analytical data were obtained for all new compounds.

Carbocations. The ions **4** were prepared by slow addition of the appropriate precursor, either as a solution in SO₂ClF at ~−78 °C or as a powder to a solution of FSO₃H/SbF₅ (1:1 M)/SO₂ClF cooled to −78 °C, with rapid vortex mixing. The concentration of the "magic acid" was 3 M and those of the ions were ~0.5 M based on the assumption of complete ionization of the alcohol.[32] The resulting solutions were transferred to NMR tubes via a precooled double-ended syringe, as detailed previously.[32]

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(32) Kelly, D. P.; Brown, H. C. *Aust. J. Chem.* **1976**, *29*, 957–965.

NMR Spectra. ¹³C NMR spectra were recorded at −80 °C of solutions in 8-mm NMR tubes containing a concentric capillary (3-mm o.d.) of acetone-d_6 and Me₄Si on a Varian CFT-20 spectrometer, using 8192 data points, 6000-Hz spectral width, and a 45° pulse angle. Chemical shifts are ±0.1 ppm from external Me₄Si.

Photochemical [3 + 2] Cycloaddition Reactions of Alkynones. Diverse Fates of Two Similar Vinylcarbene Intermediates and Reactions of a Cyclopropenol

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Contribution from the Laboratories of The Rockefeller University, New York, New York 10021. Received July 11, 1983
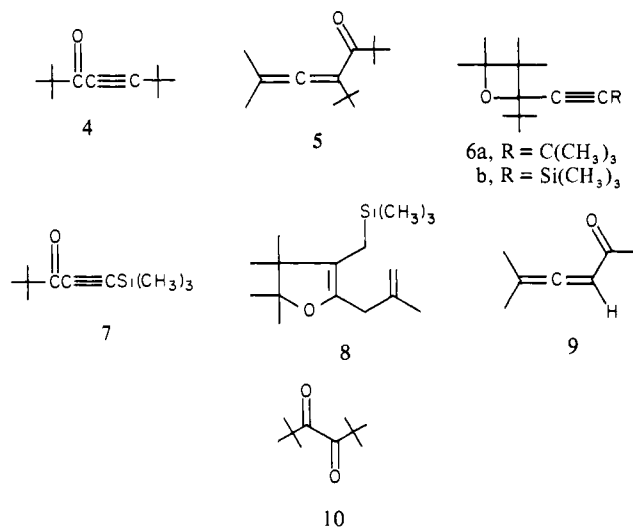
Abstract: Irradiation of alkynone **4** with tetramethylethylene (**2**) in wet benzene furnishes in high yield the simple cyclopropenol **11a**. Thermolysis of **11a** gives the conjugated allenic ketone **5** with loss of C₃H₆; treatment of **11a** with sodium hydride leads to **19**, and on standing in inert solvent at room temperature **11a** ejects acetone. In contrast the related alkynone **7** adds **2** photochemically to yield **25**, which rearranges at 75 °C to **8**. In explanation of the difference in reaction paths of **4** and **7** it is suggested that carbene **12** cyclizes to a cyclopropene from the singlet, while carbene **26** abstracts hydrogen intramolecularly from the triplet state.

Photochemical reaction of conjugated alkynones with several simple olefins yields novel [3 + 2] cycloaddition products for which a carbene intermediate has been proposed,[1] as well as the expected[2] oxetanes; this is illustrated for 3-pentyn-2-one (**1**) and tetramethylethylene (**2**). More recently we found that the oxetanes
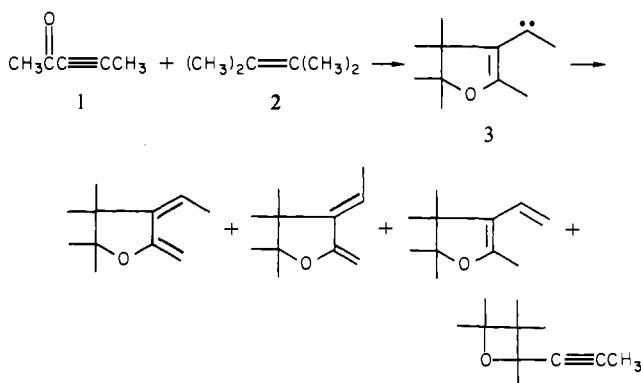
arise from the excited singlet state of the alkynone and that the [3 + 2] products come from a quenchable triplet.[3] There is also good experimental evidence for the carbenes (as **3**), including isolation of products of O–H bond insertion in alcoholic solvents.[3] In the present work we have now explored addition of tetramethylethylene to two α,β-acetylenic ketones in which no simple 1,2 or 1,4 hydrogen shifts are available for carbene stabilization. Irradiation of **4** with **2** in benzene, followed by removal of solvent, distillation, and preparative vapor-phase chromatography (VPC) of the volatile products furnished allenic ketone **5** in ~25% yield

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(1) Hussain, S.; Agosta, W. C. *Tetrahedron* **1981**, *37*, 3301.
(2) Jorgenson, M. J. *Tetrahedron Lett.* **1966**, 5811. Kwiatkowski, G. T.; Selley, D. B. *Ibid.*, **1968**, 3471.
(3) Saba, S.; Wolff, S.; Schröder, C.; Margaretha, P.; Agosta, W. C. *J. Am. Chem. Soc.* **1983**, *105*, 6902.

along with a small amount of oxetane **6a**. The constitution of **5** formally requires the surprising addition to **4** of *one-half* molecule of tetramethylethylene. In the course of elucidating the mech-

anism of this apparently extraordinary transformation, we examined the reaction of the closely related trimethylsilyl-substituted ketone **7** with **2**. Here the same procedure yields some **6b** and 68% of **8**, in which rearrangement of the *tert*-butyl group has occurred. Further investigation has provided explanations for these and other unusual transformations, as well as insight into the interesting question of the spin state of the reactive carbene and its influence on the course of subsequent reaction. Details are presented below.

Ketone **4** was available through reaction of pivalaldehyde with the Grignard reagent formed from *tert*-butylacetylene followed by oxidation with Jones's reagent.[4] Following the procedure

mentioned above, reaction of **4** with **2** furnished **6a** and **5**, the structure of which was deduced from its infrared (IR) and nuclear magnetic resonance (NMR) spectra [IR 1950 (allene), 1668 cm⁻¹ (carbonyl); ¹H NMR δ 1.80 (s, 6 H), 1.16 (s, 9 H), 1.10 (s, 9 H); ¹³C NMR δ 208.5, 204.1 (allene and carbonyl)].[5] This assignment was substantiated by oxidation of **5** with ruthenium tetroxide to form pivalil (**10**), identified through comparison with an authentic sample.[6]

Omission of the distillation after irradiation of **4** and **2** in benzene and then trituration of the residue left on removal of solvent furnished a new crystalline product. Once this substance was obtained pure, we recognized it as a 1:1 adduct of **2** and **4** containing an added equivalent of water. This led us to conduct the irradiation in benzene saturated with water, and under these conditions the new adduct was isolated in 91% yield merely by evaporation of solvent after photolysis. We assign cyclopropenol structure **11a** to this compound on the basis of its spectroscopic properties, origin, and the transformations summarized below. Its IR spectrum shows both free and hydrogen-bonded hydroxyls, absorption at 1800 cm⁻¹ typical of a cyclopropene,[7] and no carbonyl or enol ether absorption; in the ¹H NMR spectrum there are two hydroxyl protons and in the ¹³C NMR spectrum two carbinyl carbon atoms (73.3 and 67.7 ppm). Both ¹H and ¹³C NMR spectra indicate that the methyl groups of the side chain are all magnetically nonequivalent, suggesting that rotation of the chain is restricted, presumably as a result of nonbonded interactions and intramolecular hydrogen bonding between the two hydroxyl groups. Two quite significant spectroscopic features of **11a** are the signals at 133.3 and 126.9 ppm in the ¹³C NMR spectrum; these are at relatively high field for disubstituted olefinic carbon atoms and are in the region typical of fully substituted cyclopropenes.[8]

We may account for the formation of **11a** in the following manner. The original purpose in photolysis of **2** and **4** was to explore the fate of carbene **12**, which is the expected[1,3] initial [3 + 2] cycloadduct. With no 1,2 and 1,4 hydrogen transfer

11a, R = H
b, R = CH₃

12

13

14

15
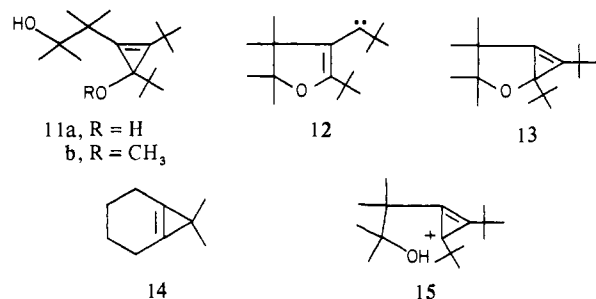
possible for stabilization, **12** can cyclize to the isomeric cyclopropene,[7,9] yielding bicyclic ether **13**. This may well be too strained to survive long at ambient temperature,[10] but attack of water could trap **13** through protonation followed by ring cleavage to give the

cyclopropenium ion **15**. Subsequent addition of hydroxide ion would then provide **11a**. Thus, both the unusual structure of the product and the peculiar reaction with water in hydrocarbon solvent can be rationalized as the consequences of a well-known rearrangement occurring in **12**. Earlier investigators looked without success for the related cyclization of a 3-furylmethylene to a cyclopropene.[11] In addition to the hydrogen-transfer reactions mentioned above, previously prepared 3-furylmethylenes and their 4,5-dihydro derivatives have also reacted by intramolecular aromatic substitution,[3] addition of oxygen,[12] dimerization,[11] and insertion into the hydrocarbon solvent.[11,12] These last possibilities are doubtless disfavored in **12** by the bulky *tert*-butyl groups, and this fact probably accounts for the smooth isomerization of **12** to **13**.

The first reaction of **11a** that we consider in support of its structure is thermal fragmentation. Distillation (pot temperature 100–150 °C/0.5 torr) converts **11a** to **5** with loss of three carbon atoms. The detailed mechanism of this process is not yet known, but the simplest postulate is that **11a** reclose to **13**,[13] which then

13

11a

16

17

18

19

20

21
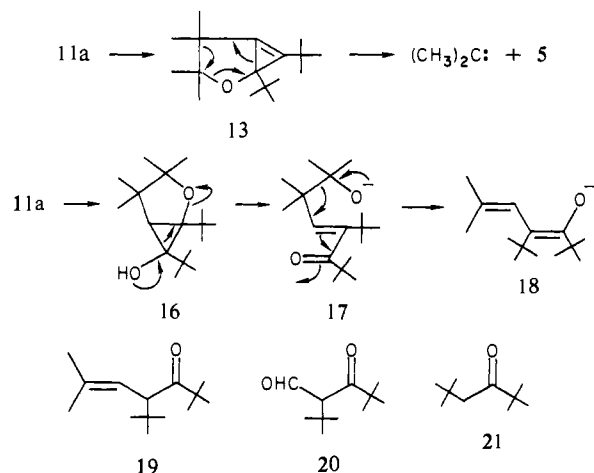
can fragment to dimethylcarbene and **5** as shown. Since there is good evidence for isomerization of simple alkylcyclopropenes to vinyl carbenes at temperatures as low as 150 °C,[14] the direct extrusion of dimethylcarbene from **11** appears possible. We found VPC evidence for formation of small amounts of propylene in this reaction but did not prove its presence. This thermolysis of **11a** then accounts for our original observation of the formation of **5** from **4** and half an equivalent of tetramethylethylene (**2**).

Other transformations of **11a** involve base-catalyzed opening of the cyclopropenol. Exposure of the diol to sodium hydride in tetrahydrofuran leads to **19** (84%) in a degradation that may be rationalized as follows. Base-catalyzed addition of the side-chain hydroxyl to the cyclopropene double bond furnishes **16**.[15] Further reaction with base gives **17** as shown, and this cleaves to acetone and enolate **18**. Final α protonation yields the isolated product, the structure of which was secured by oxidative degradation. Treatment of **19** with ruthenium tetroxide led to β-ketoaldehyde **20**, which was characterized by IR and proton NMR spectra and then directly oxidized with Jones's reagent[16] and decarboxylated. The resulting *tert*-butyl neopentyl ketone (**21**) was identical with an authentic sample.[17]

(4) For previous syntheses and characterization of **4** see the following: Dehmlow, E. V.; Dehmlow, S. S.; Marschner, F. *Chem. Ber.* **1977**, *110*, 154. Hauptmann, H.; Mader, M. *Tetrahedron Lett.* **1977**, 3151. Schröder, C. "Diplomarbeit"; Universität Hamburg, 1982. We thank Mr. Schröder for a generous sample of **4**. For synthesis of **7** see: Birkofer, L.; Richtzenhain, K. *Chem. Ber.* **1979**, *112*, 2829.

(5) These IR and ¹H NMR values are in good accord with those reported for the simpler 5-methyl-3,4-hexadien-2-one (**9**): Willy, W. E.; Thiessen, W. E. *J. Org. Chem.* **1970**, *35*, 1235. Dumont, C.; Vidal, M. *Bull. Soc. Chim. Fr.* **1973**, 2301.

(6) Leonard, N. J.; Mader, P. M. *J. Am. Chem. Soc.* **1950**, *72*, 5388. The structures of other products formed in the oxidation of **5** will be discussed elsewhere, as will independent synthesis of **5**.

(7) Closs, G. L. *Adv. Alicyclic Chem.* **1966**, *1*, 53.

(8) Albert, K.-A.; Dürr, H. *Org. Magn. Reson.* **1979**, *12*, 687. Günther, H.; Seel, H. *Ibid.* **1976**, *8*, 299.

(9) Padwa, A. *Org. Photochem.* **1974**, *4*, 261. Hartzler, H. D. In "Carbenes"; Moss, R. A., Jones, M., Jr., Eds.; Wiley, New York, 1975; Vol. 2, Chapter 2, pp 57–73.

(10) The bicycloheptene **14**, for example, rearranges rapidly at temperatures above –40 °C: Closs, G. L.; Böll, W. A.; Heyn, H.; Dev, V. *J. Am. Chem. Soc.* **1968**, *90*, 173.

(11) Hoffman, R. V.; Orphanides, G. G.; Shechter, H. *J. Am. Chem. Soc.* **1978**, *100*, 7927.

(12) Gilchrist, T. L.; Pearson, D. P. J. *J. Chem. Soc. Perkin Trans. 1* **1976**, 1257.

(13) This intramolecular etherification is analogous to the spontaneous formation of bis(cyclopropenyl) ethers on treatment of cyclopropenium ions with water: Breslow, R.; Chang, H. W. *J. Am. Chem. Soc.* **1961**, *83*, 2367.

(14) Streeper, R. D.; Gardner, P. D. *Tetrahedron Lett.* **1973**, 767.

(15) The addition of alkoxides to simple cyclopropenes occurs readily: Shields, T. C.; Gardner, P. D. *J. Am. Chem. Soc.* **1967**, *89*, 5425.

(16) Bowers, A.; Halsall, T. G.; Jones, E. R. H.; Lemin, A. J. *J. Chem. Soc.* **1953**, 2548. Djerassi, C.; Engle, R. R.; Bowers, A. *J. Org. Chem.* **1956**, *21*, 1547.

(17) This sample was prepared by a modification of a published procedure: Whitmore, F. C.; Heyd, J. W. *J. Am. Chem. Soc.* **1938**, *60*, 2030.

Cycloaddition Reactions of Alkynones

*J. Am. Chem. Soc., Vol. 106, No. 8, 1984* 2365

If the reaction of **11a** with sodium hydride is carried out in the presence of methyl iodide, two new products are found along with a small amount of **19**. The first of these is **22**, from methylation of **17**. The geometry assigned to **22** rests on the appearance of
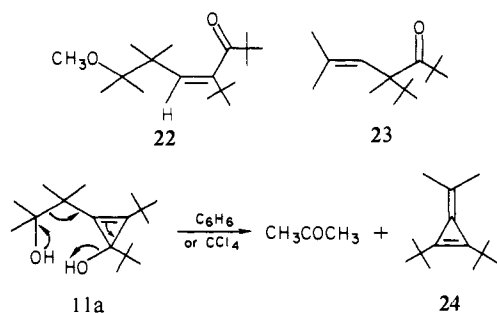
the olefinic hydrogen at 5.68 ppm in its NMR spectrum.[18] The double bond in **22** is sufficiently hindered that the compound is inert to oxidation with potassium permanganate in benzene containing dicyclohexano-18-crown-6.[19] Reaction with ruthenium tetroxide and sodium periodate in a two-phase system[20] proceeded quite slowly to give pivalil (**10**) as the only identified product. The second new substance from **11a** under these conditions was ketone **23**, the product of α methylation of enolate anion **18**.

The behavior of the only other cyclpropenol known to us is controlled by an ester grouping also present on the three-membered ring,[21] and these reactions of **11a** are accordingly of general interest. Although little is known about cyclopropenols, they are clearly reactive and unstable systems.[21,22] It is not surprising then that **11a** decomposes over a period of hours at room temperature in benzene or carbon tetrachloride. Among the products is acetone, which may be accounted for as shown. The alkylidenecyclopropene **24** probably would not survive these conditions,[22,23] and indeed we obtained no other volatile products from this decomposition. The stability of this cyclopropenol no doubt is significantly enhanced by the steric shielding of its many methyl groups[24] and by the fact that it crystallizes spontaneously upon concentration of the reaction mixture in which it is formed. In contrast, irradiation of **2** and **4** in benzene containing methanol rather than water furnishes monomethyl ether **11b** as an oil that was characterized spectroscopically but decomposed on attempted purification. In keeping with the mechanism depicted above for generation of allene **5** from **11a**, thermolysis of **11b** also led to **5**.

Turning attention now to trimethylsilyl alkynone **7**,[4] we found here also that avoidance of distillation and preparative VPC led to a relatively unstable primary [3 + 2] photoproduct. Direct purificaton by column chromatography of the reaction product from irradiation of **7** and **2** in benzene yielded **25** in 53% yield. The structure and stereochemistry of **25** are supported by its spectroscopic properties, particularly the AB quartet for the cyclopropane protons (0.735 and 0.707 ppm, *J* = 6.1 Hz) and the resonance of the olefinic proton at usually high field (s, 4.63 ppm). The geminal trimethylsilyl group should not affect this proton greatly,[25] but such shielding by the nearby spiro-fused cyclopropane

a, X = C; b, X = Si
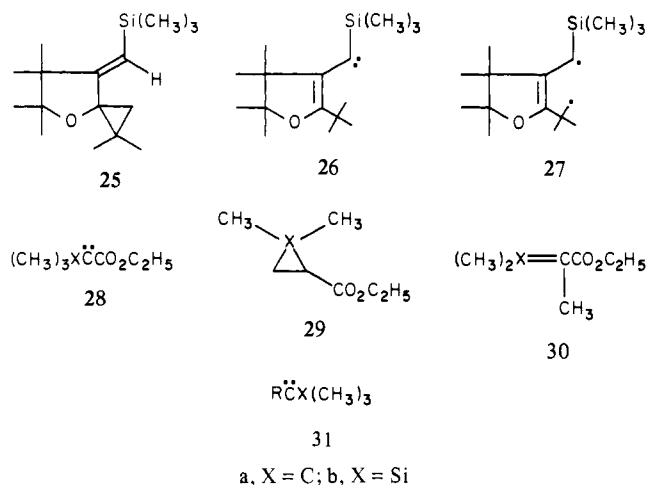
ring is reasonable[26] in the indicated geometry of the alkene. Furthermore, molecular models suggest an almost impossible degree of steric congestion in the other geometric isomer. An attractive path to this product involves hydrogen abstraction in the expected[1,3] carbene **26** to yield **27**, which may then collapse to **25**. At 75 °C in benzene solution **25** rearranges with a half-life of 49 min, yielding **8** quantitatively.[27]

The striking divergence in behavior of the two closely related ketones **4** and **7** invites consideration and explanation. Previous studies of silylcarbenes indicate that they possess normal carbene reactivity,[28,29] although not necessarily the same as that of the related all-carbon species. Carbene **28a** from *tert*-butyldiazoacetic ester rearranges to **29a** and **30a**, while the trimethylsilylcarbene **28b** yields neither **29b** nor **30b** but rather inserts into solvent.[29] The explanation that has been offered[29] for this difference is the instability of the carbon–silicon double bond and the greater bond length of the carbon–silicon single bond relative to the carbon–carbon bond.[30] We suggest that an attractive explanation for the dissimilar behavior of **4** and **7** is that carbenes **12** and **26** rearrange from different spin states. Isomerization of singlet vinyl carbenes to cyclopropenes is very favorable,[9,31] and hydrogen abstraction, as postulated for conversion of **26** to **25**, is generally considered to be a triplet process.[32] This difference would nicely rationalize the mutually exclusive paths followed by **12** and **26**. The argument based on steric effects used earlier to account for product differences within another series of vinyl carbenes[33] would seem inappropriate for distinguishing **12** and **26**. Furthermore, the suggestion that these two carbenes react from different spin states finds some support in application of the remarkably simple and successful correlation[34] between the singlet–triplet energy gap of a carbene [*E*(S) − *E*(T)] and the empirical resonance substituent constants σ°_R[35] associated with the substituents on the carbene; this relationship is given in eq 1. Use of the reported[35] values of σ°_R for trimethylsilyl and simple alkyl groups in this

(18) For comparison the olefinic hydrogens of *E*- and *Z*-3-methyl-3-penten-2-one appear at 6.64 and 5.77 ppm, respectively: McGreer, D. E.; Chiu, N. W. K.; Vinje, M. G. *Can. J. Chem.* **1965**, *43*, 1398.

(19) Sam, D. J.; Simmons, H. E. *J. Am. Chem. Soc.* **1972**, *94*, 4024. Lee, D. G. In "Oxidation in Organic Chemistry"; Trahanovsky, W. S.; Ed.; Academic Press: New York, 1982; Part D, Chapter 2 and references therein.

(20) Nakata, H. *Tetrahedron* **1963**, *19*, 1959 and references cited therein.

(21) DeBoer, C. D. *J. Chem. Soc., Chem. Commun.* **1972**, 377. Komendantov, M. I.; Domnim, I. N.; Kenbaeva, R. M.; Grigorova, T. N. *Zh. Org. Khim.* **1973**, *9*, 1420.

(22) Billups, W. E.; Blakeney, A. J. *J. Am. Chem. Soc.* **1976**, *98*, 7817.

(23) Stang, P. J.; Mangum, M. G. *J. Am. Chem. Soc.* **1975**, *97*, 3854. Billups, W. E.; Lin, L.-J. *Tetrahedron Lett.* **1983**, *24*, 1683.

(24) For examples of such stabilization in other types of cyclopropenes, see ref 22 and also: Ciabattoni, J.; Nathan, E. C., III *J. Am. Chem. Soc.* **1969**, *91*, 4766.

(25) In both *E*- and *Z*-1-(trimethylsilyl)-1-hexene the C(1) hydrogen signal appears below 5.3 ppm: Neumann, H.; Seebach, D. *Chem. Ber.* **1978**, *111*, 2785.

(26) Jackman, L. M.; Sternhell, S. "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry"; 2nd ed.; Pergamon Press: Oxford, 1969; p 98 and references cited therein.

(27) For other examples of this rearrangement of *cis*-1-methyl-2-vinylcyclopropanes see: Ellis, R. J.; Frey, H. M. *J. Chem. Soc.* **1964**, 5578.

(28) Seyferth, D.; Dow, A. W.; Menzel, H.; Flood, T. C. *J. Am. Chem. Soc.* **1968**, *90*, 1080.

(29) Schöllkopf, U.; Hoppe, D.; Rieber, N.; Jacobi, V. *Liebigs Ann. Chem.* **1969**, *730*, 1.

(30) In view of the subsequent discovery that even fully substituted silacyclopropanes are exceptionally reactive (Seyferth, D.; Annarelli, D. C. *J. Am. Chem. Soc.* **1975**, *97*, 2273; *J. Organomet. Chem.* **1976**, *117*, C51), it seems uncertain that **29b** would have been detected (ref 29) if it had been formed.

(31) Pincock, J. A.; Murray, K. P. *Can. J. Chem.* **1979**, *57*, 1403.

(32) Kirmse, W. "Carbene Chemistry"; 2nd ed.; Academic Press: New York, 1971; Chapter 7.

(33) Baron, W. J.; Hendrick, M. E.; Jones, M., Jr. *J. Am. Chem. Soc.* **1973**, *95*, 6286.

(34) Mueller, P. H.; Rondan, N. G.; Houk, K. N.; Harrison, J. F.; Hooper, D.; Willen, B. H.,; Liebman, J. F. *J. Am. Chem. Soc.* **1981**, *103*, 5049.

(35) Taft, R. W.; Hehre, W. J.; Topsom, R. O. *Prog. Phys. Org. Chem.* **1976**, *12*, 159.

$$E(S) - E(T) = 84.5\sum \sigma^{\circ}_{R} + 13 \qquad (1)$$

equation leads to the prediction that the difference between singlet–triplet gaps for **31a** and **31b**, ($[E(S) - E(T)]_{31a} - [E(S) - E(T)]_{31b}$), should be about -14 kcal/mol. That is, whatever the gap is in **31a**, it should be ~14 kcal/mol more favorable for the triplet in **31b**. It would of course be more informative to estimate specific energy gaps for **31a** and **31b** ($R = CH_3OCH=CH$ or equivalent), which would structurally approximate **12** and **26**. Unfortunately, however, no σ°_R value is available for β-methoxyvinyl or other appropriate groups. Two extreme assumptions are that σ°_R for β-methoxyvinyl is (1) the same as for methoxyl $(-0.45)^{35}$ or alternatively (2) the same as for vinyl (-0.03).^{35} These assumptions yield a singlet–triplet gap of -34 and $+1$ kcal/mol, respectively, for **31a** ($R = CH_3OCH=CH$). Such a spread of possible values is too broad to be useful, but it does incorporate the interesting range in which the all-carbon species **31a** ($R = CH_3OCH=CH$) is predicted to be a ground-state singlet and the corresponding silicon-containing **31b** a ground-state triplet. Such a difference would lend strong support to our suggestion that **12** reacts from the singlet state and **26** from the triplet. At the very least, the relationship of eq 1 implies that a trimethylsilyl-substituted carbene (as **26**) is much more likely to have a triplet ground state than is the related all-carbon species (as **12**).

Experimental Section

Materials and Equipment. General procedures have been described previously.^{36} All VPC was carried out by using a Varian Aerograph Model 920 gas chromatograph with one of the following columns: A, 22.5% Carbowax 20 M, 8 ft; B, 25% QF-1, 3 ft; and C, 22.5% Carbowax 20 M, 4 ft. All columns were packed in 0.25-in. aluminum tubing with 45/60 Chromosorb W. Uranium glass filters were used in all photolyses. In addition to a Varian T-60A NMR spectrometer, a Nicolet/Oxford NT-300 (300 MHz) instrument was also employed. Unless otherwise noted, all pure compounds were obtained as colorless oils; products are usually listed in order of their elution upon VPC.

Preparation of 2,2,6,6-Tetramethyl-4-heptyn-3-one (4). First *tert*-butylacetylene (4.93 g, 60 mmol) was converted to its salt by reaction with ethylmagnesium bromide (22.5 mL of a 2.8 M solution, 63 mmol) in THF (70 mL), and pivalaldehyde (5.0 g, 58 mmol) was then added. Standard workup gave crude carbinol (9.95 g) which was treated with Jones's reagent^{16} in the usual way. The usual workup and distillation gave slightly yellow **4** (7.43 g, 77%), bp 72–4 °C (11 mm), having IR and NMR spectra comparable with those published.^{4}

Photolysis of 4 with 2,3-Dimethyl-2-butene (2). A solution of **4** (499 mg, 3 mmol) and **2** (2.525 g, 30 mmol) in C_6H_6 (80 mL) was irradiated overnight. VPC analysis (column A, 125 °C) indicated little remaining **4**. Solvent was removed in vacuo and the residue was bulb-to-bulb distilled (80–125 °C, 0.5 mm) to afford a yellow oil (562 mg). VPC analysis indicated five components in the indicated ratios and $\sim50\%$ of material eluted as broad peaks at long retention time. The first component (12%) was **4**. The second component was **5** (63%): IR 2980 (s), 2925 (m), 2885 (m), 1950 (w), 1670 (s), 1475 (m), 1458 (m) 1387 (w), 1359 (m), 1127 (m), 1041 (w), 892 (m) cm^{-1}; NMR (60 MHz) δ 1.80 (s, 6 H), 1.16 (s, 9 H), 1.10 (s, 9 H); ^{13}C NMR δ 208.46, 204.12, 110.94, 98.55, 45.05, 34.75, 29.83, 27.96, 19.99. Anal. ($C_{14}H_{24}O$) C, H. The third component (7%) was **6a**: IR 3055 (w), 2980 (s), 2945 (s), 2880 (m), 2235 (w), 1477 (m), 1450 (m), 1382 (m), 1365 (m), 1362 (m), 1262 (m), 1087 (m), 1017 (m), 961 (m), 936 cm^{-1} (m); NMR (60 MHz) δ 1.47 (s, 3 H), 1.33 (s, 3 H), 1.26, 1.25 (both s, total 12 H), 1.20 (s, 3 H), 1.08 (s, 9 H); mass spectrum m/z 193.1599 [(M – *t*-Bu)$^+$, calcd for $C_{13}H_{21}O$, 193.1592]. The fourth (12%) and fifth (6%) components have not been identified. Subsequent irradiations of **4** (499 mg, 3 mmol) and **2** (1.26 g, 15 mmol) in C_6H_6 (100 mL) contained H_2O (250 μL) and were complete in 16–18 h. VPC analysis on column A at 150 °C indicated formation primarily of one long retention time product. This peak was not observed on old Carbowax 20 M columns or on columns prepared from other stationary phases. Solvents were removed in vacuo without external heating to afford ~730 mg of a crystalline residue. Further purification, normally unnecessary for subsequent reactions, was achieved by trituration with cold pentane yielding pure **11a**: mp 78–80 °C; IR (CHCl$_3$) 3645 (w), 3430 (s, br), 2980 (s), 2890 (s), 1800 (br, w), 1459 (s), 1381 (s), 1360 (s), 1143 (s), 948 cm^{-1} (s); ^{1}H NMR (300 MHz) δ 3.60 (br s, 1 H), 2.27 (br s, 1 H), 1.271, 1.257, 1.250 (all s, 15 H), 1.204,

1.192 (both s, 6 H), 1.021 (s, 9 H); ^{13}C NMR δ 133.28, 126.87, 73.33, 67.68, 43.51, 35.86, 31.62, 30.80, 28.80, 26.71, 25.93, 23.80, 23.66. Anal. ($C_{17}H_{32}O_2$) C, H. In solution, the cyclopropenol decomposes rapidly, but when crystalline, it can be stored at -20 °C indefinitely.

Thermolysis of 1,3-Di-*tert*-butyl-2-(2-hydroxy-1,1,2-trimethylpropyl)-2-cyclopropen-1-ol (11a). Crude crystalline **11a** (978 mg, obtained from 4 mmol of **4**) in a 100-mL pear-shaped flask fitted with a short-path distillation apparatus was heated from 25 to 150 °C at 0.5 torr over a period of 0.75 h. The distillate was taken up in pentane, washed with H_2O, and concentrated. VPC analysis (column A, 150 °C) showed a similar distribution of products as described above. The major component was collected and identified as **5** (124 mg, 15%).

Oxidation of 4-*tert*-Butyl-2,2,6-trimethyl-4,5-heptadien-3-one (5) with Ruthenium Tetroxide. To an anhydrous CCl_4 solution (10 mL) of RuO_4, prepared from RuO_2 (77 mg, 0.576 mmol) and 0.25 N $NaIO_4$, was added allene **5** (37.7 mg, 0.181 mmol). The mixture was stirred at 25 °C for 0.5 h before 2-propanol was added to destroy excess oxidant. VPC analysis (column B, 120 °C) indicated the formation of three compounds. The first-eluted, yellow component was identified as pivalil (**10**) by comparison of its IR and NMR spectra with those of an authentic sample obtained by oxidation of pivaloin.^{6} The structures of the additional products will be discussed elsewhere.

Treatment of 11a with Sodium Hydride. To a suspension of NaH (600 mg of a 60% oil dispersion, 15 mmol) in dry THF (25 mL) was added dropwise **11a** (519 mg, obtained from 2 mmol of **4**) dissolved in THF (25 mL). The mixture was stirred at 25 °C for 3 days before H_2O was added to destroy excess NaH. VPC analysis of the residue obtained after concentration of the pentane extract (column A, 150 °C) indicated the formation of one compound. Bulb-to-bulb distillation gave virtually pure **19** (343 mg, 84%): bp 80–110 °C (0.5 mm); IR 2985 (s), 2925 (s), 2885 (s), 1700 (s), 1475 (m), 1388 (m), 1360 (m), 1058 (s), 1000 (m), 889 cm^{-1} (m); NMR (60 MHz) δ 5.11 (br d, $J = 11$ Hz, 1 H), 3.52 (d, $J = 10.5$ Hz, 1 H), 1.73 and 1.67 (both d, $J = 1.5$ Hz, 6 H), 1.06 (s, 9 H), 0.91 (s, 9 H). Anal. ($C_{14}H_{26}O$) C, H.

Oxidation of 4-*tert*-Butyl-2,2,6-trimethyl-5-hepten-3-one (19) with Ruthenium Tetroxide. To a solution of RuO_4 (prepared from RuO_2, 160 mg, 1.2 mmol) in CCl_4 (20 mL) was added **19** (80 mg, 0.38 mmol). The mixture was stirred for 1 h at 25 °C before 2-propanol was added. After filtration and concentration, VPC analysis (column A, 150 °C) indicated the formation of one compound which was collected and identified as **20**: IR 2990 (s), 2925 (m), 2890 (m), 2845 (w), 2730 (w), 1726 (s), 1692 (s), 1474 (m), 1394 (w), 1366 (m), 1319 (w), 1068 (m), 989 (m), 969 cm^{-1} (w); NMR (60 MHz) δ 9.51 (d, $J = 5$ Hz, 1 H), 3.58 (d, $J = 5$ Hz, 1 H), 1.07 (s, 18 Hz). Crude **20** in acetone was treated with excess Jones's reagent^{16} for 1 h at 15 °C. Standard workup and preparative VPC yielded **21**, identical in all respects to an authentic sample.^{17}

Treatment of 4 with Sodium Hydride and Iodomethane. To a suspension of NaH (800 mg of a 60% oil dispersion, 20 mmol) in dry THF (25 mL) containing CH$_3$I (3.55 g, 25 mmol) was added **11a** (730 mg, from 3 mmol of **4**) in THF (20 mL). After the mixture was stirred at 25 °C for 3 days, water was added and the mixture was extracted with pentane. The residue obtained after removal of pentane was bulb-to-bulb distilled to give 700 mg that VPC analysis (column A, 150 °C) indicated to be a three-component mixture. The first component (6%) was **19**. The second component (21%) was **23**: IR 2990 (s), 2945 (s), 2895 (s), 1688 (s), 1475 (m), 1386 (m), 1356 (m), 1030 (w), 960 (m), 861 cm^{-1} (m); NMR (60 MHz) δ 5.25 (m, 1 H), 1.75 (d, $J = 2$ Hz, 3 H), 1.57 (d, $J = 2$ Hz, 3 H), 1.35 (s, 3 H), 1.17 (s, 9 H), 0.96 (s, 9 H). Anal. ($C_{15}H_{28}O$) C, H. The third component (73%) was **22**: IR 2990 (s), 2880 (m), 2845 (w), 1676 (s), 1475 (w), 1387 (w), 1374 (m), 1360 (m), 1135 (s), 1064 cm^{-1} (w); NMR (300 MHz) δ 5.68 (s, 1 H), 3.19 (s, 3 H), 1.24, 1.23, 1.22 (all s, total 15 H), 1.09 (s, 9 H); CI mass spectrum, m/z 283.2639 [(M + 1)$^+$, calcd for $C_{18}H_{35}O_2$, 283.2637].

Formation of Acetone in the Decomposition of 4. A C_6H_6 solution (100 mL) of **11a** (from photolysis of 499 mg of **4**) was allowed to stand at room temperature until VPC analysis indicated a peak with the retention time of acetone and no remaining **11a**. The solution was transferred to a distillation apparatus and distilled to give ~5 mL of a fraction with bp 65–75 °C. After dinitrophenylhydrazine reagent^{37} (15 drops) was added, the mixture was heated on a steam bath for 5 min and cooled. Solvent was removed in vacuo and the residue was recrystallized from aqueous ethanol to afford acetone DNP, mp 122–123 °C, mixture mp 123–124 °C, authentic compound mp 124 °C (lit.^{38} mp 126 °C), IR virtually identical with that of authentic compound.

Photolysis of 4 and 2 in Benzene–Methanol. A mixture of **4** (333 mg, 2 mmol), **2** (1.5 mL, 12 mmol), C_6H_6 (100 mL), and MeOH (800 μL, 20 mmol) was irradiated until little **4** remained (16 h). Solvent was

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removed in vacuo to yield crude **11b** (547 mg): IR 3450 (br), 2990 (s), 2885 (m), 2840 (w), 1800 (w), 1475 (m), 1378 (m), 1358 (m), 1066 cm^{-1} (s). Thermolysis of **11b** following the method described above for **11a** also gave **5** (62 mg, 15%).

Photolysis of 4,4-Dimethyl-1-(trimethylsilyl)-1-pentyn-3-one (7) and 2,3-Dimethyl-2-butene (2). A solution of **7**[4] (456 mg, 2.5 mmol) and **2** (1.052 g, 12.5 mmol) in C_6H_6 (50 mL) was irradiated in the usual fashion. After 6 h, VPC analysis (column, C, 115 °C) indicated ~10% of **7** remaining and the formation of two products. Removal of solvent and bulb-to-bulb distillation of this residue (80–130 °C, 0.1 torr) yielded an oil (525 mg, 80%) that was subjected to preparative VPC. First eluted was **6b** (12%): IR 3055 (w), 2975 (s), 2165 (w), 1477 (m), 1384 (m), 1360 (m), 1244 (s), 1069 (s), 832 cm^{-1} (s); NMR (60 MHz) δ 1.43, 1.31, 1.25, 1.17, 1.07 (all s, total 21 H), 0.19 (s, 9 H). Anal. ($C_{16}H_{30}OSi$) C, H. The second component (68%) was **8**: IR 3100 (w), 2975 (s), 1679 (w), 1652 (w), 1384 (w), 1374 (w), 1362 (m), 1241 (s), 1189 (s), 941 (m), 880 (m), 840 cm^{-1} (s); NMR (60 MHz) δ 4.73 (m, 2 H), 2.68 (br s, 2 H), 1.72 (m, 3 H), 1.31 (s, 2 H), 1.20 (s, 3 H), 0.88 (s, 3 H), 0.06 (s, 9 H). Anal. ($C_{16}H_{30}OSi$) C, H.

Flash chromatography[39] using 1.5% Et_2O/hexanes of the oil (277 mg) obtained from the photolysate gave **25** (141 mg, 51%): IR 3075 (w), 2985 (s), 2875 (m), 1622 (m), 1385 (m), 1370 (m), 1363 (m), 1245 (s),

1147 (m), 969 (m), 871 (m), 847 (s), 780 cm^{-1} (w); NMR (300 MHz) δ 4.68 (s, 1 H), 1.15, 1.13, 1.12, 1.10, 1.03, 0.94 (all s, 18 H), 0.735 (d, *J* = 6.0 Hz, 1 H), 0.707 (d, *J* = 6 Hz, 1 H), 0.175 (s, 9 H); mass spectrum *m/z* 266.2070 (M$^+$, calcd for $C_{16}H_{30}SiO$, 266.2074).

Thermolysis of (*E*)-1,1,5,5,6,6-Hexamethyl-7-((trimethylsilyl)-methylene)-4-oxaspiro[2.4]heptane (25). Solutions of **25** in C_6D_6 in sealed tubes were heated and monitored by NMR spectroscopy. At 100 °C, **25** quantitatively rearranged to **8** within 0.5 h; at 75.0 °C, 47% of **25** had rearranged in 0.75 h.

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Interaction of Thiones with Molecular Diiodine.[1] The Crystal Structures of Dithizone–Diiodine, Ethylenethiourea–Bis(diiodine), Bis(ethylenethiourea)–Tris(diiodine), Bis(dithizone)–Heptakis(diiodine), and 1-(1-Imidazolin-2-yl)-2-thioxoimidazolidinium Triiodide–(Ethylenethiourea–Diiodine)

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Abstract: The crystal structures of four neutral charge-transfer molecular compounds formed between dithizone or ethylenethiourea, as donors, and diiodine, as acceptor, are described. Dithizone–I_2 is monoclinic (*a* = 12.233 (8) Å, *b* = 11.713 (8) Å, *c* = 12.030 (8) Å, β = 102.8 (1)°, *Z* = 4, space group *P2₁/n*; R_F = 0.059) and contains discrete moieties of the molecular formula with the diiodine fragment approximately normal to the dithizone fragment. Ethylenethiourea–2(I_2) is triclinic (*a* = 10.276 (7) Å, *b* = 9.176 (6) Å, *c* = 6.792 (5) Å, α = 105.1 (1)°, β = 81.0 (1)°, γ = 96.4 (1)°, *Z* = 2, space group *P$\bar{1}$*; R_F = 0.041) and contains discrete moieties of the molecular formula; the moiety as a whole has the shape of a twisted U. 2(Ethylenethiourea)–3(I_2) is triclinic (*a* = 9.362 (6) Å, *b* = 9.176 (6) Å, *c* = 7.434 (5) Å, α = 116.9 (1)°, β = 72.5 (1)°, γ = 114.7 (1)°, *Z* = 1, space group *P$\bar{1}$*; R_F = 0.063) and has a centrosymmetric twisted-chain structure with three iodine molecules held between the two donor molecules; this structure is similar to that of bis(((triphenylphosphine sulfide-*S*)iodine)–*I*)iodine (Bransford; Meyers *Cryst. Struct. Commun.* **1978**, *7*, 697–702). 2(Dithizone)–7(I_2) is triclinic (*a* = 13.312 (8) Å, *b* = 20.637 (7) Å, *c* = 9.746 (6) Å, α = 101.8 (1)°, β = 87.1 (1)°, γ = 109.4 (1)°, *Z* = 1, space group *P$\bar{1}$*; R_F = 0.086) and has a centrosymmetric, branched twisted chain of iodine molecules held at its ends by strong sulfur–iodine interactions. Intermediate between these neutral structures and the polyiodide salts is the salt–molecule complex 1-(1-imidazolin-2-yl)-2-thioxoimidazolidinium triiodide–(ethylenethiourea–diiodine) (monoclinic, *a* = 11.102 (7) Å, *b* = 11.193 (7) Å, *c* = 9.551 (6) Å, β = 110.0 (1)°, *Z* = 2, space group *P2₁*; R_F = 0.051), which contains discrete moieties of ethylenethiourea–I_2 together with the cations and anions of the second component. For these compounds, and some others, the values of *d*(S–I) plotted against *d*(I–I) fall on an approximately hyperbolic curve.

Diiodine (I_2) forms 1:1 molecular compounds of the charge-transfer type with a variety of molecules containing oxygen, nitrogen, sulfur, or selenium heteroatoms. Many crystal structures have been reported.[3,4] Diiodine in combination with ionic iodide

species (as I$^-$ or I₃$^-$) forms a large range of oligomeric anionic polyiodides; again many crystal structures have been reported.[5,6]

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