaction of 1b with 2b. A mixture of 2.2 g (8.2 mmol) of **1b** and 4.0 g (41 mmol) of diethylketene (**2b**) was heated in a sealed tube for 2 h at 137 °C. Diethylketene dimer was removed by bulb-to-bulb distillation at 110 °C, 0.5 torr. The residue, 3.1 g, was chromatographed, yielding 1.50 g (50%) of **3d**, an oil: NMR ($CDCl_3$) δ 7.30 (s, 4 H), 3.72 (d, J = 17, 1 H), 3.10 (d, J = 17, 1 H), 2.4–1.4 (m, 4 H), 1.3–0.3 (m, 15 H), −0.11 (s, 3 H), −0.41 (s, 3 H); IR (film) 5.61, 7.95, 9.12, 10.41, 11.92, 12.84; UV (CH_3OH) λ_{max} 268 nm (ϵ 231); MS, m/e 366. Anal. Calcd for $C_{20}H_{31}ClO_2Si$: C, 65.45; H, 8.52. Found: C, 65.99;[21] H, 8.68.

Further elution yielded 0.90 g (30%) of **4d**, an oil: NMR ($CDCl_3$) δ 8.05 (d, J = 8, 2 H), 7.54 (d, J = 8, 2 H), 3.80 (s, 2 H), 2.5–1.5 (m, 4 H), 1.2–0.8 (m, 15 H), 0.11 (s, 6 H); IR (film) 5.91, 6.27, 7.96, 9.14, 11.93, 12.80; UV (CH_3OH) λ_{max} 250 nm (ϵ 14431); FDMS, m/e 366. Anal. Calcd for $C_{20}H_{31}ClO_2Si$: C, 65.45; H, 8.52. Found: C, 65.43; H, 8.67.

An additional 0.40 g (13%) of a mixture of **3d** and **4d** was obtained to give a total yield of 93%.

Reaction of 1c with 2b. A mixture of 1.0 g of diethylketene (10.2 mmol) and 1.0 g (4.27 mmol) of **1c** was heated without solvent at 96 °C for 2 h, giving a 74:26 mixture (NMR) of **3f** and **4f** at partial conversion. Heating for an additional 39 h caused complete disappearance of the starting material, and a product mixture containing **3f** and **4f** in the ratio 68:32 was obtained. Diethylketene dimer was distilled bulb to bulb (2 torr, 120 °C) and the residue (1.29 g) was chromatographed, yielding 1.09 g (77%) of fractions containing different proportions of **3f** and **4f**. Compound **3f** could not be obtained in pure form, and attempts to partially hydrolyze a mixture of **3f** and **4f** afforded an inseparable mixture of **3f** and **6f**. The spectral characteristics of 90% pure **3f** were in accord with the assigned structure: NMR ($CDCl_3$) δ 7.6–7.1 (m, 5 H), 3.83 (d, J = 17, 1 H), 3.12 (d, J = 17, 1 H), 2.3–1.3 (m, 4 H), 1.3–0.3 (m, 15 H), −0.14 (s, 3 H), −0.41 (s, 3 H); IR (film) 5.61.

Prolonged heating of a mixture of **3f** and **4f** followed by chromatography gave pure **4f**: NMR ($CDCl_3$) δ 8.0–7.3 (m, 5 H), 3.70 (s, 2 H), 2.3–1.6 (m, 4 H), 1.0–0.6 (m, 15 H), 0.08 (s, 6 H); IR (film) 5.91, 6.25, 7.95, 10.36, 11.93, 12.79; MS, m/e 332. Anal. Calcd for $C_{20}H_{32}O_2Si$: C, 72.23; H, 9.62. Found: C, 72.34; H, 9.80.

Reaction of 1d with 2b. A mixture of 1.36 g (5.15 mmol) of **1d**, 2.0 g (20.4 mmol) of **2b**, and 2 g of CCl_4 was refluxed for 3 h. Chromatography gave 1.41 g (76%) of a 1:1 (NMR) mixture of **3h** and **4h**, which

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could not be conveniently separated by chromatography or GLC. Partial hydrolysis of the mixture gave an inseparable mixture of **3h** and **6h**. The presence of **3h** was inferred from the NMR spectrum (3.92, d, J = 17; 3.20, d, J = 17) and the IR absorption at 5.61. Pure **4h** was obtained by heating the mixture at 135 °C for 10 h, leaving an oily residue: NMR ($CDCl_3$) δ 8.01 (d with fine splitting, J = 9, 2 H), 6.94 (d with fine splitting, J = 9, 2 H), 3.90 (s, 3 H), 3.80 (s, 2 H), 2.23 (q, J = 8, 2 H), 2.03 (q, J = 8, 2 H), 0.95 (t, J = 8, 6 H), 0.96 (s, 9 H), 0.13 (s, 6 H); IR (film) 5.91, 6.20, 7.93, 8.52, 12.02, 12.85; FDMS, m/e 362. Anal. Calcd for $C_{21}H_{34}O_3Si$: C, 69.56; H, 9.45. Found: C, 69.45; H, 9.53.

Preparation of 4c. A mixture of 1.0 g of **1b** (3.72 mmol) and 0.78 g (4.02 mmol) of **2a** was refluxed with 5 g of CCl_4 for 20 h. Chromatography afforded 1.82 g (>100%) of an oil, pure by NMR except for traces of solvent. Crystals of **4c** were obtained when the product was stored in methanol at −20 °C overnight, mp 69.5–70.5 °C: NMR ($CDCl_3$) δ 7.9–7.1 (m, 14 H), 3.82 (s, 2 H), 0.70 (s, 9 H), −0.15 (s, 6 H); IR (KBr) 5.94, 6.17, 6.30, 7.98, 8.18, 9.88, 10.15, 12.02, 14.30; FDMS, m/e 462. Anal. Calcd for $C_{28}H_{31}ClO_2Si$: C, 72.62; H, 6.75. Found: C, 72.79; H, 6.69.

Hydrolysis of **4c** with acetone–water–HCl yielded the diketone **6c**, which exhibited appropriate spectral and analytical data.

Preparation of 4e. A mixture of 1.0 g of **2a** (5.15 mmol), 1.2 g of **1c** (5.15 mmol), and 2 g of CCl_4 was allowed to react for 3 days at room temperature. Chromatography afforded 1.74 g (79%) of an oil which crystallized on standing. Recrystallization from methanol afforded compact white crystals of **4e**, mp 77–78 °C: NMR ($CDCl_3$) δ 8.0–7.2 (m, 15 H), 3.91 (s, 2 H), 0.74 (s, 9 H), −0.12 (s, 6 H); IR (KBr) 5.93, 6.12, 8.02, 8.10, 9.96, 10.22, 11.93, 12.07, 12.83, 13.21, 14.26; λ_{max} (CH_3OH) 245 nm (ϵ 23 290); FDMS, m/e 428. Anal. Calcd for $C_{28}H_{32}O_3Si$: C, 78.45; H, 7.53. Found: C, 78.37; H, 7.33.

Hydrolysis of **4e** in acetone–water–HCl gave the diketone **6e**, mp 125–126 °C (lit.[17] mp 127 °C).

Preparation of 4g. After chromatography, diphenylketene (1.0 g, 5.15 mmol) and **1d** (1.36 g 5.15 mmol) yielded 2.27 g (96%) of **4g**, pure by NMR. Recrystallization from CH_3OH and then from heptane yielded crystals, mp 76–78 °C: NMR ($CDCl_3$) δ 7.93 (d, 1 H), 7.36 (s, 5 H), 7.30 (s, 5 H), 6.9 (d, 1 H); IR (KBr) 5.95, 6.25, 7.98, 8.15, 8.52, 10.17, 12.04, 12.79, 14.25; λ_{max} (CH_3OH) 268 nm (ϵ 25 320); FDMS, m/e 458. Anal. Calcd for $C_{29}H_{34}O_3Si$: C, 75.94; H, 7.47. Found: C, 76.06; H, 7.46.

Hydrolysis of **4g** in acetone–water–HCl gave the diketone, **6g**, mp 107–108 °C (lit.[17] mp 108 °C).

Measurement of the Relative Amounts of 4d and 3d Produced in the Reaction of 1b with 2b. A mixture of 0.24 g (0.9 mmol) of **1b** and 0.28 g (2.9 mmol) of **2b** was heated at 96 °C for 4 h. The ratio of **4d**:**3d** as well as the conversion (assuming that all **1b** was converted to **4d** and **3d**) was calculated from the integrated NMR spectrum. Within experimental error, there was no difference in **4d**:**3d** from 15% to 85% conversion, and a value **4d**:**3d** = 0.25 ± 0.05 represents the average of four measurements.

Pyrolysis of 5 in 1a. A mixture of 19.4 mg of **5**, 8.8 mg of *n*-octadecane, and 480 mg of **1a** was heated at 138 °C for 4 h. GLC analysis indicated that **4i** had been formed in 22% yield.

Competitive Reaction of 1a and 1b with 2b. A mixture of 0.18 g (1.14 mmol) of **1a**, 0.50 g (1.86 mmol) of **1b**, and 0.05 g (0.51 mmol) of **2b** was heated at 99 °C for 4 h, causing the disappearance of most of the yellow color of diethylketene. The integrated NMR spectrum showed **3d**, **4d**, and **3b** in the molar ratio of 4:1:12. Assuming pseudo-first-order kinetics, **1a** then reacts about 4 times faster with **2b** than does **1b**. Any deviation from the pseudo-first-order approximation will increase this rate difference. The rate difference was not determined with any greater precision because of the inability to measure **3d** by a method other than NMR spectroscopy.

Registry No. 1a, 66031-93-4; **1b**, 90720-21-1; **1c**, 66324-10-5; **1d**, 80676-78-4; **1e**, 84850-50-0; **2a**, 525-06-4; **2b**, 24264-08-2; **3a**, 90720-22-2; **3b**, 90720-23-3; **3c**, 90720-24-4; **3d**, 90720-25-5; **3e**, 90720-26-6; **3f**, 90720-27-7; **3g**, 90720-28-8; **3h**, 90720-29-9; **3i**, 90720-30-2; **4a**, 90720-31-3; **4b**, 90720-32-4; **4c**, 90720-33-5; **4d**, 90720-34-6; **4e**, 90720-35-7; **4f**, 90720-36-8; **4g**, 90720-37-9; **4h**, 90720-38-0; **4i**, 90720-39-1; **5**, 90720-40-4; **6c**, 90720-41-5; **6e**, 16877-30-8; **6f**, 90720-42-6; **6g**, 16877-31-9; **6h**, 90720-43-7; **6i**, 90720-44-8.

Chemistry of Singlet Oxygen. 47. 9,10-Dicyanoanthracene-Sensitized Photooxygenation of Alkyl-Substituted Olefins

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Abstract: 9,10-Dicyanoanthracene (DCA) sensitizes the photooxygenation of 1-methylcyclohexene (**1**), 1,2-dimethylcyclohexene (**2**), and cholesterol (**3**) in acetonitrile and benzene. For all three olefins, the products are the same as those formed by reaction with singlet oxygen. The quantum yields for product formation and the solvent deuterium isotope effects for this reaction in acetonitrile and benzene are in good agreement with the values calculated assuming a singlet oxygen mechanism. These results indicate that singlet oxygen is the reactive intermediate rather than radical ions.

Previously we have shown 9,10-dicyanoanthracene (DCA)-sensitized photooxyygenation of phenyl-substituted olefins occurs exclusively by an electron-transfer pathway (Scheme I).[1] These compounds are essentially unreactive to singlet oxygen. In a later study of a singlet-oxygen-reactive olefin, 1,1-diphenyl-2-methoxyethylene, Steichen and Foote found tentative evidence that both singlet oxygen and electron-transfer mechanisms were operating.[2] Santamaria has provided chemical evidence for the production of singlet oxygen from DCA.[3] More recently, we have demonstrated directly by laser spectroscopy that DCA can sensitize the formation of $^1O_2$ in substantial yield by several mechanisms.[4,5] DCA-sensitized photooxygenation can therefore occur by two distinct pathways: electron transfer (Scheme I) and $^1O_2$. This complication led us to determine the mechanism by which several

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