tion of **3t** with 2 equiv of 30% H_2O_2 for 12 h at 25 °C yielded the sulfone (65%), mp 200.5–202 °C, from ethyl acetate. Anal. Calcd for $C_{20}H_{15}NO_4S$: 365.07219; C, 65.74; H, 4.14; N, 3.83; S, 8.77. Found: *m/e* 365.07228; C, 65.75; H, 4.14; N, 3.82; S, 8.82.

***p*-[(*p*-Methylphenyl)sulfonyl]benzophenone.** Reaction of **1** (2.56 mmol) with p-$MeC_6H_4SO_2Na{\cdot}2H_2O$ (2.56 mmol) in 30 mL of DMF for 12 h at 25 °C gave a black solution. Treatment with brine and ether extraction gave 0.15 g (22%) of the keto sulfone: mp 199–200 °C; IR (KBr) 1650, 1595, 1395, 1320, 1290, 1160, 1100, 750, 690, 670 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 8.06–7.27 (m, 13 H), 2.42 (s, 3 H). Anal. Calcd for $C_{20}H_{16}O_3S$: 336.08202; C, 71.41; H, 4.79; S, 9.53. Found: *m/e* 336.08180; C, 71.33; H, 4.88; S, 9.69.

***p*-(Phenylsulfonyl)benzophenone**: mp 142.5–143.5 °C; IR (KBr) 1645, 1445, 1390, 1315, 1290, 1155, 1100, 745, 705, 685 cm^{-1}. Calcd for $C_{19}H_{14}O_3S$: 322.06637. Found: *m/e* 322.06493.

1,1-Diphenyl-1-[(dimethoxy)phosphinyl]-2,2-dinitroethane (2a): mp 133 °C dec; IR (KBr) 3050, 2990, 1595, 1580, 1510, 1450, 1375, 1330, 1255, 1060, 1040, 700 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.44–7.05 (m, 10 H), 3.46 (d, 6 H, J_{P-H} = 11.5 Hz), 7.73 (d, 1 H, J_{P-H} = 11 Hz). Calcd for $C_{16}H_{17}N_2O_7P$: 380.07735. Found: *m/e* 380.07706.

1,1-Diphenyl-1-(diethoxyphosphinyl)-2,2-dinitroethane (2b): mp 128–129 °C dec. Anal. Calcd for $C_{18}H_{21}N_2O_7P$: 408.10865; C, 52.94; H, 5.18; N, 6.86; P, 7.58. Found: *m/e* 408.10817; C, 53.7; H, 5.46; N, 6.88; P, 7.57.

1,1-Diphenyl-1-(dimethoxythiophosphinyl)-2,2-dinitroethane (2c): mp 137 °C dec. Calcd for $C_{16}H_{17}N_2O_6PS$: 396.05450. Found: *m/e* 396.05548.

4,4-Diphenyl-5,5-dinitro-2-pentanone (2e): mp 137 °C; ^{1}H NMR ($CDCl_3$) δ 8.18 (s, 1 H), 7.1 (s, 10 H), 3.52 (s, 2 H), 1.69 (s, 3 H). Anal. Calcd for $C_{17}H_{16}N_2O_5$: 328.10593; C, 62.19; H, 4.91; N, 8.53. Found: *m/e* 328.10540; C, 61.99; H, 5.11; N, 8.40.

2,2-Dimethyl-5,5-diphenyl-6,6-dinitro-3-hexanone (2f): mp 146–147 °C; ^{1}H NMR ($CDCl_3$) δ 8.52 (s, 1 H), 7.17 (s, 10 H), 3.63 (s, 2 H), 0.76 (s, 9 H). Anal. Calcd for $C_{20}H_{22}N_2O_5$: 370.15288; C, 64.85; H, 5.98; N, 7.56. Found: *m/e* 370.15268; C, 65.05; H, 5.98; N, 7.54.

Registry No. **1**, 15795-74-1; **2a**, 97807-29-9; **2b**, 97807-30-2; **2c**, 97807-31-3; **2d**, 97807-32-4; **2e**, 97807-34-6; **2f**, 97807-33-5; **2g**, 97807-35-7; **2h**, 97807-37-9; **2i**, 97807-38-0; **2j**, 97807-36-8; **2k**, 38554-49-3; **3s**, 97807-39-1; **3t**, 97807-43-7; **3u**, 97807-40-4; **3v**, 97807-42-6; **3w**, 97807-41-5; **3x**, 97807-44-8; **3y**, 97807-45-9; **a**·K, 54057-98-6; **b**·K, 54058-00-3; **c**·K, 80866-15-5; **d**·K, 71774-85-1; **e**·Li, 62415-84-3; **f**·Li, 70367-67-8; **g**·Li, 55905-98-1; **h**·K, 82101-71-1; **i**·K, 15590-26-8; **j**·K, 865-33-8; **k**·K, 151-50-8; **l**·K, 28273-55-4; **m**·K, 7758-09-0; **n**·K, 26652-46-0; **o**·K, 19294-29-2; **p**·K, 127-08-2; **q**·K, 10387-40-3; **r**·K, 865-47-4; **s**·K, 10577-48-7; **t**·K, 3111-52-2; **u**·K, 40645-42-9; **v**·K, 71367-29-8; **w**·K, 31367-69-8; **x**·K, 40973-72-6; **y**·K, 100-67-4; **z**·K, 1122-93-6; p-$MeC_6H_4SO_2H{\cdot}Na$, 824-79-3; EtOH·K, 917-58-8; KOH, 1310-58-3; $Ph_2C(OMe)_2$, 2235-01-0; p-$PhSO_2C_6H_4COPh$, 54687-39-7; p-(p-$MeC_6H_4SO_2$)C_6H_4COPh, 97807-46-0; benzophenone, 32488-48-5; 1-nitro-1-(phenylsulfinyl)-2,2-diphenylethylene, 97825-40-6; 1-nitro-1-(phenylsulfonyl)-2,2-diphenylethylene, 97807-47-1.

Some [2 + 2] and [3 + 2] Photocycloadditions of α,β-Acetylenic Ketones

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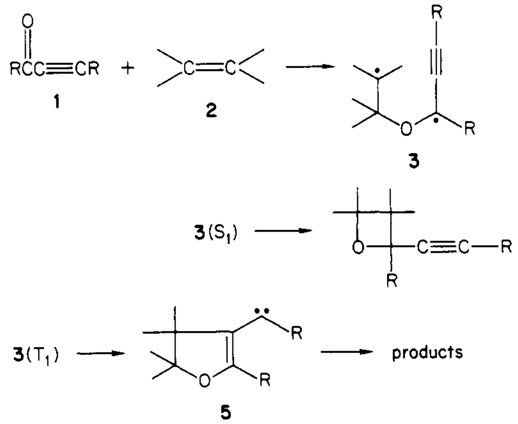
Photocycloaddition between 4,4-dimethyl-1-phenyl-2-pentyn-1-one (**7**) and the alkoxyalkenes **8** and **13** occurs in both the [2 + 2] and [3 + 2] fashions. Studies on the reaction of **7** and **13** indicate that formation of both types of product is quenched at the same rate by naphthalene and that these processes follow Stern–Volmer kinetics with $k_q\tau \sim 9.2$ M^{-1}. With 3-pentyn-2-one (**6**), **8** gives only [2 + 2] product **17**. Ketone **7** reacts with 2-butyne to yield the [3 + 2] adduct **18** and with 1,1-dimethylallene (**20**) to yield the [2 + 2] adducts **21** and **22**. These results may be contrasted with the earlier observation that triplets of ketones **6** and **7** yield essentially only [3 + 2] products from simple alkenes.

Previous studies have revealed that photochemical cycloaddition between α,β-acetylenic ketones (**1**) and simple olefins (**2**) proceeds along two paths.[3,4] The 1,4-biradical (**3**) formed from the ketone singlet and olefin closes to an oxetane (**4**), but **3** from the ketone triplet and olefin cyclizes in the [3 + 2] fashion to a vinyl carbene (**5**). Products are then formed by way of various well-precedented processes that depend on the specific substituents in **5**.[3-5] These earlier investigations concerned reactions of 3-pentyn-2-one (**6**), related alkynones, and 4,4-dimethyl-1-phenyl-2-pentyn-1-one (**7**) with simple alkenes such as tetramethylethylene, isobutylene, and 2-butene. In the present work our purpose was to examine these cyclo-



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[1] The Rockefeller University.

[2] Universität Hamburg.

[3] Saba, S.; Wolff, S.; Schröder, C.; Margaretha, P.; Agosta, W. C. *J. Am. Chem. Soc.* **1983**, *105*, 6902.

[4] Hussain, S.; Agosta, W. C. *Tetrahedron* **1981**, *37*, 3301.

[5] Wolff, S.; Agosta, W. C. *J. Am. Chem. Soc.* **1984**, *106*, 2363.

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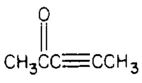
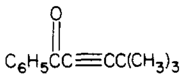


$CH_3C(=O)C{\equiv}CCH_3$

6



$C_6H_5C(=O)C{\equiv}CC(CH_3)_3$

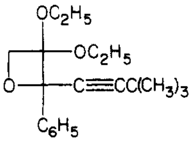
7

$CH_2{=}C(OC_2H_5)_2$

8

additions with alkoxyalkenes, as well as with acetylenic and allenic systems. We chose 7 as our primary ketone substrate, a choice motivated by several considerations. Since [3 + 2] cycloaddition appears to be a triplet reaction and intersystem crossing is rapid in aromatic ketones, it seemed reasonable that the [3 + 2] process would be particularly favored in 7. We have reported, for example, that 7 adds tetramethylethylene essentially exclusively in the [3 + 2] fashion.[3] A second reason for using 7 here was our recognition that, while [2 + 2] cycloaddition of alkoxyalkenes to saturated ketones has been familiar for years,[6,7] there is little information on reaction of electron-rich olefins with aromatic ketones of any sort.[8] A final practical attraction of 7 is that on [3 + 2] addition it yields a vinyl carbene (as 5) that bears a *tert*-butyl substituent and stabilizes itself by aromatic substitution, forming an indene derivative.[3] Previous experience has shown that hydrogen-bearing groups, such as methyl, on the carbene lead to 1,2-hydrogen shifts and formation of difficulty handled 3-vinyl-4,5-dihydrofurans as products.[3,4] In the paragraphs that follow we report photocycloadditions involving two alkoxyalkenes, an alkyne, and an allene.

We first examined the reaction of 7 with ketene diethyl acetal (8). Irradiation (λ > 340 nm) of a benzene solution of these addends yielded two products, oxetane 9 (50%) and the unstable indenofuran 10 (18%), the structures of which were apparent from their spectroscopic properties. Further support for the structure of 9 came when, on attempted deketalization using pyridinium tosylate in aqueous acetone,[9] the oxetane was transformed into allenic ester 11. There is good precedent for the acid-catalyzed loss of formaldehyde from 9 to form 12[10] and also for the hydrolysis of an alkynyl-substituted ketene acetal such as 12 to give either an allenic or an acetylenic ester.[11] Formation of 10 can be rationalized as shown, through [3 + 2] addition of 7 and 8 (as 3 → 5), aromatic substitution by the carbene,[3] and finally aromatization of the dihydrofuran with loss of ethanol. Addition of 7 to ethyl vinyl ether (13) in benzene proceeded analogously to furnish oxetanes 14 and 15 and indenofuran 16.[12] The regiochemistry observed in 9, 14, and 15 [alkoxy substitutents at C(3) rather than C(2)] is that typically favored in additions of these alkoxyalkenes to saturated ketones.[6-8]



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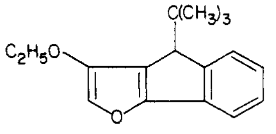

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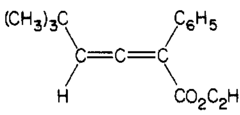

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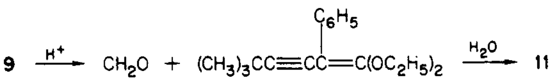
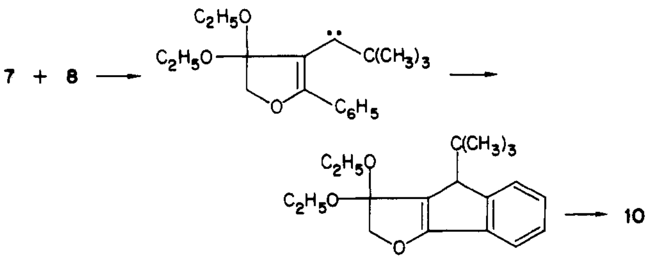


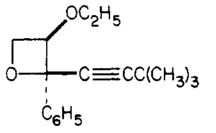
$9 \xrightarrow{H^+} CH_2O + (CH_3)_3CC{\equiv}CC(C_6H_5){=}C(OC_2H_5)_2 \xrightarrow{H_2O} 11$

12



$CH_2{=}CHOC_2H_5$

13



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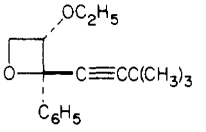

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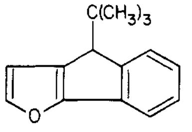

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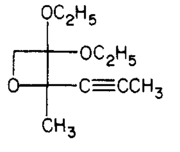

17

This observation of both [2 + 2] and [3 + 2] adducts from 7 and the two ethoxyalkenes suggests that either these electron-rich olefins capture 7 singlets before intersystem crossing or else, unlike previous experience, the triplet biradical (as 3) in these cases closes in both the [3 + 2] and [2 + 2] fashions. Even though intersystem crossing is rapid in aromatic ketones, the first possible explanation required at least some consideration since the rate of interaction of electron-rich alkenes with ketone carbonyls is known to be a function of the ionization potential of the alkene [1,2-diethoxyethylene is, for example, much more reactive than ethoxyethylene (13)[8,13]]. In addition, as noted above, there is little known in general about addition of such electron-rich olefins to aromatic ketones. We investigated the origin of 14–16 through study of the quenching of the reaction between 13 and 7. In these experiments naphthalene quenched the appearance of all three products at essentially the same rate; Stern–Volmer kinetics[14] were followed, and $k_q\tau$ was ~9.2 M^{-1}.[15] We conclude that 14–16 all come from the same quenchable triplet species, whose lifetime is ~2 ns.[16a] The triplet biradical from alkoxyalkenes then closes in both the [2 + 2] and [3 + 2] fashions. The reasons for this difference between simple olefins and alkoxyalkenes remain to be elucidated. It has been suggested in connection with a related process that the [3 + 2] closure occurs directly from the triplet biradical without prior spin inversion to the singlet.[16b] If this is correct, two simple rationalizations for

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(7) Turro, N. J.; Wriede, P. A. *J. Am. Chem. Soc.* **1970**, *92*, 320.

(8) Jones, G., II. *Org. Photochem.* **1981**, *5*, 1.

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(10) Kohler, E. P.; Richtmyer, N. K. *J. Am. Chem. Soc.* **1930**, *52*, 2038. Büchi, G.; Inman, C. G.; Lipinsky, E. S. *Ibid.* **1954**, *76*, 4327.

(11) Gusev, B. P.; Tsurgozen, L. A.; Kucherov, V. F. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1971**, 141.

(12) In hexane as solvent preparative photolysis gave appreciable amounts of the two diastereomeric pinacols formed through reductive dimerization.

(13) Yang, N. C.; Hui, M. H.; Shold, D. M.; Turro, N. J.; Hautala, R. R.; Dawes, K.; Dalton, J. C. *J. Am. Chem. Soc.* **1977**, *99*, 3023. Schore, N. E.; Turro, N. J. *Ibid.* **1975**, *97*, 2482.

(14) Wagner, P. J. In "Creation and Detection of the Excited State"; Marcel Dekker: New York, 1971; Vol. 1, Part A, p 173.

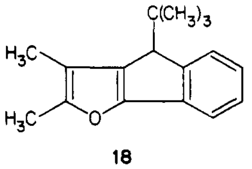
(15) This may be compared to $k_q\tau$ ~20.7 M^{-1} for quencing by naphthalene of the reaction between 3-pentyn-2-one and tetramethylethylene[3]. Information about two minor higher adducts of 7 and 13 observed spectroscopically in the quenching studies is given in the Experimental Section.

(16) (a) Wagner, P. J.; Kochevar, I. *J. Am. Soc.* **1968**, *90*, 2232. (b) Rao, V. B.; Wolff, S.; Agosta, W. C. *Ibid.* **1985**, *107*, 521.

the [2 + 2] cyclization of the triplet alkoxyalkene-derived biradical are attractive. This species, in comparison with the biradical from simple olefins, could undergo intersystem crossing to the singlet more rapidly or undergo [3 + 2] cyclization more slowly. These need not be mutually exclusive, and either could permit competitive spin inversion and [2 + 2] cyclization of the triplet biradical species.

In light of these results it was interesting to examine the cycloaddition between pentynone **6** and ketene diethyl acetal (**8**). The same preference for [2 + 2] addition was noted, and the only product obtained was oxetane **17**.

We next studied the addition of 2-butyne to **7**. The [3 + 2] product **18** was formed smoothly (60%) along with a small amount of a 2:1 adduct **19** that was rather unstable and reverted thermally to **18**. Adduct **19** was not obtained analytically pure, but its structure and stereochemistry could be assigned. The regiochemistry of photoaddition of aldehydes and ketones to furans is known to be as shown for **19**, with the oxygen of the carbonyl group adding α rather than β on the furan ring.[17] This orientation in **19** is supported by the presence in its NMR spectrum of a methyl signal at 1.74 ppm, a position typical[18] of methyl on a ketal carbon atom. The appearance of the second unique methyl signal at 0.82 ppm strongly suggests the relative stereochemistry of the oxetane ring with cis vicinal methyl and phenyl groups. From spectra of known oxetanes[4,19] it appears that shielding from an adjacent cis phenyl should shift this methyl above 1.0 ppm, but with inverted stereochemistry of the phenyl and alkynyl substituents, the methyl should resonate at 1.1 ppm or lower field.[20] The *tert*-butyl group is assigned cis to the furan methyls inasmuch as models indicate that it effectively shields one side of the furan ring from [2 + 2] addition of **7** to form the oxetane.



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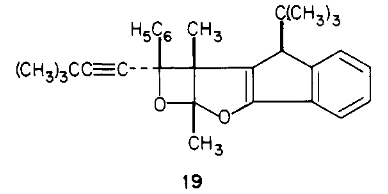
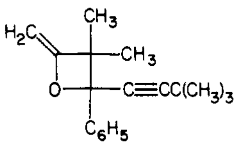


19

$CH_2{=}C{=}C(CH_3)_2$

20



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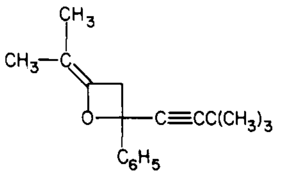

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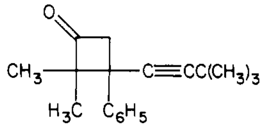

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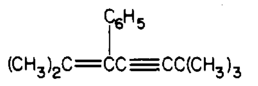

$(CH_3)_2C{=}C(C_6H_5)C{\equiv}CC(CH_3)_3$

24

Finally, irradiation of **7** and 1,1-dimethylallene (**20**) yielded a mixture of the two possible oxetane adducts **21** and **22**. Attempted chromatographic separation of these products gave **21** without difficulty, but **22** underwent rearrangement to the isomeric cyclobutanone **23**. These same products were obtained quantitatively on heating the mixture of **21** and **22** at 100 °C in benzene. Alternatively, upon gas chromatography at 150 °C **21** lost ketene to furnish **24**. In reaction with allene **20** then, the acetylenic ketone behaves as saturated ketones do.[21] Other examples of rearrangement and fragmentation of α-alkylideneoxetanes similar to those of **21** and **22** are well-known.[21]

Experimental Section

General Information. All VPC was carried out by using a Varian Aerograph Model 920 gas chromatograph with one of the following columns: A, 10% QF-1, 2 ft; B, 10% Carbowax, 5 ft; C, 10% OV-101, 2 ft. All columns were packed in 0.25-in. aluminum tubing with 45/60 Chromosorb W. Unless otherwise stated, all IR spectra were recorded for CCl_4 solution and NMR for $CDCl_3$ solution, the former on a Perkin-Elmer Model 237 B spectrophotometer and the latter on a Nicolet/Oxford NT-300 (300 MHz) spectrometer. In addition, a Varian T-60A (60 MHz) NMR spectrometer was used. Unless otherwise stated, all pure compounds were obtained as colorless oils; products are usually listed in their order of elution upon VPC.

General Procedure for Photolyses. A solution of pure alkynone in anhydrous benzene (3–4 mg/mL; 0.02–0.04 M) contained in a toroidal Pyrex glass vessel was irradiated under N_2 with a Hanovia 450-W medium-pressure mercury arc lamp employing uranium glass filter. In all cases required olefin/acetylene (8–10-fold molar excess) was added to the alkynone in benzene, and a stream of nitrogen gas was bubbled through this solution for 30 min prior to irradiation.

Photolysis of 4,4-Dimethyl-1-phenyl-2-pentyn-1-one (7) with 1,1-Diethoxyethylene (8). A solution of **7**[3] (0.186 g, 1 mmol) in anhydrous benzene (50 mL, 0.02 M) containing **8** (0.928 g, 8 mmol) was photolyzed. TLC analysis indicated completion of reaction in 5 h and showed the presence of two major components. Benzene was distilled off, and the residue was subjected to flash chromatography[22] using 10% ether in hexane as eluent to obtain **10** (18%) and **9** (50%). **10**: unstable, blue-green fluorescence; IR 3090 (w), 2980 (s), 2920 (m), 2895 (m), 1608 (w), 1580 (m), 1535 (m), 1480 (m), 1380 (m), 1365 (m), 1245 (m), 1220 (w) cm^{-1}; ^1H NMR (60 MHz) δ 7.0–7.6 (m, 4 H, Ar), 7.06 (s, 1 H, furan H), 3.95 (q, 2 H, $J = 6.5$ Hz, OCH_2CH_3), 3.43 (s, 1 H, CH), 1.40 (t, 3 H, $J = 6.5$ Hz, CH_2CH_3) 1.06 (s, 9 H, $C(CH_3)_3$); mass spectrum, m/z 256.1465 (M^+; calcd for $C_{17}H_{20}O_2$, 250.1463). **9**: IR 3080 (w), 3040 (w), 3000 (s), 2950 (m), 2910 (m), 2235 (w), 1480 (s), 1390 (m), 1368 (s), 1325 (m), 1275 (m), 1248 (m), 1203 (s), 1190 (s), 1120 (m), 1040 (m), 980 (m), 940 (m) cm^{-1}; ^1H NMR (300 MHz) δ 7.46–7.66 (m, 2 H, Ar), 7.22–7.38 (m, 3 H, Ar), 4.71 (d, 1 H, $J = 6.7$ Hz, OCH_2), 4.53 (d, 1 H, $J = 6.7$ Hz, OCH_2), 3.7–3.81 (m, 1 H, OCH_2CH_3), 3.42–3.55 (m, 1 H, OCH_2CH_3), 3.25–3.35 (m, 1 H, OCH_2CH_3), 3.06–3.16 (m, 1 H, OC_2CH_3), 1.31 (s, 9 H, $C(CH_3)_3$), 1.286 (t, 3 H, $J = 6.6$ Hz, CH_2CH_3), 0.847 (t, 3 H, $J = 7.0$ Hz, CH_2CH_3). Anal. Calcd for $C_{19}H_{26}O_3$: C, 75.46; H, 8.67. Found: C, 75.47; H, 8.45.

Ethyl 5,5-Dimethyl-2-phenyl-2,3-hexadienoate (11). Oxetane **9** (0.05 g, 0.16 mmol) was dissolved in acetone (10 mL) with water (0.5 mL), and pyridinium tosylate (0.1 g) was added. This solution was heated at reflux under N_2 for 2.5 h, when TLC analysis indicated the disappearance of starting material. Aqueous workup, extraction with ether (2 × 30 mL), and flash chromatography[22] (25% ether in hexane) yielded pure **11** (0.021 g, 54%): IR 3085 (w), 3050 (w), 2980 (s), 2915 (m), 2890 (m), 1950 (w), 1725

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(s), 1494 (w), 1450 (w), 1360 (m), 1275 (m), 1248 (w), 1218 (m), 1180 (m), 1125 (m), 1040 (m), 1025 (m) cm^{-1}; ^{1}H NMR δ 7.51–7.54 (m, 2 H, Ar), 7.25–7.35 (m, 3 H, Ar), 5.78 (s, 1 H), 4.18–4.34 (m, 2 H, $\mathrm{OC}\mathit{H}_2\mathrm{CH}_3$), 1.31 (t, 3 H, J = 7.1 $\mathrm{CH_2C}\mathit{H}_3$), 1.17 (s, 9 H, $C(CH_3)_3$); mass spectrum, m/z 244.1451 (M$^+$; calcd for $C_{16}H_{20}O_2$, 244.1463).

Photolysis of 4,4-Dimethyl-1-phenyl-2-pentyn-1-one (7) with Ethyl Vinyl Ether (13). A solution of **7** (0.186 g, 1 mmol) and freshly distilled **13** (0.576 g, 8 mmol) in benzene (50 mL, 0.02 M) was irradiated. VPC analysis on column A after 5 h indicated disappearance of the starting material. Benzene was distilled off, and the residue subjected to flash chromatography.[22] Elution yielded indenofuran **16** (hexane) followed by oxetanes **14** and **15** (10% ether in hexane). **16** (0.021 g, 10%): unstable oil with blue-green fluorescence; IR 2960 (m), 2950 (s), 2930 (m), 2865 (m), 1617 (w), 1475 (m), 1430 (m), 1365 (m), 1225 (w), 1140 (m), 1075 (m), 1020 (w), 895 (m) cm^{-1}; ^{1}H NMR δ 6.8–7.6 (m, 5 H, Ar and furan H), 6.27 (d, J = 1.8 Hz, 1 H, furan H), 3.19 (s, 1 H, CH), 0.92 (s, 9 H, $C(CH_3)_3$); mass spectrum, m/z 212.1196 (M$^+$; calcd for $C_{15}H_{16}O$, 212.1201). **14** (0.021 g, 8%): IR 3075 (w), 3048 (w), 2993 (s), 2948 (m), 2245 (w), 1450 (m), 1365 (w), 1275 (m), 1170 (w), 1120 (m), 973 (w), 950 (w), 903 (m) cm^{-1}; ^{1}H NMR δ 7.66–7.69 (m, 2 H, Ar), 7.25–7.42 (m, 3 H, Ar), 4.87 (dd, J = 6.9, 6.9 Hz, 1 H, OCH), 4.59 (dd, J = 5.5, 6.7 Hz, 1 H, OCH_2), 4.45 (dd, J = 5.5, 6.9 Hz, 1 H, OCH_2), 3.2–3.3 (m, 1 H, $\mathrm{OC}\mathit{H}_2\mathrm{CH}_3$), 3.04–3.14 (m, 1 H, $\mathrm{OC}\mathit{H}_2\mathrm{CH}_3$), 1.31 (s, 9 H, $C(CH_3)_3$), 0..80 (t, J = 7.0 Hz, 3 H, $\mathrm{CH_2C}\mathit{H}_3$); mass spectrum, m/z 256.1585 (M$^+$; calcd for $C_{17}H_{22}O_2$, 258.1618). **15** (0.02 g, 8%): IR 3075 (w), 3040 (w), 2985 (s), 2950 (w), 2910 (m), 2245 (w), 1450 (m), 1370 (w), 1348 (w), 1278 (m), 1245 (w), 1178 (w), 1130 (w), 955 (m) cm^{-1}; ^{1}H NMR δ 7.62–7.65 (m, 2 H, Ar, 7.25–7.42 (m, 3 H, Ar), 4.59–4.68 (m, 2 H, OCH_2), 4.235 (dd, J = 6.8, 6.8 Hz, 1 H, OCH), 3.69–3.75 (m, 1 H, $\mathrm{OC}\mathit{H}_2\mathrm{CH}_3$) 3.26–3.36 (m, 1 H, $\mathrm{OC}\mathit{H}_2\mathrm{CH}_3$), 1.34 (s, 9 H, $C(CH_3)_3$), 1.24 (t, J = 7.02 Hz, 3 H, $\mathrm{CH_2C}\mathit{H}_3$); mass spectrum, m/z 258.1601 (M$^+$; calcd for $C_{17}H_{22}O_2$, 258.1618).

Photolysis of 4,4-Dimethyl-1-phenyl-2-pentyn-1-one (7) with 2-Butyne. A solution of **7** (0.186 g, 1 mmol) and 2-butyne (0.432 g, 8 mmol) in benzene (50 mL, 0.02 M) was photolyzed. VPC analysis (column A, 160 °C) indicated the completion of reaction in 5 h. Benzene was distilled off, and residue was purified by flash chromatography[22] Elution with hexane yielded compound **18** followed by **19** with 10% ether in hexane. **18** (0.145 g, 60%): IR 3075 (w), 2975 (s), 2890 (m), 1625 (w), 1395 (m), 1370 (m), 1225 (w), 1130 (w), 860 (m) cm^{-1}; ^{1}H NMR δ 7.15–7.60 (m, 3 H, Ar), 7.01 (ddd 1 H, J = 1.3, 7.5, 7.5 Hz, Ar), 3.34 (br s [$w_{1/2}$ ~1.5 Hz), 1 H, CH) 2.32 (d, J = 0.5 Hz, 3 H, CH_3), 2.04 (d, J = 0.6 Hz, 3 H, CH_3), 1.02 (s, 9 H, $C(CH_3)_3$); mass spectrum, m/z 240.1512 (M$^+$; calcd for $C_{17}H_{20}O$, 240.1514). **19** (0.063 g, 15%): colorless low-melting solid; IR 3090 (w), 2983 (s), 2950 (m), 2885 (m), 2245 (w), 1625 (w), 1450 (m), 1400 (m), 1375 (m), 1360 (m), 1270 (m), 1210 (w), 1150 (w), 1120 (w), 950 (m), 870 (m), 853 (w) cm^{-1}; ^{1}H NMR δ 7.16–7.66 (m, 9 H, Ar), 3.88 (s, 1 H, CH), 1.74 (s, 3 H, CH_3), 1.12 (s, 9 H, $C(CH_3)_3$), 0.89 (s, 9 H, $C(CH_3)_3$), 0.82 (s, 3 H, CH_0); compound is highly unstable thermally, and VPC on column A (160 °C) gives **18** and **7** quantitatively.

Photolysis of 3-Pentyn-2-one (6) with 1,1-Diethoxyethylene (8). Pentynone **6** (0.082 g, 1 mmol) and **8** (0.928 g, 8 mmol) were dissolved in benzene (30 mL, 0.03 M), and the solution was photolyzed. VPC analysis (column B, 150 °C) after 100 h of photolysis showed about 50% conversion. Benzene was removed, and the residue was purified by flash chromatography (10% ether in hexane) to yield unreacted 3-pentyn-2-one and **17** (0.085 g, 43%): IR 3000 (s), 2950 (m), 2905 (m), 2250 (w), 1440 (m), 1370 (w), 1325 (m), 1205 (s), 1115 (m), 1050 (s), 945 (m) cm^{-1}; ^{1}H NMR δ 4.46 (d, J = 6.8 Hz, 1 H, OCH_2), 4.39 (d, J = 6.8 Hz, 1 H, OCH_2), 3.43–3.54 (m, 1 H, $\mathrm{OC}\mathit{H}_2\mathrm{CH}_3$), 3.21–3.35 (m, 3 H, $\mathrm{OC}\mathit{H}_2\mathrm{CH}_3$), 1.92 (s, 3 H, CH_3), 1.60 (s, 3 H, CH_3), 1.26 (t, J = 7.0 Hz, 3 H, $\mathrm{CH_2C}\mathit{H}_3$), 1.24 (t, J = 7.0 Hz, 3 H, $\mathrm{CH_2C}\mathit{H}_3$). Anal. Calcd for $C_{11}H_{18}O_3$: C, 66.64; H, 9.15. Found: C, 66.61; H, 9.20.

Photolysis of 4,4-Dimethyl-1-phenyl-2-pentyn-1-one (7) with 1,1-Dimethylallene (20). A benzene solution (0.02 M) of **7** (0.186 g, 1 mmol) and **20**[23] (0.68 g, 10 mmol) was irradiated for 6 h. Solvent was removed by distillation, and crude residue upon preparative VPC (column C, 150 °C) yielded **24** and **23** in a 1:1 ratio (70% yield). When solvent from the photolysate was removed at room temperature under vacuum and residue purified by preparative TLC (5% ether in hexane), **21** and **23** were obtained in nearly quantitative yield with ~3% of oxetane **22** present as contamination in **21**. Oxetane **21** and **23** were also quantitatively formed when crude photolysate was heated in a sealed tube for 1 h at 100 °C. **21**: IR 3060 (w), 3040 (w), 2980 (s), 2930 (s), 2820 (m), 2225 (w), 1598 (w), 1455 (m), 1380 (w), 1275 (s), 1193 (m), 1125 (m) cm^{-1}; ^{1}H NMR δ 7.25–7.65 (m, 5 H, Ar), 4.19 (d, J = 3.8 Hz, 1 H), 3.77 (d, J = 3.8 Hz, 1 H), 1.54 (s, 3 H, CH_3), 1.27 (s, 9 H, $C(CH_3)_3$), 0.734 (s, 3 H, CH_3); mass spectrum, m/z 254.1672 (M$^+$; calcd for $C_{18}H_{22}O$, 254.1671). **22**: ^{1}H NMR (data are obtained after subtracting the values of **21** from the mixture) δ 7.25–7.65 (m, 5 H, Ar), 3.61 (dq, J = 1.5, 14.2 Hz, 1 H), 3.25 (dq, J = 1.4, 14.0 Hz, 1 H), 1.62 (br s, 3 H, CH_3), 1.44 (br s, 3 H, CH_3), 1.28 (s, 9 H, $C(CH_3)_3$). **24**: IR 2970 (s), 2935 (m), 2860 (w), 2205 (m), 1600 (w), 1450 (m), 1370 (m), 1275 (m), 1235 (w), 1195 (w) cm^{-1}; ^{1}H NMR δ 7.29–7.31 (m, 5 H, Ar), 2.09 (s, 3 H, CH_3), 1.79 (s, 3 H, CH_3), 1.26 (s, 9 H, $C(CH_3)_3$); mass spectrum, m/z 212.1559 (M$^+$; calcd for $C_{16}H_{20}$, 212.1565). **23**: IR 2960 (s), 2930 (m), 2860 (m), 2205 (w), 1790 (s), 1463 (m), 1380 (w), 1370 (m), 1275 (w), 1150 (w) cm^{-1}; ^{1}H NMR δ 7.35–7.39 (m, 5 H, Ar), 3.81 (d, J = 17.0 Hz, 1 H), 3.39 (d, J = 17.1 Hz, 1 H), 1.42 (s, 3 H, CH_3), 1.24 (s, 9 H, $C(CH_3)_3$), 0.71 (s, 3 H, CH_3); mass spectrum, m/z 254.1678 (M$^+$; calcd for $C_{18}H_{22}O$, 254.1671).

Stern–Volmer Quenching of Addition of 13 to 7 by Naphthalene. Solutions of **7** (0.1 M) and **13** (0.4 M) in benzene containing naphthalene (11 concentrations, 0.0–0.15 M) were irradiated at $\lambda \sim 350$ nm and analyzed gas chromatographically with tetradecane as internal standard. Distribution of products **14–16** was invariant with quencher concentration, and a plot of Φ_0/Φ vs. [Q] was linear with slope 9.2 ± 0.6 M^{-1}. Two additional minor products (10–15% total) were detected by GC-MS. From the presence of m/z 444 in their mass spectra they were taken to be 2:1 adducts of **7** with **13**. Their formation was quenched much more efficiently by naphthalene than that of **14–16**.

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