Tetrahedron Vol. 37, No. 19, pp. 3301 to 3305, 1981
Printed in Great Britain

0040-4020/81/193301-05$02.00/0
Pergamon Press Ltd.

PHOTOCHEMICAL [3 + 2] CYCLOADDITION OF α,β-ACETYLENIC KETONES WITH SIMPLE OLEFINS

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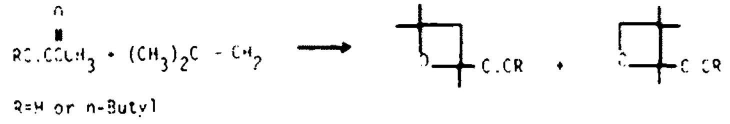
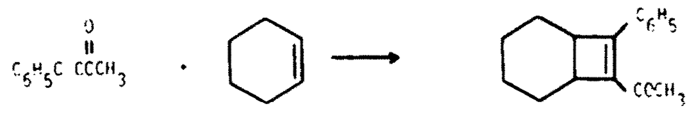
(*Received in USA April 1981*)

Abstract—Irradiation of 3-pentyn-2-one (**1**) in the presence of tetramethylethylene, isobutylene, and *cis*- and *trans*-2-butene leads to vinyldihydrofurans **3**, **5**, **6**, **8**, and **9** (Table 1) in a novel [3 + 2] photochemical cycloaddition reaction. A related adduct **13** is formed between tetramethylethylene and 5,5-dimethyl-3-hexyn-2-one (**2**). A mechanism incorporating an initial biradical that closes to a carbene (eqn 3) is proposed to account for these reactions.

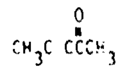
We describe here several examples of a new photochemical cycloaddition reaction between α,β-acetylenic ketones and simple olefins. Investigations of the photochemistry of such ynones[1] have been much less extensive than those involving conjugated enones, and there are rather few previous studies in this area. Earlier work has shown that both alkynyloxetanes[2,3] and acylcyclobutenes[3,4] can be formed on irradiation of acetylenic ketones with alkenes. For example, addition of isobutylene to 3-butyn-2-one or 3-octyn-2-one yields in each case a mixture of the two possible oxetanes (eqn 1),[2] while reaction of cyclohexene with 4-phenyl-3-butyn-2-one leads only to addition at the triple bond and formation of a cyclobutene (eqn 2).[3] These previously reported reactions then are obvious analogues of photochemical processes that have been well studied in saturated and α,β-olefinic ketones of various structural types.[5] In contrast, the cycloadditions reported in the present work are [3 + 2] reactions resulting from a novel photochemical transformation. The products formed are accompanied by varying amounts of alkynyloxetanes but apparently no acylcyclobutenes.



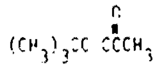
(1)



(2)



$CH_3\overset{O}{C}C{\equiv}CCH_3$

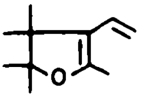
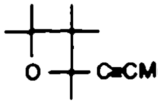
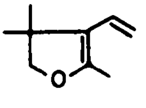
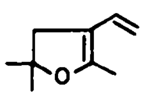
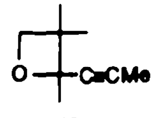
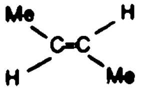
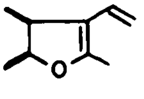
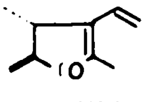
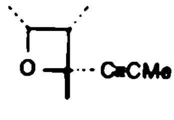
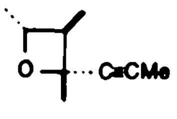
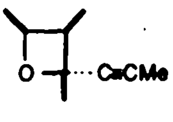
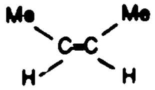
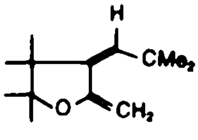


$(CH_3)_3CC{\equiv}C\overset{O}{C}CH_3$

2

In our investigations to date we have used 3-pentyn-2-one (**1**)[6] and the related t-Bu-substituted ketone **2**[7] as representative simple acetylenic ketones. Irradiation of these ketones in benzene solution through uranium glass-filtered light (λ > 340 nm) in the presence of various olefins leads to the results summarized in Table 1. Yields indicated are for high conversions and have not been optimized. The furanoid products are relatively sensitive to both heat and oxygen and are, therefore, easily destroyed; this leads to some reduction in the isolated yields. The indicated structures of the photoproducts were deduced from their IR, proton NMR, and UV spectroscopic properties given in detail in the Experimental. For the vinyldihydrofurans from **1**, UV absorptions were in reasonable agreement with the reported spectrum of the open chain model diene **15** (λ_{max} 247 nm, ε 18500).[8] NMR spectra for these products were similarly in accord with the extensive data available for **16**, **17**, and several similar alkoxy dienes.[9] For the oxetanes the most important spectral data are IR absorption typical of disubstituted alkynes at ~2250 cm^{-1} (w), the absence of carbonyl absorption in the IR, and NMR spectra that compare favorably with those previously recorded for alkynyl-oxetanes.[2,3] The stereochemical assignments for dihydrofurans **8** and **9** and for oxetanes **10**–**12** are based on the relative positions of methyl and methine signals in their NMR spectra. For **8** and **9** the result is in general agreement with earlier conclusions for the closely related tetramethyldihydrofurans **18** and **19**;[10] for the oxetanes **10**–**12** the assignments are in accord with the reported spectra of tetramethyloxetanes **20**[11] and **21**,[11] as well as other related

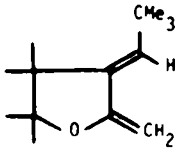
Table 1. Products of cycloadditions reactions

Ketone	Olefin	Products, (yield)
1	$Me_2C{=}CMe_2$	 3 (77%)  4 (8%)
1	$Me_2C{=}CH_2$	 5 (11%)  6 (12%)  7 (40%)
1		 8 (7%)  9 (41%)  10 (2%)  11 (19%)  12 (1%)
1		8 (10%) 9 (17%) 10 (8%) 11 (12%) 12 (2%)
2	$Me_2C{=}CMe_2$	 13 (47%)

compounds.[12] The structure of the product 13 formed from t-butyl ketone 2 and tetramethylethylene follows from NMR and UV spectra that require a conjugated diene system (λ_{max} 245 nm, ϵ 15,850) containing a terminal methylene group and one additional olefinic hydrogen atom along with two pairs of identical Me groups. On gas chromatography at 100° 13 is partially converted to an isomer 14 having a very similar NMR spectrum but in which the UV absorption has shifted to 235 nm (ϵ 17,400). This isomer 14 is unstable and reverts to 13 on heating in inert solvent.[13] In each of these compounds the t-Bu group is in a severely hindered environment, and its quite low field NMR signal (δ 1.22 ppm in each case) independently suggests this crowding. From earlier work it is known that such low field resonance is characteristic of a t-Bu group that is both directly attached to a double bond and also unusually hindered.[14]

The UV spectra indicate considerably greater deviation of the butadiene chromophore from planarity in 14 than in 13.[15] It was not feasible, however, to deduce from this information the geometric configuration of these isomers. Molecular models reveal severe hindrance in both compounds but do not suggest clearly which should have the more twisted butadiene system. Instead, we have drawn a tentative stereochemical assignment from observation of nuclear Overhauser effects (NOE's) in 13. Irradiation at the position of the signal for the t-Bu-group in 13 causes considerable enhancement of the olefinic signals at 5.21 and 4.31 ppm, but not that at 4.43 ppm, indicating that both the lone olefinic proton and one of the terminal methylene protons are sufficiently close to the t-Bu group to permit energy transfer. The condition is met in the geometry assigned to 13 but not in that of 14.

We have also examined the reaction of 1 with *cis*-2-butene at low conversion and found that at short irradiation times the products 8–12 are formed in virtually the same ratio as in preparative photolysis. Analysis of the butene recovered from such a reaction indicated the presence of only a minute amount of *trans*-2-butene. These results require that the *trans*-dimethyl-substituted dihydrofuran 9 and oxetane 11 arise directly from cycloaddition of 1 with *cis*-2-butene and not from some secondary reaction with *trans*-2-butene generated during the photolysis.



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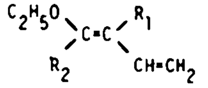
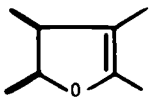


15, $R_1 = R_2 = CH_3$

16, $R_1 = CH_3$, $R_2 = H$

17, $R_1 = H$, $R_2 = CH_3$



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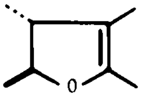

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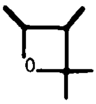

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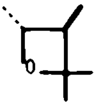

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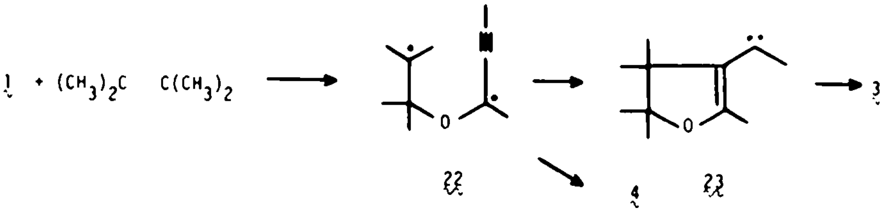
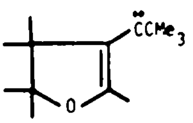


(3)

The simplest mechanism that readily accounts for our observations is given in eqn (3), using as an example the reaction of tetramethylethylene with ketone 1. This involves as a first step formation of biradical intermediate 22. Such intermediates are generally implicated in photochemical formation of oxetanes,[5] and this probable route to 4 is shown. Alternatively, 22 could cyclize at the α-carbon atom of the triple bond and furnish unsaturated carbene 23. Hydrogen migration[16] would then give the observed vinyldihydrofuran 3. Loss of stereochemical integrity in products formed from the 2-butenes can be explained in the usual way through bond rotation in the biradical prior to ring closure to the carbene. This explanation is already widely accepted[5] for loss of stereochemistry in cycloadditions leading to oxetanes.

It was this possible mechanism that initially led us to investigate the addition of tetramethylethylene to ketone 2, since we were curious about the fate of the postulated carbene if it could not undergo 1,2 shift of hydrogen. The bismethylenetetrahydrofuran 13 obtained in this reaction can be accounted for by assuming that in this case carbene 24 intramolecularly abstracts[16] a hydrogen atom from the Me group at C(2), and that the resulting biradical 25 relaxes to the more stable olefin, 13.

As we pointed out above, these [3 + 2] cycloadditions are a new photo-chemical reaction of α,β-acetylenic ketones. There are at least formal precedents for this behavior, however, in two thermal self-addition reactions of dimethyl acetylenedicarboxylate. There is no mechanistic information available in either of these isolated cases, but for each the suggested first step is [3 + 2] dimerization of the acetylenic ester to yield the carbene intermediate 26.[17] Less closely related to the new transformations reported here are the various photochemical additions of two double bonds to one triple bond, generating bicyclopropyl systems,[4,18–20] for which



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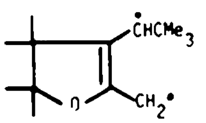

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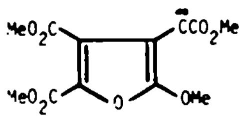

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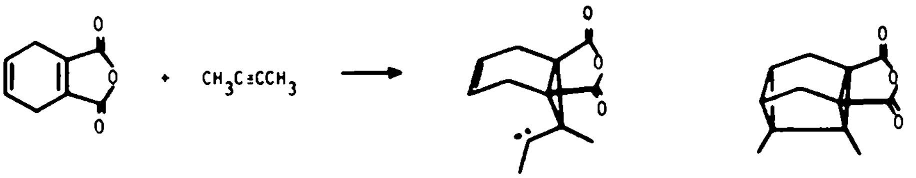

(4)

a carbene mechanism has been put forward.[19,21] The original example is the addition of 2-butyne to dihydrophthalic anhydride,[18] and this is shown in eqn (4) with the suggested[21] carbene intermediate. In light of these earlier observations the mechanism advanced in eqn (3) appears reasonable. Work is now in progress to provide evidence supporting this suggestion.

EXPERIMENTAL

Equipment. All vpc was carried out using a Varian Aerograph Model 700 Autoprep or 920 gas chromatograph employing one of the following columns: A, 1/4 in. × 12 ft, 25% UCON 50-HB-2000 on Chromosorb WNAW 45/60; B, as A, but 15 ft; C, 1/8 in. × 15 ft stainless steel, Porapak Q. Columns A and B were prepared from aluminum tubing and were operated at a helium flow rate of 80–90 ml/min; column C was operated at 22 ml/min.

All IR and NMR (60 MHz) spectra were recorded for CCl_4 solutions, the former on a Perkin–Elmer Model 237B spectrophotometer and the latter on a Varian T-60A spectrometer. All 220-MHz NMR spectra were recorded for $CDCl_3$ solutions on a Varian HR-220 spectrometer. Chemical shifts are reported in ppm relative to internal tetramethylsilane (~ 1% v/v; 0 ppm). All UV spectra were recorded in 95% ethanol on a Cary Model 14 spectrophotometer. Samples for elemental analysis were usually repurified by vpc before combustion. Unless otherwise indicated, all pure photoproducts were obtained as colorless oily liquids.

General procedure for photolysis of alkynones. A soln of the pure alkynone in anhyd benzene (5 mg/ml; 0.04–0.06 M) contained in a toroidal Pyrex glass vessel fitted with a side arm and standard taper 14/20 joint was irradiated under N_2 with a Hanovia 450-W medium-pressure mercury lamp cooled in a Pyrex immersion-well employing uranium glass as filter. In all cases, required olefin (5-fold molar excess) was added to the alkynone soln prior to irradiation. In the case of irradition with the butenes, the following procedure was adopted. The soln of the alkynone was prepared as usual in a toroidal vessel and was cooled to 0°. The desired butene was bubbled slowly through the chilled ketone soln until the total volume of the soln had increased by 10–15 ml. This was then irradiated under N_2 as described above. No more cooling was found necessary during irradiation.

Pent-3-yn-2-one (**1**) was prepared in 72% yield by a published method[6] except that thermolysis of triphenylphosphine diacetylmethylene was carried out at 12 mm and the product was collected in a receiver cooled by Dry-Ice acetone. However, vpc of the product (column A, 110°) indicated this to be a mixture of two components which were isolated. The major component (~ 88% of the mixture) was identified as pent-3-yn-2-one on the basis of the following data: IR (cm^{-1}) 2959 (w), 2290 (w), 2225 (s), 1675 (s), 1415 (m), 1350 (s), 1230 (s), 1210 (m), 1010 (w), 950 (m); NMR δ 2.2 (s), 2.0 (s), of equal intensity. (Found: C, 72.95; H, 7.47. Calc. for C_5H_6O: C, 73.14; H, 7.37%).

The minor component showed strong IR bands at 1960, 1930 and 1685 cm^{-1} and an NMR spectrum consistent with its being the allenic isomer of **1**, penta-3,4-dien-2-one.

5,5-Dimethylhex-3-yn-2-one (**2**) was prepared according to the procedure of Wilson *et al.*[7] The product was purified by column chromatography (silica, ether-petroleum ether, 1:9) followed by VPC (column A, 130°); IR (cm^{-1}) 2990 (s), 2955 (w), 2940 (w), 2875 (w), 2225 (s), 2190 (m), 1675 (s), 1475 (w), 1450 (w), 1415 (w), 1360 (s), 1355 (s), 1265 (s), 1195 (s), 1015 (w), 985 (w), 920 (m). NMR δ: 2.19 (s, 3H); 1.29 (s, 9H). (Found: C, 77.41; H, 9.79. Calc. for $C_8H_{12}O$: C, 77.37; H, 9.74%).

Photolysis of pent-3-yn-2-one with 2,3-dimethyl-2-butene. A soln of pent-3-yn-2-one (900 mg, 11.0 mmol) in anhyd benzene (180 ml, 0.06 M) containing tetramethylethylene (4.62 g, 55.0 mmol) was photolyzed for 12 hr according to the general procedure (~ 90% conversion). Vpc of the crude mixture (column A, 110°) showed two products in a ratio of about 10:1 (in order of increasing vpc retention time). These were isolated and identified respectively as **3** and **4**.

Compound **3**: IR (cm^{-1}): 3000 (s), 2975 (s), 1650 (s), 1390 (s), 1385 (s), 1365 (m), 1325 (w), 1250 (s), 1145 (w), 1115 (m), 962 (m), 860 (s), 690 (m); NMR (220 MHz) δ 6.26 (dd, J = 11.5, 17.9 Hz, 1 H), 5.01 (dd, J = 17.9, 1.4 Hz, 1H), 4.75 (dd, J = 11.5, 1.4 Hz, 1 H), 1.82 (s, 3 H), 1.21 (s, 6 H), 1.17 (s, 6 H). UV λ_{max} 252 nm, log ϵ = 4.04. (Found: C, 79.41; H, 10.82. Calc. for $C_{11}H_{18}O$: C, 79.46; H, 10.92%).

Compound **4**: IR (cm^{-1}): 3025 (s), 2990 (s), 2950 (s), 2250 (w), 1480 (w), 1450 (w), 1390 (m), 1370 (s), 1365 (m), 1260 (m), 1210 (w), 1150 (s), 1110 (m), 1070 (s), 970 (w), 940 (m), 875 (m); NMR (60 MHz) δ 1.82 (s, 3H), 1.36 (s, 3 H), 1.29 (s, 3 H), 1.16 (s, 6 H), 1.06 (s, 3 H). (Found: 79.45; H, 10.99. Calc. for $C_{11}H_{18}O$: C, 79.46; H, 10.92%).

Photolysis of pent-3-yn-2-one with 1,1-dimethylethylene. A soln of pent-3-yn-2-one (1.06 g, 12.95 mmol) in anhyd benzene (210 ml) containing 1,1-dimethylethylene was irradiated as described in the general procedure. Vpc (col A, 100°), showed the formation of three products with retention times respectively of 13, 16 and 28 min. Irradiation was stopped after ~97% of the starting material had been consumed (46 hr). The products were isolated and identified as **6**, **5** and **7**, respectively.

Compound **6**: IR (cm^{-1}): 3125 (w), 3010 (s), 2950 (m), 2880 (m), 1660 (s), 1600 (w), 1450 (w), 1440 (w), 1420 (w), 1385 (s), 1365 (m), 1275 (s), 1210 (w), 1150 (m), 1070 (w), 1015 (w), 965 (m), 865 (s). NMR (60 MHz) δ 6.23 (dd, J = 11, 16 Hz, 1 H), 4.64 (dd, J = 11, 2 Hz, 1 H), 4.40 (dd, J = 16, 2 Hz, 1 H), 2.40 (m, 2 H), 1.76 (m, 3 H), 1.33 (s, 6 H). (Found: C, 78.34; H, 10.16. Calc. for $C_9H_{14}O$: C, 78.21; H, 10.21%) UV λ_{max}250 nm, log ϵ = 4.24.

Compound **5**: IR (cm^{-1}): 3140 (w), 3000 (s), 2950 (s), 2900 (s), 1650 (s), 1460 (s), 1440 (m), 1390 (s), 1380 (s), 1365 (s), 1310 (w), 1255 (m), 1185 (s), 1015 (m), 980 (m), 880 (m), 865 (s). NMR (60 MHz) δ 6.03 (dd, J = 11, 17 Hz, 1 H), 4.85 (dd, J = 17, 2 Hz, 1 H), 4.64 (dd, J = 11, 2 Hz, 1 H), 3.77 (s, 2 H), 1.76 (m, 3 H), 1.30 (s, 6 H). (Found: C, 78.15; H, 10.27. Calc. for $C_9H_{14}O$: C, 78.21; H, 10.21%). UV λ_{max} 245 nm, log ϵ = 4.21.

Compound **7**: IR (cm^{-1}): 3000 (s), 2950 (s), 2890 (s), 2260 (w), 1465 (m), 1445 (m), 1380 (m), 1365 (s), 1270 (m), 1240 (w), 1195 (m), 1120 (m), 1080 (m), 975 (s), 840 (s); NMR (60 MHz) δ 4.00 (s, 2 H), 1.89 (s, 3 H), 1.45 (s, 3 H), 1.30 (s, 3 H), 1.15 (s, 3 H). (Found: C, 78.04; H, 10.37. Calc. for $C_9H_{14}O$: C, 78.21; H, 10.21%)

Photolysis of pent-3-yn-2-one with cis-2-butene. A soln of the alkynone (1.1 g, 13.4 mmol) in anhyd benzene (220 ml) containing *cis*-2-butene was irradiated according to the general procedure for 28 hr (~ 88% conversion). Vpc (col B, 100°) showed formation of five products with retention times respectively of 30, 39, 46, 55, and 59 min. These were isolated and identified as **9**, **11**, **8**, **10**, and **12**, respectively.

Compound **9**: IR (cm^{-1}): 3110 (w), 2990 (m), 2940 (m), 2875 (w), 1650 (s), 1590 (w), 1450 (m), 1440 (w), 1385 (m), 1370 (m), 1340 (w), 1290 (w), 1220 (s), 1025 (m), 975 (m), 925 (m), 875 (s). NMR (220 MHz) δ 6.37, (dd, J = 11, 17.5 Hz, 1 H), 4.83 (d, J = 17.5 Hz, 1 H), 4.78 (d, J = 11 Hz, 1 H), 4.15 (dq, J = ~6.5, 6.3 Hz, 1 H), 2.70 (dq, J = ~6.5, 6.7 Hz, 1 H), 1.84 (s, 3 H), 1.25 (d, J = 6.3 Hz, 3 H), 1.15 (d, J = 6.7 Hz, 3 H). UV: λ_{max} 260 nm, log ϵ 4.06. (Found: C, 78.36; H, 10.04. Calc. for $C_9H_{14}O$: C, 78.21; H, 10.21%).

Compound **11**: IR (cm^{-1}): 2990 (s), 2940 (s), 2890 (m), 2240 (w), 1450 (m), 1440 (m), 1380 (w), 1375 (w), 1365 (m), 1275 (w), 1250 (m), 1215 (m), 1110 (w), 1020 (s), 935 (s), 880 (m), 850 (m). NMR (220 MHz) δ 4.37 (dq, J = ~6.5, 6.2 Hz, 1 H), 2.35 (dq, J = ~ 6.5, 7.0 Hz, 1 H), 1.91 (s, 3 H), 1.58 (s, 3 H), 1.34 (d, J = 6.2 Hz, 3 H), 1.16 (d, J = 7.0 Hz, 3 H). (Found: C, 78.49; H, 10.27. Calc. for $C_9H_{14}O$; C, 78.21; H, 10.27%).

Compound **8**: IR (cm^{-1}): 3100 (w), 2990 (m), 2975 (m), 2940 (m), 2980 (m), 1655 (s), 1590 (w), 1440 (w), 1385 (m), 1375 (s), 1335 (w), 1320 (w), 1220 (s), 1160 (w), 1060 (m), 1010 (m), 975 (w), 910 (w), 865 (m), NMR (220 MHz) δ 6.38 (dd, J = 10.9, 17.2 Hz, 1 H), 4.84 (d, J = 17.2 Hz, 1 H), 4.81 (d, J = 10.9 Hz, 1H), 4.56 (dq, J = ~6.5, 6.6 Hz, 1 H), 2.91 (dq, J = ~6.5, 6.9 Hz, 1 H), 1.84 (s, 3 H), 1.35 (d, J = 6.6 Hz, 3 H), 0.98 (d, J = 6.9 Hz, 3 H). UV: λ_{max} 260 nm, log ϵ = 4.00 (Found: C, 78.0; H, 10.0. Calc. for $C_9H_{14}O$: C, 78.21; H, 10.21%).

Compound **10**: IR (cm^{-1}): 3010 (s), 2950 (s), 2250 (w), 1465 (m), 1450 (m), 1440 (m), 1375 (s), 1365 (m), 1260 (m), 1225 (s), 1050 (s), 1025 (m), 885 (m). NMR (220 MHz) δ 4.80 (dq, J = ~ 7.0, 6.5 Hz, 1 H), 2.77 (dq, J = 7.0, 7.5 Hz, 1 H), 1.89 (s, 3 H), 1.65 (s, 3 H), 1.31 (d, J = 6.5 Hz, 3 H), 1.14 (d, J = 7.4 Hz, 3 H). (Found: C, 78.13; H, 10.12. Calc. for $C_9H_{14}O$: C, 78.21; H, 10.21%).

Compound **12**: IR (cm^{-1}): 3000 (s), 2950 (m), 2250 (w), 1465 (m), 1375 (s), 1365 (m), 1250 (w), 1030 (m), 1015 (w), 860 (w). NMR (220 MHz) δ 5.00 (dq, $J = \sim 7.0$, 6.5 Hz, 1 H), 3.09 (dq, $J = \sim 7.0$, 7.6 Hz, 1 H), 1.88 (s, 3 H), 1.46 (s, 3 H), 1.23 (d, $J = 6.5$ Hz, 3 H), 1.06 (d, $J = 7.5$ Hz, 3 H). (Found: C, 78.50; H, 10.20. Calc. For $C_9H_{14}O$: C, 78.21, H, 10.21%).

Photolysis of pent-3-yn-2-one with trans-*2-butene*: A soln of the ketone (648 mg, 7.9 mmol) in anhyd benzene (130 ml) containing *trans*-2-butene was irradiated according to the general procedure. Progress of the reaction was followed by vpc (col A, 110°) which showed the formation of five products as in the case of *cis*-2-butene. The products were isolated (vpc) and identified as **9**, **11**, **8**, **10**, and **12**.

Photolysis of 5,5-dimethylhex-3-yn-2-one with 2,3-dimethyl-2-butene. A soln of the ketone (1.2 g, 9.6 mmol) in anhyd benzene (240 ml, 0.04 M) containing 2,3-dimethyl-2-butene (1.61 g, 19.2 mmol) was irradiated according to the general procedure for 18 hr (~ 80% conversion). NMR of the crude photolysate after solvent removal (rotary evaporator) indicated the formation of a single product later identified as **13** (see below). However, vpc of the mixture (col A, 100°) led to the isolation of two products with retention time respectively of 71 and 78 min. These were isolated and identified as **14** and **13**. It was evident that **14** was being produced from **13** during isolation by vpc.

Compound **14**: IR (cm^{-1}): 2990 (s), 2975 (s), 2925 (m), 2890 (m), 1650 (m), 1595 (m), 1475 (m), 1455 (m), 1445 (w), 1385 (m), 1370 (m), 1360 (s), 1350 (w), 1255 (s), 1225 (w), 1188 (w), 1110 (s), 1015 (w), 995 (m), 980 (s), 840 (w). NMR (60 MHz) δ 5.23 (s, 1 H), 4.43 (br s, 1 H), 4.23 (br s, 1 H), 1.22 (s, 9 H), 1.06 (s, 3 H), 0.92 (s, 3 H). UV: λ_{max} 235 nm, log $\epsilon = 4.24$.

Compound **13**: IR (cm^{-1}): 3000 (s), 2990 (s), 2925 (m), 2890 (m), 1630 (m), 1590 (m), 1460 (m), 1435 (w), 1385 (m), 1370 (m), 1360 (s), 1330 (m), 1290 (m), 1255 (m), 1215 (w), 1160 (m), 1140 (m), 1125 (m), 1035 (m), 1015 (s), 985 (w), 850 (w). NMR (60 MHz), δ 5.21 (poorly resolved d, $J \sim 2$ Hz; 1 H), 4.43 (poorly resolved d, $J \sim 2$ Hz, 1 H), 4.31 (s, 1 H), 1.22 (s, 9 H), 1.08 (s, 3 H), 0.92 (s, 3 H). UV λ_{max} 245 nm, log $\epsilon = 4.20$. (Found: C, 80.89; H, 11.57. Calc. For $C_{14}H_{24}O$: C, 80.70; H, 11.61%).

Photolysis of pent-3-yn-2-one with cis-*2-butene at low conversion.* A soln of the ketone (120 mg, 1.46 mmol) in anhyd benzene (60 ml, 0.024 M) containing *cis*-2-butene was irradiated for 4 hr as described above. Vpc (col A, 100°) showed ~ 12% conversion of the ketone. Analysis of the butenes in this mixture by direct injection on column C indicated $\leq 1\%$ *trans*-2-butene. Similar analysis of the butene before photolysis indicated ~ 0.5% *trans*-2-butene. (Retention times were *cis*-2-butene, 35.6 min; *trans*-2-butene, 33.0 min) The ratios of the products formed at 12% conversion (column A, 100°) was virtually the same as those reported above.

Acknowledgements—We thank Drs. Steven Wolff and David Cowburn for their advice and assistance and both the National Science Foundation and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

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