J. Org. Chem. **1993**, *58*, 6629–6633

Reactions of Methyl(2,5,5-trimethyl-1-cyclopenten-1-yl)carbene and the Photochemistry of 2-(1-Propynyl)-2,5,5-trimethylcyclopentanone

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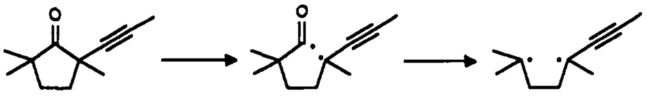
Dienes 7 and 8 are formed both on photolysis of 1 and on triplet decomposition of diazo compound 14. These observations appear to imply that biradical 3, a photochemical intermediate formed from 1, closes to carbene 9, from which 7 and 8 result on migration of hydrogen. It is shown, however, that dienes 7 and 8 are secondary products formed both on photolysis of 1 and on decomposition of 14. Photodimer 28 is also formed on irradiation of 1, and it is suggested that 28 arises by 1,3 acyl shift of 1 to allenic ketone 29 followed by head-to-head dimerization of 29 at the β,γ double bond.

In a previous investigation, Rudolph, Margaretha, and Agosta demonstrated that irradiation of cyclopentanone 1 leads by way of α-cleavage to 2 and subsequent decarbonylation to 3.[2] Hydrogen transfer in 2 gives both isomers of aldehyde 4, while cyclization and fragmentation of 3 furnish 5 and 6, respectively. In addition to these straightforward products, the two isomeric dienes 7 and 8 are also formed in this reaction, and it was suggested that they were the product of 1,5 closure of 3 to vinyl carbene 9, followed by hydrogen migration.[2] Our laboratories have studied a number of other cyclizations of alkyl propargyl 1,4 biradicals to vinyl carbenes[3,4] but none from a biradical so simple as 3. Formation of 7 and 8 from 9 requires a secondary hydrogen shift in cisoid dienes 10 and 11, which are reasonable[5] products from 9 or else unexpected migration of a ring allylic hydrogen atom in 9. In the original study there was no evidence for 10 or 11[2] and so to clarify the origin of 7 and 8 we have examined the products formed from independently prepared singlet and triplet carbene 9. In the course of this work we have also reinvestigated the photochemistry of 1.[6] We now report the following: (1) Dienes 7 and 8 are indeed among the products resulting from triplet-sensitized formation of 9, in keeping with the originally proposed intermediacy of 9 in the photochemistry of 1. (2) Dienes 7 and 8 are also formed on irradiation of 1 in pentane, as previously reported. (3) Despite these auspicious observations, dienes 7 and 8 are secondary products in both these reactions. As we explain below, there is no reason to consider carbene 9 an intermediate in the observed photochemistry of 1. (4) Irradiation of 1 at higher concentration than previously employed furnishes a dimer of 1 in addition to the products previously reported. These points are discussed below.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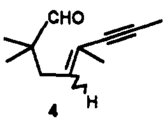
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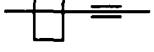
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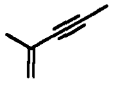
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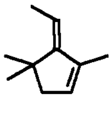
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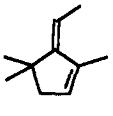
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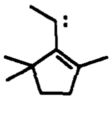
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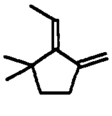
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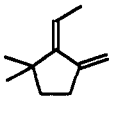
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Preparation and Reactions of Carbene 9. Ketone 12, prepared as previously described,[7] was converted to its tosylhydrazone and thence into the corresponding sodium salt 13 on treatment with sodium methoxide in methanol. Heating a suspension of 13 in benzene furnished a reddish solution of diazo compound 14,[8] which was partially purified before use. Both 13 and 14 were employed as precursors of carbene 9 under various conditions. A suspension of thoroughly dried 13 in pentane was decomposed to singlet 9 on direct irradiation through Pyrex ($\lambda > 280$ nm).[8] This furnished a mixture of isomeric hydrocarbons that consisted mainly of 11 and 15 plus a small amount of 17. Qualitatively similar results were obtained when a solution of diazo compound 14 was photolyzed in pentane. The major products arise by 1,2 (15) and 1,4 (11) hydrogen shifts in 9, both well-precedented reactions of singlet vinylcarbenes.[9] Bicyclic hydrocarbon 17 can be explained as the product of carbene–carbene rearrangement[10] of 9 to 16, followed by insertion into the adjacent methyl group, as shown in eq 1. If 13 is not carefully dried before irradiation, residual methanol that is present from preparation of 13 traps carbenes 9 and 16 to give methyl ethers 18 and 19, respectively, as the major products. Irradiation of 13 in solvent methanol yielded only 18. Heating a suspension of 13 in benzene

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[1] Institut für Organische Chemie, Universität Hamburg.

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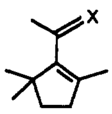
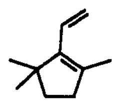


12, X = O
13, X = NNTs$^-$ Na$^+$
14, X = N_2



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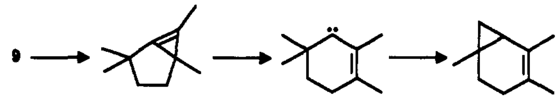

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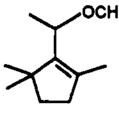

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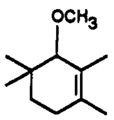

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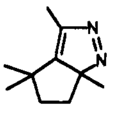

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for 12 h at reflux furnished pyrazole **20** as the main product,[11] along with minor amounts of **11** and **17**.

Triplet **9** was available from sensitized decomposition of **13** and **14**.[12] What appeared to be the best results were obtained using acetone as solvent and sensitizer for decomposition of **14**. These conditions gave dienes **10**, **11**, and **15**, along with **7**. With 5 equiv of benzophenone in solvent pentane as sensitizer for **14**, these same products plus a small amount of **17** were formed. Using less benzophenone gave more **17** and less **7** and **10**, suggesting that **17** arises only from singlet **9** and that **7** and **10** are triplet products. Similar results were obtained with benzophenone as sensitizer for decomposition of **13**. Products and yields for the various singlet and triplet reactions of **13** and **14** are gathered in Table I.

Formation of **7** from **9** specifically under triplet conditions was of course very interesting, since this is one geometric isomer of the diene originally suggested to arise from **1** by way of **9**.[2] Further observations, however, showed that **7** has no mechanistic significance in the chemistry of **9**. An NMR sample of **10** in chloroform-*d* slowly rearranged to **7** on standing, suggesting that this allylic isomerization can be catalyzed by traces of acid. More significantly, on irradiation in acetone under the conditions used to decompose diazo compound **14**, a sample of **10** (containing a small amount of **7**) was isomerized quantitatively to **7**. Thus, **7** can be explained as a secondary product from carbene **9**. Irradiation of **10** in pentane led to no reaction, suggesting that photochemical isomerization of **10** is mediated by triplet acetone. Diene **15** was recovered unchanged from similar irradiation in acetone.

The structures of these hydrocarbons and methyl ethers rest on spectroscopic data, particularly 300-MHz ^{1}H NMR, together with the following observations. Diene **15** was independently available on treatment of enol triflate **21**[7] with tributylvinylstannane in the presence of tetrakis(triphenylphosphine)palladium.[7] The NOESY spectrum of **10** confirmed the assigned stereochemistry of the ethylidene group. The hydrocarbons of particular interest, **7** and **8**, were independently prepared through dehydration of **22**, which was available on borohydride reduction of **12**. Treatment of **22** with 2,4-dinitrobenzenesulfenyl chloride gave sulfenate **23**, which immediately underwent [2,3] sigmatropic rearrangement to the allylic sulfoxide and then elimination to form largely dienes **7** and **8**, along with smaller amounts of **10**, **11**, and **15**.[13] The 1:1 mixture of **7** and **8** obtained was not separable under any chromatographic conditions tried.

Table I. Products Derived from Photolysis or Thermolysis of 13 and 14

entry	substrate	condns[a]	products (yields, %)			
1	13	B	18 (40)	19 (15)	11 (6)	15 (5)
2	13	A	17 (3)		11 (26)	15 (35)
3	13	C	17 (8)		11 (15)	15 (15)
4	13	D	17 (8)	10 (15)	11 (13)	15 (7)
5	13	E	17 (10)	10 (18)	11 (15)	15 (5)
6	14	A	17 (20)		11 (18)	15 (30)
7	14	C	17 (35)		11 (16)	15 (15)
8	14	D	17 (10)	10 (10)	11 (15)	15 (12)
9	14	E		10 (55)	11 (6)	15 (8)
10	13	F	17 (24)		11 (5)	20 (62)

[a] Conditions: (A) pentane, photolysis; (B) pentane, salt with trace amounts of methanol, photolysis; (C) pentane + 1.0 equiv of benzophenone, photolysis; (D) pentane + 5.0 equiv of benzophenone, photolysis; (E) acetone, photolysis; (F) benzene, reflux.

Photochemistry of 1. Before the experiments with carbene **9** were completed, we had also begun reinvestigation of the photochemistry of **1**. Irradiation ($\lambda > 280$ nm) of a dilute solution ($\sim$0.01 M) of **1** in pentane yielded products **4**–**8**, as reported.[2] Efforts to quench these reactions of **1** (0.05 M in pentane) with piperylene (up to 1.05 M) led to no change in the nature or distribution of products. Attempts to triplet-sensitize photolysis of **1** (0.05 M) in acetone as solvent led to much slower reaction with no change in the products. Some, if not all, reaction of **1** under these conditions resulted from its competitive direct absorption of light. These results are consistent with reaction of **1** from S_1. The 1,3 acyl shift in β,γ unsaturated ketones is specifically a singlet reaction,[14] and α-cleavage from the singlet is observed in highly substituted alkanones.[15] This behavior of **1** led us to question the postulated pathway to **7** and **8** through cyclization of biradical **3** to carbene **9** because there is considerable evidence in other systems that such cyclization takes place only in triplet alkylpropargyl biradicals.[3] In addition, we have previously reported that singlet biradical **24** formed on loss of nitrogen from the related 1,1-diazene does not cyclize to **25**.[16]

These observations led us to seek some other explanation for the presence of **7** and **8** in the photolysis mixture from **1**. A possible alternative route to these dienes is through α-cleavage of the appropriate isomer of aldehyde **4**, 1,5 cyclization of resulting radical **26** to **27**, and finally abstraction of hydrogen from solvent (eq 2). Under the conditions used for photolysis of **1**, the mixture of aldehydes **4** reacted smoothly to give **7** and **8** as the only volatile products. These dienes then are secondary products that have no mechanistic significance in the photochemistry of **1**. These various experiments imply that the photochemistry of **1** proceeds from S_1 and that there is no opportunity to observe whether or not triplet **3** closes to **9**.

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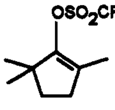

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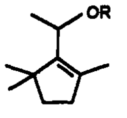
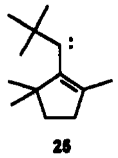


22, R = H

23, R = $SC_6H_3(NO_2)_2$

24



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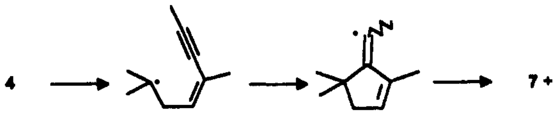

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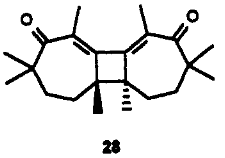
Photodimer of 1. One unexpected finding in our investigation was the formation of a previously unnoted dimer of 1. Irradiation of 1 at higher concentration (0.15 M) than that previously used (0.01 M) led to much slower photolysis and a new highly crystalline major product (55%), accompanied by 4–8 in reduced yield. Spectroscopic data indicated that this new product was a symmetrical dimer of 1, and as we have reported elsewhere,[17] X-ray analysis revealed that it is the trans-fused head-to-head dimer 28. The simplest pathway to this novel product is α-cleavage of 1 to 2 followed by closure to cycloheptadienone 29, which then dimerizes. Formation of 29 formally requires a 1,3 acyl shift, for which there is precedent in the photochemistry of other β,γ acetylenic and olefinic ketones.[14] Dimerization of 29 to 28 requires selective[18] head-to-head [2 + 2] cycloaddition at the β,γ double bond. Selective formation of a head-to-head dimer has precedent in the spontaneous head-to-head self-addition of 1,2-cycloheptadiene (30).[19a] To the best of our knowledge, formation of 28 is the first evidence for dimerization of an allenic ketone.[19b] Selective reaction only at the β,γ double bond is, therefore, noteworthy. Efforts to trap 29 with a variety of agents failed.[20] Since 28 is formed only from relatively concentrated solutions of 1, allenic ketone 29 appears to be destroyed by processes competitive with its dimerization. When 28 is formed, it must competitively absorb light,[21] and this presumably accounts for the slower photochemical reaction of 1 at higher concentration.



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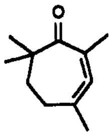

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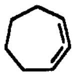

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Experimental Section

General Procedures. All operations were carried out under an inert atmosphere (argon) unless otherwise mentioned. Melting points were determined by using a Thomas-Hoover capillary melting point apparatus and are corrected. IR spectra were determined on a Perkin-Elmer 1870 Fourier transform spectrometer either neat or in KBr pellets, and absorption values are given in reciprocal centimeters (cm^{-1}) (s, strong, m, medium; w, weak; br, broad). NMR spectra were recorded on a General Electric QE300 (300 MHz for protons) instrument and are reported in parts per million (ppm) downfield from tetramethylsilane as an internal standard (δ) in $CDCl_3$ (unless otherwise mentioned: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad). Low-resolution mass spectral analyses were performed on a Hewlett-Packard HP5890/5988A GC/MS. High-resolution mass spectral analyses were performed on VG-70250 magnetic sector instrument. All spinning disk chromatographic separations were carried out on a Chromatotron (Harrison Model-7924 T) using silica gel coated (1-, 2-, or 4-mm thick) glass rotors. Analytical gas chromatography (GLC) was carried out on a Hewlett-Packard HP5890 instrument using an Alltech Econo-Cap (30-m × 0.25-mm) SE-30 capillary column with a film thickness of 0.25 μm. Preparative GLC was carried out on a Varian Aerograph Model 920 or a Gow-Mac 550P instrument using a 25% QF-1 on Chromosorb-W (10 ft × 0.25 in.) column. All organic extracts were washed with saturated aqueous NaCl and dried over anhydrous $MgSO_4$ prior to solvent removal. All solutions for photolyses were purged with argon for a period of 15 min prior to irradiation. A medium-pressure 450-W Hanovia mercury arc lamp was used for irradiations. All solvents were purified and/or dried before use wherever it was deemed necessary. Yields of isolated compounds are expressed in grams and percentage while estimated yields (by capillary GLC) are expressed only in percentage.

Tosylhydrazone of 1-Acetyl-2,2,5-trimethylcyclopent-5-ene. To a solution of 1-acetyl-2,2,5-trimethylcyclopent-5-ene[7] (12) (1 g, 6.57 mmol) in anhydrous ethanol (3 mL) was added tosylhydrazine (1.225 g, 6.57 mmol). The reaction mixture was heated under reflux for a period of 1 h and was cooled to room temperature. Addition of cold water precipitated a white solid. This was crystallized from methanol to obtain pure tosylhydrazone as a white crystalline solid (1.96 g, 91%) (mp 142–143 °C): IR (KBr pellet) 3209 (s), 2965 (s), 2943 (s), 2925 (s), 2862 (s), 2837 (s), 1647 (m), 1597 (s), 1496 (m), 1442 (s), 1377 (s), 1344 (s), 1329 (s), 1163 (s), 1094 (m), 1056 (m), 1020 (m), 904 (s); ^1H NMR δ 7.853 (d, J = 7.5 Hz, 2 H), 7.286 (d, J = 9.15 Hz, 2 H), 2.414 (s, 3 H), 2.236 (t, J = 6.9 Hz, 1 H), 1.195 (s, 3 H), 1.897–1.961 (m, 1 H), 1.587 (s, 3 H), 1.568–1.613 (m, 2 H), 1.345 (s, 1 H), 0.948 (s, 3 H), 0.944 (s, 3 H). Anal. Calcd for $C_{17}H_{24}N_2SO_2$: C, 63.75; H, 7.50; N, 8.75. Found: C, 63.75; H, 7.51; N, 8.84.

Irradiation of Sodium Salt 13 in Methanol. A mixture of the above tosylhydrazone (160 mg, 0.55 mmol) and MeONa (30 mg, 0.55 mmol) was stirred in dry methanol (20 mL) for 1 h while being flushed with argon. The resultant clear solution was irradiated using a 450-W lamp for 3 h. A pink color started appearing in about 30 min, which became intense in 2 h. By the end of the irradiation the solution had turned colorless. This was evaporated to dryness under vacuum, and the residual oil was subjected to chromatography to obtain 1-(1-methoxyethyl)-2,2,5-trimethylcyclopent-5-ene (18) (55 mg, 65%): IR (neat) 2943 (s), 2865 (s), 2817 (s), 1667 (w), 1462 (m), 1372 (m), 1209 (m), 1118 (s), 1088 (s); ^1H NMR δ 3.839 (q, J = 6.6 Hz, 1 H), 3.191 (s, 3 H), 2.206 (m, 2 H), 1.753 (s, 3 H), 1.618 (m, 2 H), 1.323 (d, J = 6.60 Hz, 3 H), 1.048 (s, 3 H), 1.011 (s, 3 H); ^{13}C NMR δ 14.615 (q), 21.878 (q), 27.173 (q), 28.026 (q), 35.801 (t), 40.120 (t), 47.071 (s), 55.787 (q), 74.115 (d), 134.227 (s), 141.989 (s); LRMS (EI) 168 (M^+, 2), 153 (1), 137 (2), 122 (2), 121 (10), 112 (100), 105 (5), 97 (66), 93 (3), 67 (9); HRMS m/z 168.1530 $(M)^+$, calcd for $C_{11}H_{20}O$ 168.1514.

General Procedure for Irradiation of 13 in Pentane or Acetone. A mixture of the tosylhydrazone (500 mg, 1.56 mmol) and MeONa (93 mg, 1.71 mmol) in anhydrous MeOH (20 mL) was stirred under inert atmosphere for 1 h and was evaporated to dryness in a rotary evaporator. Sodium salt 13 thus obtained as a white solid was kept under high vacuum for 48 h and stirred in dry pentane or acetone for 2 h while being flushed with argon to obtain a finely devided suspension. This slurry was irradiated while being stirred vigorously for 6 h. The irradiated suspension was taken up in ether, washed with water and brine, dried, and evaporated. The oil thus obtained was subjected to preparative GLC to isolate pure products.

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[18] Gas chromatographic and mass spectral evidence indicates formation of at least four other dimers in a combined yield of ~10%.

[19] (a) Bottini, A. T.; Frost, K. A., II; Anderson, B. R.; Dev, V. *Tetrahedron* **1973**, *29*, 1975 and references cited therein. (b) Eaton, P. E.; Stubbs, C. E. *J. Am. Chem. Soc.* **1967**, *89*, 5722. (c) Johnson, R. P. *Chem. Rev.* **1989**, *89*, 1111.

[20] Reagents tried included methanol, furan, methyl acrylate, acrylonitrile, 1,1-dimethylallene, and dimethyl fumarate.

[21] UV of 28: λ_{max} 281 nm (ε 7708), 288 (8676).

The irradiation of **13** (prepared from 500 mg of tosylhydrazone) in pentane gave **11** (55 mg, 26%), **15** (74 mg, 35%), and **17** (7 mg, 3%).

(*Z*)-1-Ethylidene-2-methylene-5,5-dimethylcyclopentane (11): IR (neat) 2950 (s), 2865 (s), 1652 (w), 1616 (w), 1453 (m), 1382 (m), 1361 (w), 1155 (w), 1013 (m), 879 (s), 811 (m) cm^{-1}; ^{1}H NMR (C_6D_6) δ 5.438 (q, J = 7.2 Hz, 1 H), 5.270 (s, 1 H), 5.185 (s, 1 H), 2.355 (tt, J = 7.5, 2.1 Hz, 2 H), 1.804 (d, J = 7.2 Hz, 3 H), 1.405 (t, J = 7.5 Hz, 2 H), 1.036 (s, 6 H); ^{13}C NMR (C_6D_6) δ 149.218 (s), 149.142 (s), 117.750 (d), 110.321 (t), 43.585 (s), 39.413 (t), 31.913 (t), 28.800 (q), 15.399 (q); LRMS (EI) 136 (M$^+$, 20), 121 (100), 105 (13), 93 (20), 91 (34), 79 (23); HRMS m/z 136.1257 (M)$^+$, calcd for $C_{10}H_{16}$ 136.1252.

1,3,3-Trimethyl-2-vinyl-1-cyclopentene (15): IR (neat) 3099 (s), 2943 (s), 1709 (m), 1641 (m), 1592 (w) 1453 (m), 1375 (m), 1361 (m), 1209 (w), 1145 (w), 1109 (w), 989 (s), 897 (s); ^{1}H NMR δ 6.320 (dd, 1 H, J = 11.7, 6.3 Hz), 5.219 (d, 1 H, J = 17.4 Hz), 5.072 (d, 1 H, J = 11.7 Hz), 2.262 (t, 2 H, J = 6.9 Hz), 1.747 (s, 3 H), 1.545–1.747 (m, 2 H), 1.142 (s, 6 H); ^{13}C NMR δ 15.033 (q), 27.266 (q), 35.753 (t), 40.180 (t), 46.654 (s), 113.672 (t), 130.318 (d), 136.814 (s), 141.216 (s); LRMS (EI) 136 (M$^+$, 29), 121 (100), 93 (50), 91 (27), 77 (26); HRMS m/z 136.1259 (M)$^+$, calcd for $C_{10}H_{16}$ 136.1252.

2,3,6-Trimethylbicyclo[4.1.0]hept-2-ene (17): IR (neat) 2939 (s), 2866 (s), 1647 (s), 1457 (m), 1376 (m), 1068 (w), 887 (w); ^{1}H NMR δ 1.696–1.773 (m, 3 H), 1.728 (s, 3 H), 1.528 (s, 3 H), 1.498–1.412 (m, 1 H), 1.085 (s, 3 H), 0.752 (dd, J = 8.10, 3.90 Hz, 1 H), 0.623 (dd, J = 4.20, 3.90 Hz, 1 H), 0.445 (dd, J = 8.1, 4.20 Hz, 1 H), ^{13}C NMR δ 127.441 (s), 121.034 (s), 28.516 (t), 27.417 (t), 25.620 (q), 24.890 (d), 19.241 and 19.061 (overlapped q), 18.916 (s), 17.573 (t); LRMS (EI) m/z 136 (M$^+$, 44), 121 (60), 108 (58), 105 (49), 93 (100), 91 (63), 79 (41); HRMS m/z 136.1256 (M)$^+$, calcd for $C_{10}H_{16}$ 136.1252.

Irradiation of **13** (prepared from 500 mg of tosylhydrazone) containing traces of methanol in pentane gave **11** (13 mg, 6%), **15** (11 mg, 5%), **18** (105 mg, 40%), and **19** (39 mg, 15%).

1,2,4,4-Tetramethyl-3-methoxy-1-cyclohexene (19): IR (neat 2927 (s), 2864 (s), 2818 (s), 1684 (w), 1453 (m), 1368 (m), 1326 (w), 1311 (w), 1205 (m), 1113 (m), 1091 (m), 843 (m); ^{1}H NMR δ 3.523 (s, 3 H), 2.902 (s, 1 H), 1.916 (m, 2 H), 1.730 (s, 3 H), 1.610 (s, 3 H), 1.543–1.641 (m, 1H), 1.613 (s, 3 H), 1.140–1.211 (m, 1 H), 0.978 (s, 3H), 0.827 (s, 3 H), LRMS (EI) 168 (M$^+$, 21), 153 (76), 137 (4), 122 (10), 121 (100), 112 (25), 105 (16), 97 (15), 93 (49), 67 (17); HRMS m/z 168.1528 (M)$^+$, calcd for $C_{11}H_{20}O$ 168.1514.

Irradiation of **13** (prepared from 500 mg of tosylhydrazone) in pentane containing 5 equiv of benzophenone gave **10** (32 mg, 15%), **11** (27 mg, 13%), **15** (15 mg, 7%), and **17** (17 mg, 8%). Irradiation of **13** (prepared from 500 mg of tosylhydrazone) in acetone gave **10** (18%), **11** (15%), **15** (5%), and **17** (10%).

(*E*)-2-Ethylidene-1-methylene-3,3-dimethylcyclopentane (10): IR (neat) 2955 (s), 2864 (s), 1652 (w), 1623 (w), 1453 (m), 1382 (w), 1361 (w), 1155 (w), 978 (w), 865 (s), 822 (m); ^{1}H NMR (C_6D_6) δ 5.908 (q, J = 7.5 Hz, 1 H), 5.218 (s, 1 H), 4.763 (s, 1 H), 2.293 (tt, J = 7.5, 2.1 Hz, 2 H), 1.649 (br d, J = 7.5 Hz, 3 H), 1.409 (t, J 7.5 Hz, 2 H), 1.156 (s, 6 H), ^{13}C NMR (C_6D_6) δ 151.708 (s), 148.200 (s), 115.521 (d), 101.010 (t), 42.408 (s), 42.191 (t), 31.598 (t), 27.422 (q), 13.610 (q); LRMS (EI) m/z 136 (M$^+$, 21), 121 (100), 105 (13), 93 (40), 91 (35), 79 (22); HRMS m/z 136.1256 (M)$^+$, calcd for $C_{10}H_{16}$ 136.1252.

Thermolysis of 13. A suspension of the sodium salt **13** prepared from 500 mg of tosylhydrazone as described above and rigorously dried under vacuum was refluxed for a period of 12 h in dry benzene (20 mL). The reaction mixture was then washed with water and brine and dried over sodium sulfate. The benzene was distilled out via a Vigreux column, and the remaining crude mixture was chromatographed to obtain **11** (11 mg, 5%), **17** (36 mg, 24%), and **20** (159 mg, 62%).

1,4,6,6-Tetramethyl-2,3-diazabicyclo[3.3.0]oct-4-ene (20): IR (neat) 2961 (s) 2869 (s), 1657 (m), 1461 (m), 1422 (m), 1367 (m), 1320 (m), 1177 (w), 1155 (w), 1081 (w), 965 (w); ^{1}H NMR δ 2.485 (ddd, J = 13.2, 6.6, 6.3 Hz, 1H) 2.353 (s, 3 H), 2.220 (ddd, J = 13.5, 5.4, 0.6 Hz, 1 H) 2.100 (dd, J = 12.0, 6.6 Hz, 1 H), 1.460 (s, 3 H), 1.376 (dd, J = 12.0, 4.2 Hz, 1 H), 1.312 (s, 3 H), 1.210 (s, 3 H); ^{13}C NMR δ 168.692 (s), 144.846 (s), 105.717 (s), 48.761 (t), 34.118 (s), 30.237, 28.524, and 27.850 (overlapped q), 18.938 (q), 12.204 (q); LRMS (EI) 164 (M$^+$, 1), 149 (2), 136 (11), 121 (67), 105 (11), 80 (100); HRMS m/z 164.1311 (M)$^+$, calcd for $C_{10}H_{16}N_2$ 164.1313.

Preparation of Diazo Compound 14. A suspension of the sodium salt **13** (1 g, 2.92 mmol) in dry benzene (25 mL) was heated under reflux until it became a clear solution (approximately 50 min). This deep red solution was evaporated to dryness in a rotary evaporator at a bath temperature of 25 °C. The soft solid mass thus obtained was stirred (10 min) with dry pentane (15 mL), and the suspension was centrifuged. The red supernatant layer was filtered through a syringe filter (swinny) into the reaction vessel. This procedure was repeated until no more red compound was extracted by the pentane. The combined pentane solution was evaporated to dryness at 25 °C to obtain the diazo compound **14** (300 mg, 64% yield) as a thick dark red liquid. All these operations were carried out under argon and absence of moisture.

General Procedure for Irradiation of Diazo Compound 14. The red diazo compound **14** (300 mg, 1.83 mmol) was dissolved in acetone or pentane (25 mL), degassed with argon, and irradiated through a uranium filter for 3 or 6 h, respectively. The solution turned colorless after this period, and it was diluted with pentane (50 mL). This solution was washed with water (3 × 30 mL) followed by brine. The pentane was distilled off at 50 °C using a water bath. The oily mass thus obtained was eluted (chromatotron) with pentane to obtain a colorless liquid which was subjected to preparative GLC for isolation of the pure products.

Irradiation of **14** (300 mg, 1.83 mmol) in pentane gave **11** (27 mg, 18%), **15** (74 mg, 30%), and **17** (49 mg, 20%). Irradiation of **14** (300 mg, 1.83 mmol) in pentane (1 equiv of benzophenone added) gave **11** (16%), **15** (15%), and **17** (35%). Irradiation of **14** (300 mg, 1.83 mmol) in pentane (5 equiv of benzophenone added) gave **10** (10%), **11** (15%), **15** (12%), and **17** (10%). Irradiation of **14** (300 mg, 1.83 mmol) in acetone gave **10** (136 mg, 55%), **11** (15 mg, 6%), and **15** (20 mg, 8%).

Synthesis of Authentic 15. To a solution of the triflate **21**[7] (2 g, 7.751 mmol) in dry THF (60 mL) was added dry LiCl (985 mg, 23.23 mmol), vinyltributyltin (2.94 g, 9.27 mmol), and tetrakis(triphenylphosphine)palladium (248 mg). This solution was heated under reflux for a period of 48 h followed by cooling to room temperature. The reaction mixture was then diluted with ether and washed with 5% ammonium hydroxide, water, and brine. This solution was then dried over sodium sulfate and concentrated. The crude product was passed through a silica gel column eluting with pentane to obtain 960 mg (92%) of the pure diene **15** with spectroscopic properties virtually identical to those given above.

1-(1-Hydroxyethyl)-2,2,5-trimethylcyclopent-5-ene (22). To a solution of the ketone **12** (2 g, 13 mmol) in anhydrous methanol (30 mL) was added $NaBH_4$ (1 g, 26 mmol), and the mixture was stirred for 6 h. Usual workup and distillation (60 °C/2 mm) furnished 1.95 g (96%) of the pure alcohol **22**: IR (neat) 3382 (br s) 2943 (s), 1663 (w), 1457 (m), 1365 (m), 1067 (s), 982 (s), 893 (s); ^{1}H NMR δ 4.415 (q, J = 6.6 Hz, 0.6 H), 3.415 (q, J = 6.9 Hz, 0.4 H), 2.1–2.2 (m, 2 H), 1.919 (br s, 1 H, OH), 1.736 (s, 3 H), 1.500–1.600 (m, 2 H), 1.307 (d, J = 6.6 Hz, 3 H), 1.029 (s, 3 H), 0.983 (s, 3 H); ^{13}C NMR δ 145.089 (s), 133.610 (s), 64.936 (d), 47.081 (s), 39.712 (t), 35.600 (t), 27.893 (q), 27.242 (q), 23.249 (q), 14.913 (q); HRMS m/z 154.1351 (M)$^+$, calcd for $C_{10}H_{18}O$ 154.1357.

Dehydration of Alcohol 22. To a solution of the alchol **22** (2.44 g, 15.8 mmol) in dry dichloromethane (75 mL) was added dry Et_3N (4.86 g, 47.5 mmol), and the mixture was cooled to −35 °C. To this cold solution was added 2,4-dinitrobenzenesulfenyl chloride (9.92 g, 39.6 mmol), and the mixture was stirred at this temperature for 45 min.[18] The temperature was then gradually allowed to reach room temperature over a period of 3 h. Pentane (300 mL) was added to this mixture and was filtered. The filtrate was passed through a silica gel column eluting with pentane to obtain a mixture of dehydrated products. These were separated by GLC to obtain **7** and **8** (1:1 mixture, 860 mg, 40%), **10** (322 mg, 15%, **11** (215 mg, 10%), and **15** (107 mg, 5%).

Irradiation of 4. A solution of the aldehyde (two isomers in 1:1 ratio) **4** (25 mg, 0.152 mmol) in pentane (20 mL) was degassed and irradiated for 12 h. A careful GLC and GC/MS analysis revealed quantitative conversion of **4** into a mixture (1:1) of **7** and **8**.

Irradiation of 10 in Pentane and in Acetone. A solution of **10** (50 mg, containing 10% **7**) in acetone (20 mL) was irradiated through Pyrex for 8 h. This was partitioned between water and pentane followed by separation of the pentane layer which contained the product. This on concentration and purification followed by NMR and GLC analysis showed **7** to be formed quantitatively. When pentane was used as a solvent under otherwise identical conditions, recovery of starting material alone resulted.

2-(1-Propynyl)-2,5,5-trimethylcyclopentanone (1). The reported[2] isomerization of 2-(2-propynyl)-2,5,5-trimethylcyclopentanone was modified as follows. A solution of the starting acetylenic ketone (5 g, 30 mmol) in anhydrous DMSO (30 mL) was added to a cold solution of *t*-BuOK (7 g, 62 mmol) in DMSO (160 mL), maintained at 10 °C, at a rate of 1 mL/min while the *t*-BuOK was stirred vigorously. After 1.5 h the reaction mixture was poured into cold water (1500 mL) and extracted with a mixture of ether and pentane (2:1) several times. These extracts were combined, dried, concentrated, and distilled (80–83 °C/13 mm) to obtain 3 g (60%) of pure **1**.

Irradiation of Acetylenic Ketone 1. A solution of the acetylenic ketone **1** (492 mg, 3 mmol) in pentane (20 mL) was irradiated through Pyrex for 72 h. The solution was concentrated to 5 mL and allowed to stand overnight. Colorless crystals of the dimer **28** appeared. The remaining mass was subjected to chromatography to obtain an additional amount of **28**. Combined weight of the dimer was 270 mg (55%) (mp 175–176 °C): UV λ_{max} (pentane) 281 (ϵ = 7708), 288 (8676); IR (KBr pellet) 2972 (s), 2920 (s), 2871 (s), 2096 (s), 1671 (s), 1476 (m), 1450 (m), 1386 (m), 1363 (m), 1306 (m), 1274 (m), 1242 (s), 1049 (s), 1023 (s), 978 (s); ^{1}H NMR δ 1.150 (s, 3 H), 1.159 (s, 3 H), 1.196 (s, 3 H), 1.290 (ddd, *J* = 2.4, 6.0, 14.1 Hz, 1 H), 1.600 (ddd, *J* = 6.0, 7.5, 14.5 Hz, 1 H), 1.810 (m, 1 H), 1.869 (s, 3 H), 2.233 (m, 1 H); ^{13}C NMR δ 19.672 (q), 22.450 (q), 25.144 (q), 26.206 (q), 28.231 (t), 36.073 (t), 47.611 (s), 49.724 (s), 131.049 (s), 144.336 (s), 212.413 (s): HRMS *m/z* 328.2375 (M)$^+$, calcd for $C_{22}H_{32}O_2$ 328.2402.

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