

Furans from Novel [3 + 2] Photocycloaddition of Alkenes to 2-(1-Alkynyl)cyclohexenones

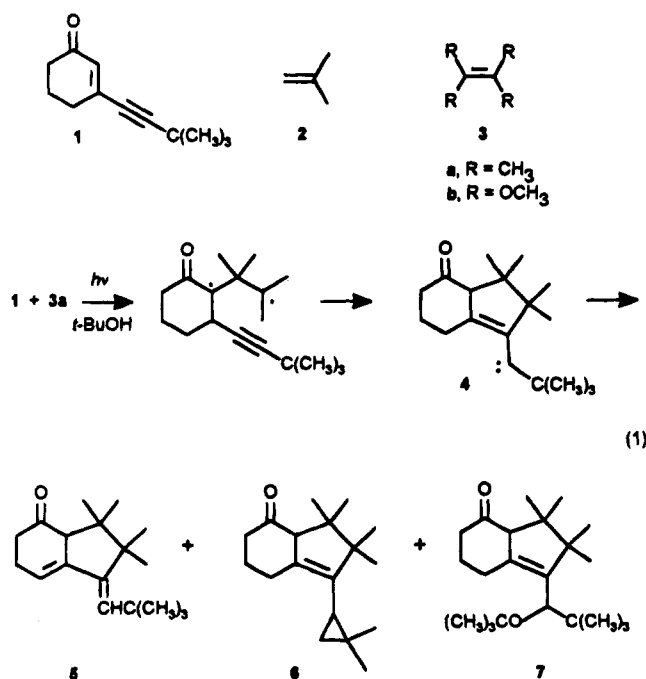
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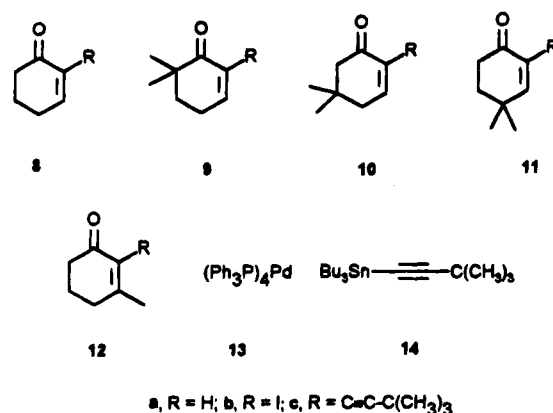
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Photocycloaddition of 2-alkynyl-substituted cyclohexenones **8c–11c** with isobutylene (**2**) and tetramethylethylene (**3a**) leads to tricyclic furans **15a–18a** and **15b–17b**, respectively, in gas chromatographic yields of ~90%. A suggested mechanism for this novel process is shown in eq 2. Tetramethoxyethylene (**3b**) gives only oxetanes **22** and **23**, and the 3-methyl-substituted ketone **12c** fails to react with **2** and **3a,b**. *tert*-Butylethylene gives [2 + 2] adduct **24** with **10c**.

Earlier investigations have shown that photocycloaddition of 3-alkynylcyclohex-2-en-1-ones such as **1** with alkenes leads to a multiplicity of photoproducts.³ As is shown for reaction of tetramethylethylene (**3a**) with **1** in



tert-butyl alcohol (eq 1), stepwise [3 + 2] cycloaddition gives carbene **4**, which leads to the products of hydrogen transfer (**5**), intramolecular insertion (**6**), and insertion into solvent (**7**), as well as isomeric substances resulting from shifts of the β,γ double bonds of **5–7** into conjugation. In addition, the various geometric and stereochemical isomers of these adducts are formed, as are small amounts of simple [2 + 2] cycloaddition products. These reactions are mechanistically interesting but the diversity of products limits their synthetic value. In the present work, we have investigated cycloaddition reactions of the isomeric 2-alkynylcyclohexenones **8c–12c**. In sharp contrast to the behavior of their 3-alkynyl isomers, ketones **8c–11c** react cleanly in a novel tandem process, in which initial [3 + 2] cycloaddition is followed by



cyclization to furnish tetrasubstituted tricyclic furans.⁴ Details of these and related observations are given below.

Preparative Experiments. Preparation of ketone **8c** began with iodination⁵ of cyclohexenone (**8a**) to form **8b**. In the presence of tetrakis(triphenylphosphine)palladium(0) (**13**), **8b** reacted with (*tert*-butylethynyl)tributylstannane (**14**) in tetrahydrofuran to form **8c**.^{6,7} The remaining ketones **9c–12c** were prepared analogously from known cyclohexenones **9a–12a**.

Photochemical Experiments. Ketones **8c–11c** were irradiated in benzene (~350 nm) saturated with isobutylene (**2**) or containing 10 equiv of tetramethylethylene (**3a**). Ketone **11c** failed to react with **3a**, presumably owing to steric hindrance, but reactions of the other ketones were monitored by gas chromatography and continued until the starting ketone had essentially disappeared (~40 h). The reaction mixture was then chromatographed over silica gel to yield the product.

Products from addition of **2** and **3a** to **8c–11c** were identified as furans **15a–18a** and **15b–17b**, respectively, on the basis of their spectroscopic properties. Complete details are given in the experimental section, but the most significant spectroscopic data for each product are

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(5) Johnson, C. R.; Adams, J. P.; Braun, M. P.; Senanayake, C. B. W.; Wovkulich, P. M.; Uskoković, M. R. *Tetrahedron Lett.* **1992**, 33, 917. Use of this new method considerably improved preparation of iodide intermediates over our earlier report (ref 4).

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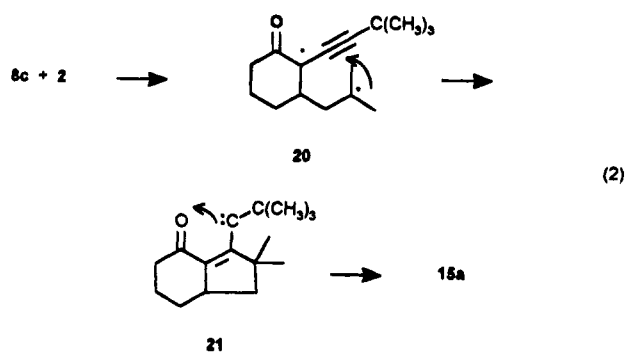
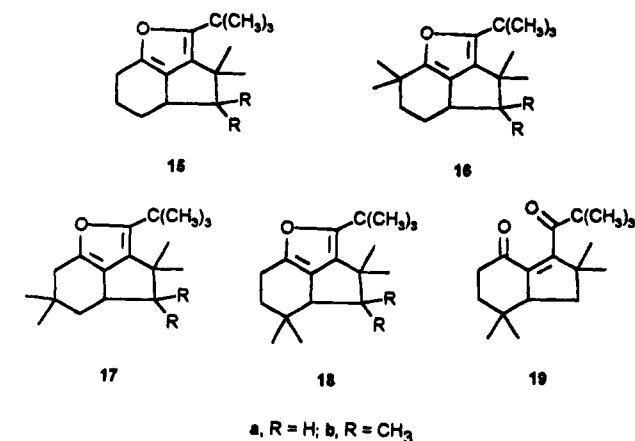
(7) For related coupling reactions of α -iodoenones, see: Negishi, E.; Owczarczyk, Z. R.; Swanson, D. R. *Tetrahedron Lett.* **1991**, 32, 4453. Johnson, C. R.; Adams, J. P.; Braun, M. P.; Senanayake, C. B. W. *Ibid.* **1992**, 33, 919.

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four ¹³C NMR signals typical of furans in the range ~130–160, the lack of carbonyl absorption in the IR spectrum, and MS evidence that each product is a 1:1 adduct.

These structural assignments were supported by the observation that in the presence of molecular oxygen, furan **18a** undergoes photochemical cleavage to furnish the corresponding enedione **19**. Such oxidative cleavage of furans, both photochemical⁸ and nonphotochemical,⁹ has been known for many years.

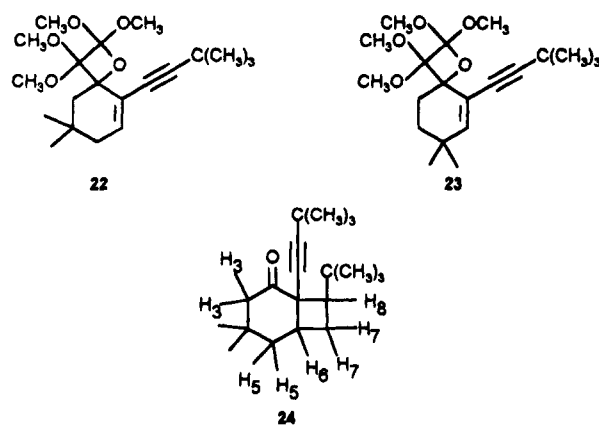
In eq 2 we give a mechanistic rationalization for the reaction between **8c** and **2**. Biradical **20**, formed on initial addition of **2** to triplet **8c**, closes on the triple bond in the now well-established¹⁰ [3 + 2] cycloaddition to yield carbene **21**. This species then cyclizes through carbene attack on the carbonyl oxygen to form the furan. Analogous cyclizations of other β-acylvinyl carbenes have been reported previously,¹¹ and there are also related reactions of all-carbon systems and of vinyl carbenes bearing other substituents.¹² Initial formation of *bis*-tertiary biradical **20** accounts for the observed regiochemistry of the *gem*-dimethyl group originating from isobutylene (**2**) in adducts **15a**–**18a**. No products were obtained having the

regiochemistry resulting from the alternative initial addition of **2** to form a primary radical center.

Each step in this suggested mechanism has precedent, but the overall process constitutes a novel one-step preparation of furans. While eq 2 provides the simplest explanation of our results, it is conceivable that an unobserved acylcyclopropene intermediate intervenes between **21** and **15a**. Both isomerization of singlet vinylcarbenes to cyclopropenes¹³ and rearrangement of triplet acylcyclopropenes to furans¹⁴ are known processes.

Gas chromatography directly on the reaction mixtures indicated that yields of the furans were ~90%. These products are sensitive to oxidation and a considerable amount of material was lost during isolation and purification. Isolated yields of purified adducts were in the range 10–67%.

We also irradiated **8c**–**11c** with tetramethoxyethylene (**3b**).¹⁵ As in reaction of **3b** with **1** and related ketones,³ the only adducts formed with **3b** were oxetanes. Ketones **10c** and **11c** yielded **22** and **23**, respectively, but surprisingly **3b** failed to add to the carbonyl groups of **9c** and



12c. We also attempted cycloadditions with the 3-methyl-substituted ketone **12c**. This ketone failed to react with **2** or **3a,b**, presumably owing to excessive steric hindrance at the ring carbon–carbon double bond. Finally, addition of *tert*-butylethylene to **10c** furnished one of the diastereomers of [2 + 2] cycloadduct **24** as the only isolated product. The regiochemistry of **24** follows from its COSY spectrum, which is given in the Experimental Section.

Experimental Section

General. ¹H NMR spectra are recorded on a Bruker WP 80 (80 MHz), a Bruker AC 250 P (250 MHz), or a Bruker AMX 400 (400 MHz). ¹³C-NMR spectra are recorded on a Bruker AC 250 P (62.9 MHz) or a Bruker AMX 400 (100.6 MHz). Chemical shifts are given downfield from tetramethylsilane (δ). Assignments are made by the DEPT method. Ultraviolet spectra are recorded on a Perkin-Elmer 552 spectrophotometer. Infrared spectra are recorded on a Perkin-Elmer FT-IR 1720 X spectrometer. Gas-liquid chromatography (GLC) was carried out on a Carlo Erba Fractovap Series 2150 instrument equipped with a 30 m SE 30 glass capillary column and a Hewlett-Packard 3394A integrator. Mass spectra are recorded on a Finnigan MAT 311A mass spectrometer equipped

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(9) See, for example: Brown, W. H.; Wright, G. F. *Can. J. Chem.* **1957**, *35*, 236.

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with a 25 m CPS/L5B column. High resolution mass spectra are recorded on a VG Analytical/Manchester 70–250 S mass spectrometer equipped with a 25 m CPSIL 7B column, using perfluorokerosene as standard. Melting points are determined with an electrothermal melting point apparatus and are uncorrected. TLCs are performed using silica gel-coated thin layer Polygram SIL G/UV 254 from Macherey-Nagel Co., Düren, Germany. Irradiations are carried out using a Rayonet RPR 100 Photochemical Reactor from The Southern New England Ultraviolet Co. with $\lambda_{\max} \sim 350$ nm. Chloroform and carbon tetrachloride are distilled from tetraphosphorus decaoxide. DMSO is distilled from calcium hydride. Ether and THF are distilled from benzophenone ketyl radical. Pyridine is distilled from potassium hydroxide. Tetrakis(triphenylphosphine)palladium(0),¹⁶ (3,3-dimethylbutynyl)tributylstannane,¹⁷ tetramethoxyethylene,¹⁵ 4,4-dimethylcyclohexen-1-one,¹⁸ 5,5-dimethylcyclohexen-1-one,¹⁹ and 6,6-dimethylcyclohexen-1-one²⁰ are prepared according to the literature. NMR spectra available as supplementary material were used as criteria of purity for new compounds for which HRMS M^+ ions were measured.

Preparation of 8b–12b. Ketones **8a–12a** were iodinated in CCl_4 –pyridine following the procedure of Johnson et al.,⁵ who used it to prepare **8b** and **12b**. Ketones **9b–11b** were purified by bulb-to-bulb distillation. For **9b**: yield, 67%; dark liquid; 1H NMR (250 MHz, $CDCl_3$) (δ) 7.67 (t, $J = 4.4$ Hz, 1 H, olefinic), 2.47 (dt, $J = 6$ Hz, $J = 4.4$ Hz, 2 H, cyclohexyl), 1.92 (t, $J = 6$ Hz, 2 H, cyclohexyl), 1.18 (s, 6 H, methyl); ^{13}C NMR (δ) (62.9 MHz, $CDCl_3$) 197.2 (q), 157.8 (t), 103.2 (q), 42.2 (q), 35.9 (s), 27.6 (s), 24.7 (p); IR (film) 1684 cm^{-1} ; GCMS (70 eV) 250 (M, 40%), 194 (M – C_4H_8 , 100%); HRMS (70 eV) m/z 249.9868 (M^+ ; calcd for $C_8H_{11}IO$, 249.9855). For **10b**: yield, 81%; yellow liquid; 1H NMR (250 MHz, $CDCl_3$) (δ) 7.63 (t, $J = 4.4$ Hz, 1 H, olefinic), 2.50 (s, 2 H, cyclohexyl), 2.33 (d, $J = 4.4$ Hz, 2 H, cyclohexyl), 1.07 (s, 6 H, methyl); ^{13}C NMR (62.9 MHz, $CDCl_3$) (δ) 192.4 (q), 157.0 (t), 102.4 (q), 50.6 (s), 43.8 (s), 34.4 (q), 27.9 (p); IR (film) 1687 cm^{-1} ; GCMS (70 eV) 250 (M, 53%), 194 (M – C_4H_8 , 100%), 166 (15%); HRMS (70 eV) m/z 249.9862 (M^+ ; calcd for $C_8H_{11}IO$, 249.9855). For **11b**: yield, 81%; yellow liquid; 1H NMR (250 MHz, $CDCl_3$) (δ) 7.47 (s, 1 H, olefinic), 2.68 and 1.94 (AA'BB', 4 H, cyclohexyl), 1.20 (s, 6 H, methyl); ^{13}C NMR (62.9 MHz, $CDCl_3$) (δ) 191.9 (q), 168.0 (t), 101.8 (q), 38.0 (q), 36.0 (s), 33.3 (s), 27.4 (p); IR (film) 1689 cm^{-1} ; GCMS (70 eV) 250 (M, 32%), 123 (100%); HRMS (70 eV) m/z 249.9855 (M^+ ; calcd for $C_8H_{11}IO$, 249.9855).

General Procedure for Preparation of 8c–12c. Under argon, the 2-iodo enone (**8b–12b**, 10 mmol), stannane **14** (5.57 g, 15 mmol), and **13** (115 mg, 0.1 mmol) were dissolved in dry THF (10 mL). The solution was stirred and heated under reflux until iodo enone had disappeared (GLC monitoring). The solution was then cooled to room temperature, and ether (100 mL) and a solution of KF (46 g) in water (200 mL) were added. The mixture was stirred vigorously for 1 h, the organic layer was separated, and the aqueous layer was extracted with ether (150 mL). Combined organic layers were dried over $MgSO_4$. Solvent was removed under reduced pressure, and the crude product was purified by column chromatography over silica (100-fold weight). For **8c**: yield, 37%; colorless solid; mp 113 °C; 1H NMR (80 MHz, $CDCl_3$) (δ) 7.15 (t, $J = 4.5$ Hz, 1 H), 2.58–1.81 (m, 6 H), 1.27 (s, 9 H); ^{13}C NMR (100.6 MHz, $CDCl_3$) (δ) 195.7 (q), 152.7 (t), 125.5 (q), 101.4 (q), 73.4 (q), 38.2 (s), 30.9 (p), 27.9 (q), 26.3 (s), 22.5 (s); IR (KBr) 1680 cm^{-1} ; GCMS (70 eV) 176 (M, 100%), 161 (M – CH_3 , 100%), 148 (M – CO, 31%); HRMS (70 eV) m/z 176.1196 (M^+ ; calcd for $C_{12}H_{16}O$, 176.1201); UV (cyclohexane) λ_{\max} 264 nm (7450). For **9c**: yield, 53%; yellow solid; mp 49 °C; 1H NMR (250 MHz, $CDCl_3$) (δ) 7.07 (t, $J = 4.4$ Hz, 1 H), 2.43 (dt, $J = 6$ Hz, $J = 4.4$ Hz, 2 H),

1.83 (t, $J = 6$ Hz, 2 H), 1.28 (s, 9 H), 1.13 (s, 6 H); ^{13}C NMR (62.9 MHz, $CDCl_3$) (δ) 200.7 (q), 151.0 (t), 123.6 (q), 100.6 (q), 74.0 (q), 41.5 (q), 35.8 (s), 30.9 (p), 27.9 (q), 24.2 (p), 23.4 (s); GCMS (70 eV) 204 (M, 38%), 189 (M – Me, 100%), 148 (M – C_4H_8 , 47%), 105 (76%); IR (KBr) 1683 cm^{-1} ; HRMS (70 eV) m/z 204.1514 (M^+ ; calcd for $C_{14}H_{20}O$, 204.1514); UV (cyclohexane) λ_{\max} 264 nm (7820). For **10c**: yield, 42%; yellow solid; mp 88 °C; 1H NMR (80 MHz, $CDCl_3$) (δ) 6.98 (t, $J = 4$ Hz, 1 H), 2.26 (d, $J = 4$ Hz, 2 H), 2.27 (s, 2 H), 1.24 (s, 9 H), 1.01 (s, 6 H); 1H NMR (80 MHz, C_6D_6) (δ) 6.61 (t, $J = 4$ Hz, 1 H), 1.98 (s, 2 H), 1.66 (d, $J = 4$ Hz, 2 H), 1.24 (s, 9 H), 0.63 (s, 6 H); ^{13}C NMR (62.9 MHz, $CDCl_3$) (δ) 196.0 (q), 150.5 (t), 124.7 (q), 101.5 (q), 73.3 (q), 51.7 (s), 40.4 (s), 33.9 (q), 31.0 (p), 28.3 (p), 28.0 (q); IR (KBr) 1688 cm^{-1} ; GCMS (70 eV) 204 (M, 51%), 189 (M – CH_3 , 54%), 148 (M – C_4H_8 , 100%), 105 (68%); HRMS (70 eV) m/z 204.1519 (M^+ ; calcd for $C_{14}H_{20}O$, 204.1514); UV (cyclohexane) λ_{\max} 264 nm (8000). For **11c**: yield, 81%; colorless solid; mp 97 °C; 1H NMR (250 MHz, $CDCl_3$) (δ) 6.87 (s, 1 H), 2.49 (t, $J = 7.2$ Hz, 2 H), 1.86 (t, $J = 7.2$ Hz), 1.27 (s, 9 H), 1.17 (s, 6 H); ^{13}C NMR (62.9 MHz, $CDCl_3$) (δ) 195.6 (q), 161.6 (t), 122.7 (q), 101.1 (q), 73.4 (q), 35.7 (s), 34.4 (s), 33.5 (q), 30.9 (p), 27.9 (q), 27.7 (p); IR (KBr) 1687 cm^{-1} ; GCMS (70 eV) 204 (M, 54%), 189 (M – CH_3 , 100%); HRMS (70 eV) m/z 204.1519 (M^+ ; calcd for $C_{14}H_{20}O$, 204.1514); UV (cyclohexane) λ_{\max} 264 nm (8530). For **12c**: yield, 38%, yellow solid; mp 56 °C; 1H NMR (250 MHz, $CDCl_3$) (δ) 2.47–2.37 (m, 4 H), 2.17 (s, 3 H), 2.00–1.90 (m, 2 H), 1.30 (s, 9 H); ^{13}C NMR (62.9 MHz, $CDCl_3$) (δ) 195.8 (q), 164.4 (q), 122.1 (q), 105.8 (q), 72.5 (q), 37.4 (s), 32.3 (s), 31.1 (p), 28.2 (q), 23.6 (p), 21.8 (s); IR (KBr) 1677 cm^{-1} ; GCMS (70 eV) 190 (M, 34%), 175 (M – CH_3 , 100%); HRMS (70 eV) m/z 190.1345 (M^+ ; calcd for $C_{13}H_{18}O$, 190.1358); UV (cyclohexane) λ_{\max} 265 nm (9840).

General Procedure for Irradiations. Irradiations were carried out in glass tubes (diameter 1 cm) containing enynone (0.25 mmol) in benzene (4 mL) and closed with a septum fitted with two needles, one reaching to the bottom of the tube and one ending above the surface of the solution. Argon was bubbled through the longer needle for 10 min, and then olefin (2.5 mmol of **3a** or **3b**) was added through the shorter needle, and argon flushing was continued for an additional 5 min. When isobutylene (**2**) was used, it was added via the longer needle until the solution was saturated. After irradiation, solvent was removed at the rotary evaporator, and the crude product was purified by column chromatography or thick-layer chromatography.

Reaction of 2-(3,3-Dimethylbutynyl)-2-cyclohexen-1-one (8c) with Isobutylene (2). For **15a**: yield of purified furan, 11%; colorless liquid; 1H NMR (250 MHz, $CDCl_3$) (δ) 2.84–1.50 and 1.20–0.72 (m, 9 H), 1.33 (s, 6 H), 1.27 (s, 9 H); ^{13}C NMR (62.9 MHz, $CDCl_3$) (δ) 154.3 (q), 142.6 (q), 137.1 (q), 129.2 (q), 58.6 (s), 43.4 (q), 33.3 (q), 32.1 (t), 30.7 (s), 30.3 (p), 29.3 (p), 28.3 (p), 25.5 (s), 23.5 (s); GCMS (70 eV) 232 (M, 17%), 217 (M – Me, 100%); IR (film) 2932 cm^{-1} ; HRMS (70 eV) m/z 232.1822 (M^+ ; calcd for $C_{16}H_{24}O$, 232.1827).

Reaction of 6,6-Dimethyl-2-(3,3-dimethylbutynyl)-2-cyclohexen-1-one (9c) with Isobutylene (2). For **16a**: yield (purified), 56%; colorless solid; mp 70 °C; 1H NMR (250 MHz, $CDCl_3$) (δ) 2.82–2.68 (m, 1 H), 2.12 (dd, $J = 11.6$ Hz, $J = 6.4$ Hz, 1 H), 1.91–1.51 (m, 4 H), 1.33 (s, 3 H), 1.30 (s, 3 H), 1.25 (s, 12 H), 1.03 (s, 3 H), 1.03–0.83 (m, 1 H); ^{13}C NMR (62.9 MHz, $CDCl_3$) (δ) 153.8 (q), 149.5 (q), 135.2 (q), 128.6 (q), 58.6 (s), 43.8 (q), 42.6 (s), 34.5 (q), 33.4 (q), 32.7 (t), 30.2 (p), 29.4 (s), 29.3 (p), 28.4 (p), 28.3 (p), 26.2 (p); IR (KBr) 2961 cm^{-1} ; GCMS (70 eV) 260 (M, 18%), 245 (M – Me, 100%); HRMS (70 eV) m/z 260.2162 (M^+ ; calcd for $C_{18}H_{26}O$, 260.2140).

Reaction of 5,5-Dimethyl-2-(3,3-dimethylbutynyl)-2-cyclohexen-1-one (10c) with Isobutylene (2). For **17a**: yield (purified), 34%; colorless liquid; 1H NMR (250 MHz, $CDCl_3$) (δ) 2.80 (m, 1 H), 2.34 (dd, $J = 16.0$ Hz, $J = 2.0$ Hz, 1 H), 2.21–2.10 (m, 2 H), 1.71 (dd, $J = 12.0$ Hz, $J = 10.6$ Hz, 1 H), 1.61 (dd, $J = 12.0$ Hz, $J = 5.2$ Hz, 1 H), 1.33 (s, 6 H), 1.27 (s, 9 H), 1.10 (s, 3 H), 1.03 (s, 3 H), 0.84 (dd, $J = 12.0$ Hz, $J = 10.4$ Hz, 1 H); 1H NMR (250 MHz, C_6D_6) (δ) 2.77 (m, 1 H), 2.32 (dd, $J = 16.0$ Hz, $J = 2.0$ Hz, 1 H), 2.17 (dd, $J = 16.0$ Hz, $J = 2.8$ Hz, 1 H), 2.06 (dd, $J = 12.0$ Hz, $J = 6.8$ Hz, 1 H), 1.74 (dd, $J = 12.0$ Hz, $J = 9.6$ Hz, 1 H), 1.45 (dd, $J = 12.0$ Hz, $J =$

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5.2 Hz, 1 H), 1.37 (s, 9 H), 1.30 (s, 6 H), 1.03 (s, 3 H), 0.87 (s, 3 H), 0.70 (dd, $J = 12.0$ Hz, $J = 10.4$ Hz, 1 H); ^{13}C NMR (62.9 MHz, CDCl_3) (δ) 154.6 (q), 143.2 (q), 135.9 (q), 129.2 (q), 58.6 (s), 44.9 (s), 43.6 (q), 38.0 (s), 36.4 (q), 33.3 (q), 31.8 (t), 30.3 (p), 29.4 (p), 29.3 (p), 28.3 (p), 26.9 (p); IR (KBr) 2960 cm^{-1} ; GCMS (70 eV) 261 (M, 13%), 245 (M - Me, 30%), 204 (M - C_4H_8 , 100%), 189 (M - C_4H_8 - CH_3 , 35%); HRMS (70 eV) m/z 260.2153 (M^+ ; calcd for $\text{C}_{18}\text{H}_{28}\text{O}$, 260.2140).

Reaction of 4,4-Dimethyl-2-(3,3-dimethylbutynyl)-2-cyclohexen-1-one (11c) with Isobutylene (2). For **18a**: yield (purified), 67%; colorless liquid; ^1H NMR (250 MHz, CDCl_3) (δ) 2.65 (m, 1 H), 2.53 (dddd, $J = 16.0$ Hz, $J = 6.4$ Hz, $J = 2.0$ Hz, $J = 2.4$ Hz, 1 H), 2.33 (dddd, $J = 16.0$ Hz, $J = 10.8$ Hz, $J = 5.6$ Hz, $J = 3.2$ Hz, 1 H), 1.91 (dd, $J = 12.0$ Hz, $J = 6.8$ Hz, 1 H), 1.82 (dd, $J = 12.0$ Hz, $J = 10.4$ Hz, 1 H), 1.75 (ddd, $J = 14.0$ Hz, $J = 10.8$ Hz, $J = 6.4$ Hz, 1 H), 1.53 (ddd, $J = 14.0$ Hz, $J = 5.6$ Hz, $J = 2.0$ Hz, 1 H), 1.32 (s, 3 H), 1.30 (s, 3 H), 1.23 (s, 9 H), 1.00 (s, 3 H), 0.47 (s, 3 H); ^{13}C NMR (62.9 MHz, CDCl_3) (δ) 154.7 (q), 141.4 (q), 136.1 (q), 129.7 (q), 51.7 (s), 43.3 (q), 41.5 (t), 40.5 (s), 33.6 (q), 33.3 (q), 30.2 (p), 29.4 (p), 28.7 (q), 22.1 (s), 18.8 (p); IR (film) 2956 cm^{-1} ; GCMS (70 eV) 260 (M, 17%), 245 (M - Me, 51%), 204 (M - C_4H_8 , 100%); HRMS (70 eV) m/z 260.2138 (M^+ ; calcd for $\text{C}_{18}\text{H}_{28}\text{O}$, 260.2140).

Reaction of 2-(3,3-Dimethylbutynyl)-2-cyclohexen-1-one (8c) with Tetramethylethylene (3a). For **15b**: yield of purified furan, 11%; colorless liquid; ^1H NMR (250 MHz, CDCl_3) (δ) 2.58–1.60 (m, 7 H), 1.20 (s, 9 H), 1.10 (s, 3 H), 1.07 (s, 3 H), 0.93 (s, 3 H), 0.50 (s, 3 H); ^{13}C NMR (62.9 MHz, CDCl_3) (δ) 154.7 (q), 142.9 (q), 133.3 (q), 128.6 (q), 56.3 (q), 48.3 (q), 42.0 (t), 33.2 (q), 30.4 (p), 25.9 (p), 25.1 (s), 24.3 (s), 23.8 (s), 23.0 (p), 21.4 (p), 20.7 (p); IR (film) 2927 cm^{-1} ; GCMS (70 eV) 260 (M, 15%), 245 (M - Me, 42%), 217 (100%); HRMS (70 eV) m/z 260.2141 (M^+ ; calcd for $\text{C}_{18}\text{H}_{28}\text{O}$, 260.2140).

Reaction of 6,6-Dimethyl-2-(3,3-dimethylbutynyl)-2-cyclohexen-1-one (9c) with Tetramethylethylene (3a). For **16b**: yield of purified furan, 10%; colorless liquid; ^1H NMR (250 MHz, CDCl_3) (δ) 2.58 (dd, $J = 10.4$ Hz, $J = 5.6$ Hz, 1 H), 1.82–1.50 (m, ~2.5 H), 1.25 (s, 12 H), 1.20 (1 H from COSY), 1.17 (s, 3 H), 1.12 (s, 3 H), 1.03 (s, 3 H), 0.97 (s, 3 H), 0.58 (s, 3 H); ^{13}C NMR (62.9 MHz, CDCl_3) (δ) 154.2 (q), 149.9 (q), 131.2 (q), 128.1 (q), 56.1 (q), 48.5 (q), 42.4 (t), 41.8 (s), 34.3 (q), 33.3 (q), 30.3 (p), 28.0 (p), 26.3 (p), 25.9 (p), 23.1 (p), 22.1 (s), 21.3 (p), 20.6 (p); IR (film) 2964 cm^{-1} ; GCMS (70 eV) 288 (M, 20%), 273 (M - Me, 47%), 245 (100%); HRMS (70 eV) m/z 288.2424 (M^+ ; calcd for $\text{C}_{20}\text{H}_{32}\text{O}$, 288.2453).

Reaction of 5,5-Dimethyl-2-(3,3-dimethylbutynyl)-2-cyclohexen-1-one (10c) with Tetramethylethylene (3a). For **17b**: yield of purified furan, 12%; colorless liquid; ^1H NMR (400 MHz, C_6D_6) (δ) 2.63 (9 lines, 1 H), 2.31 (dd, $J = 12.0$ Hz, $J = 2.4$ Hz, 1 H), 2.19 (dd, $J = 12.0$ Hz, $J = 3.2$ Hz, 1 H), 1.45 (s, 9 H), 1.26 (s, 3 H), 1.24 (dd, $J = 12.0$ Hz, $J = 5.2$ Hz, 1 H), 1.19 (s, 3 H), 1.05 (s, 3 H), 0.98 (s, 3 H), 0.93 (s, 3 H), 0.93 (1 H from COSY), 0.64 (s, 3 H); ^{13}C NMR (100.6 MHz, CDCl_3) (δ) 155.8 (q), 143.6 (q), 131.9 (q), 128.6 (q), 56.4 (q), 48.8 (q), 39.4 (t), 38.4 (s), 38.0 (s), 35.9 (q), 33.5 (q), 31.9 (p), 30.7 (p), 26.5 (p), 26.0 (p), 23.2 (p), 21.6 (p), 20.8 (p); IR (film) 2927 cm^{-1} ; GCMS (70 eV) 289 (M, 16%), 274 (M - Me, 35%), 245 (100%), 217 (11%); HRMS (70 eV) m/z 288.2451 (M^+ ; calcd for $\text{C}_{20}\text{H}_{32}\text{O}$, 288.2453).

Reaction of 5,5-Dimethyl-2-(3,3-dimethylbutynyl)-2-cyclohexen-1-one (10c) with Tetramethoxyethylene (3b). For **22**: yield, 24%; colorless liquid; ^1H NMR (250 MHz, CDCl_3) (δ) 6.27 (dd, $J = 4.4$ Hz, $J = 5.9$ Hz, 1 H), 3.57 (s, 3 H), 3.38 (s, 3 H), 3.35 (s, 3 H), 3.31 (s, 3 H), 1.97 (d, $J = 14.4$ Hz, 1 H), 1.89 (m, 2 H), 1.78 (d, $J = 14.4$ Hz, 1 H), 1.26 (s, 9 H), 1.00 (s, 3 H), 0.95 (s, 3 H); ^1H NMR (250 MHz, C_6D_6) (δ) 6.22 (t, $J = 4.4$ Hz, 1 H), 3.70 (s, 3 H), 3.37 (s, 3 H), 3.33 (s, 3 H), 3.27 (s,

3 H), 2.22 (d, $J = 14.8$ Hz, 1 H), 2.00 (d, $J = 14.8$ Hz, 1 H), 1.62 (d, $J = 4.4$ Hz, 2 H), 1.33 (s, 9 H), 1.00 (s, 3 H), 0.90 (s, 3 H); ^{13}C NMR (62.9 MHz, CDCl_3) (δ) 140.7 (t), 121.2 (q), 116.6 (q), 106.7 (q), 95.5 (q), 83.8 (q), 78.9 (q), 52.4 (p), 51.5 (p), 50.5 (p), 48.4 (p), 44.2 (s), 40.1 (s), 30.9 (p), 30.2 (p), 29.5 (q), 27.9 (q), 27.2 (p); IR (film) 1642, 1105 cm^{-1} ; GCMS (70 eV) 321 (M - OMe, 2%), 262 (19%), 261 (18%), 133 (100%); HRMS (70 eV) m/z 321.2058 [(M - CH_3O) $^+$; calcd for $\text{C}_{19}\text{H}_{29}\text{O}_4$ ($\text{C}_{20}\text{H}_{32}\text{O}_5$ - CH_3O), 321.2066].

Reaction of 4,4-Dimethyl-2-(3,3-dimethylbutynyl)-2-cyclohexen-1-one (11c) with Tetramethoxyethylene (3b). For **23**: yield, 29%; colorless liquid; ^1H NMR (250 MHz, CDCl_3) (δ) 5.95 (d, $J = 1.6$ Hz, 1 H), 3.63 (s, 3 H), 3.38 (s, 3 H), 3.37 (s, 3 H), 3.35 (s, 3 H), 2.40–2.30 (m, 1 H), 1.77–1.47 (m, 3 H), 1.23 (s, 9 H), 1.00 (s, 6 H); ^{13}C NMR (62.9 MHz, CDCl_3) (δ) 150.3 (t), 120.9 (q), 116.3 (q), 106.3 (q), 96.2 (q), 84.3 (q), 78.5 (q), 52.8 (p), 51.8 (p), 50.0 (p), 48.8 (p), 33.6 (s), 32.7 (q), 30.9 (p), 29.9 (p), 28.2 (s), 27.9 (q), 27.3 (p); IR (film) 2964, 1141 cm^{-1} ; GCMS (70 eV) 321 (M - OCH_3 , 0.9%), 247 (22%), 148 (45%), 133 (100%); HRMS (70 eV) m/z 321.2058 [(M - CH_3O) $^+$; calcd for $\text{C}_{19}\text{H}_{29}\text{O}_4$ ($\text{C}_{20}\text{H}_{32}\text{O}_5$ - CH_3O), 321.2066].

Reaction of 5,5-Dimethyl-2-(3,3-dimethylbutynyl)-2-cyclohexen-1-one (10c) with *tert*-Butylethylene. For **24**: yield of purified adduct, 12%; light yellow liquid; ^1H NMR COSY (250 MHz, C_6D_6) (δ) 2.62 (dddd, $J = 4, 9, 9, 9$ Hz, 1 H, H_e), 2.50 (dd, $J = 9, 9$ Hz, 1 H, H_b), 2.37 (dd, $J = 2, 15$ Hz, 1 H, H_{3a}), 2.19 (ddd, $J = 11, 9, 9$ Hz, 1 H, H_{7a}), 2.04 (d, $J = 15$ Hz, 1 H, H_{3b}), 1.45 (1 H, H_{5a}), 1.30 (1 H, H_{7b}), 1.12 (1 H, H_{5b}), 1.18 (s, 9 H), 1.14 (s, 9 H), 0.83 (s, 3 H), 0.77 (s, 3 H); ^{13}C NMR (62.9 MHz, CDCl_3) (δ) 209.9 (q), 94.0 (q), 78.9 (q), 50.7 (s), 48.9 (t), 47.9 (q), 41.7 (s), 40.5 (t), 35.3 (q), 32.6 (q), 30.9 (p), 28.4 (p), 27.8 (q), 27.6 (q), 27.2 (p), 26.2 (s); IR 1709 cm^{-1} ; GCMS (70 eV) 288 (M, 1.5%), 148 (100%); HRMS (70 eV) m/z 288.2448 (M^+ ; calcd for $\text{C}_{20}\text{H}_{32}\text{O}$, 288.2453).

Oxidation of Furan 18a to Enedione 19. The reaction of **11c** with **2** was carried out according to the general procedure, but the solution was not degassed with argon. GLC analysis showed appearance and then disappearance of furan **18a** with simultaneous appearance of a new product. For **19**: yield, 38%; colorless liquid; ^1H NMR (250 MHz, CDCl_3) (δ) 2.85 (dd, $J = 10.4$ Hz, $J = 6.8$ Hz, 1 H), 2.42–2.33 (m, 2 H), 1.83 (dd, $J = 12.0$ Hz, $J = 6.8$ Hz, 1 H), 1.76–1.66 (m, 2 H), 1.64 (dd, $J = 12.0$ Hz, $J = 10.4$ Hz, 1 H), 1.26 (s, 3 H), 1.20 (s, 9 H), 1.14 (s, 3 H), 1.00 (s, 3 H) and 0.90 (s, 3 H); ^{13}C NMR (62.9 MHz, CDCl_3) (δ) 215.6 (q), 198.8 (q), 136.3 (q), 52.7 (t), 48.1 (q), 43.7 (q), 43.2 (s), 38.3 (s), 36.3 (s), 32.3 (q), 29.0 (p), 27.5 (p), 27.2 (p), 26.4 (p), 19.6 (p); IR (film) 2961, 1681 cm^{-1} ; GCMS (70 eV) 220 (M - C_4H_8 , 100%), 152 (16%); HRMS (70 eV) m/z 220.1447 [(M - C_4H_8) $^+$; calcd for $\text{C}_{14}\text{H}_{20}\text{O}_2$ ($\text{C}_{18}\text{H}_{28}\text{O}_2$ - C_4H_8), 220.1463]. A control experiment indicated that, under the same conditions but in the absence of light, oxidation of **18a** to **19** occurred about 20–25% as fast.

Attempts to add **3a** to **11c**, or to add **2**, **3a**, or **3b** to **12c** under the conditions described above led to no observable reaction.

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Supplementary Material Available: Copies of ^1H NMR spectra of all new compounds (24 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.