at least some benzyl compounds. Further clarification may come from a study now in progress on a doubly ^{13}C-labeled toluene.[24]

[24] K. L. Rinehart, University of Illinois, private communication; K. L. Rinehart and A. C. Buchholz, Abstracts, 154th National Meeting of the American Chemical Society, Chicago, Ill., 1967, Paper S-85.

Acknowledgments. We are indebted to A. W. Weitkamp, of the American Oil Company, for help in gas-chromatographic purification of the diphenylmethanes and to R. D. Hites, of the American Oil Company, and M. M. Green, of the University of Michigan, for directing our attention to relevant spectroscopic literature.

The Photochemistry of Acetylenic Compounds. The Photochemical Reduction of Some Conjugated Acetylenic Carbonyl Compounds

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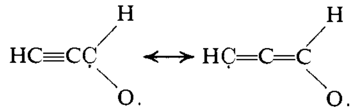
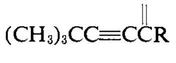
Abstract: The irradiation of 5,5-dimethyl-3-hexyn-2-one (**1**) in isopropyl alcohol produced: 2,3-dimethyl-2,3-butanediol (**3**), 2,3,6,6-tetramethyl-4-heptyn-2,3-diol (**4**), and 2,2,5,6,9,9-hexamethyl-3,7-decadiyn-5,6-diol (**5**). The irradiation of methyl 4,4-dimethyl-2-pentynoate (**2**) in methanol produced the reduction products, *cis*- and *trans*-methyl 4,4-dimethyl-2-pentenoates (**6**). These were transformed to methyl (2,2-dimethylcyclopropyl)acetate (**7**) on longer irradiation. A considerable amount (at least 60% of the total product) of higher molecular weight material was also formed. The contrasting nature of the products from the two similar starting materials is interpreted in terms of two different excited states.

Although the solution photochemistry of the carbon–carbon double bond is becoming well understood, the corresponding excited-state reactivity of the carbon–carbon triple bond in solution has received much less attention. The most common photochemical reaction involving acetylenes is the intermolecular addition of a variety of functional groups,[1] *e.g.*, the carbonyl group,[1b] the carbon–carbon double[1c] or triple bond,[1d] a nitro group,[1e] or an aromatic ring,[1f] to an acetylenic bond. Some of these reactions probably involve the addition of an electronically excited molecule to a ground-state acetylene. There are few examples of reactions in which the excitation energy is known to reside in the acetylenic molecule. The photochemical dimerizations of phenylacetylene[1f] and tolan[1d] and the several intramolecular reactions of diacetylenes[2,3] necessarily belong to this category. There are three recent reports of this reaction type. Owen[4] has interpreted the photochemical oxidation of diphenylacetylene in solution as a reaction between oxygen and triplet tolan. Jorgenson[5] has studied the photochemical addition of acetylenic ketones to olefins and has found that only the carbonyl moiety is involved in the reaction. Recently Ben-Efraim[6] has discovered an interesting reduction of conjugated diacetylenes to vinylacetylenes.

Conjugated acetylenic carbonyl compounds offer several advantages for mechanistic studies of the effect of structural variations on reactivity that conjugated olefinic carbonyl compounds do not offer. The synthesis of a variety of conjugated acetylenic ketones and esters is relatively easy and their photochemistry is not complicated by two of the common reactions of acyclic olefinic ketones, *cis–trans* isomerization and dimerization to cyclobutanes. The possibility of observing some interesting photochemistry of acetylenic carbonyl compounds was suggested by a report[7] that the excited state resulting from the first singlet–singlet, n → π* transition in propynal is best represented as a planar delocalized species



In this paper we report a study of the products obtained from the ultraviolet irradiation of compounds **1** and **2** in alcohol.



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

1, R = CH_3
2, R = OCH_3

Results

5,5-Dimethyl-3-hexyn-2-one (**1**) was prepared by the oxidation of the propargyl alcohol derived from *t*-

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[1] (a) A recent review contains many examples: R. N. Warrener and J. B. Bremner, *Rev. Pure Appl. Chem.*, **16**, 117 (1966); (b) G. Büchi, J. T. Kofron, E. Koller, and D. Rosenthal, *J. Am. Chem. Soc.*, **78**, 876, (1956); (c) R. Criegee, U. Zirngibl, H. Furrer, D. Seeback, and G. Freund, *Chem. Ber.*, **97**, 2942 (1964); (d) G. Büchi, C. W. Perry, and E. W. Robb, *J. Org. Chem.*, **27**, 4106 (1962); (e) M. L. Sheinbaum, *ibid.*, **29**, 2200 (1964); (f) D. Bryce-Smith and J. E. Lodge, *J. Chem. Soc.*, 695 (1963).

[2] E. Müller, M. Sauerbier, and J. Heiss, *Tetrahedron Letters*, 2473 (1966).

[3] E. H. White and A. A. F. Sieber, *ibid.*, 2713, (1967).

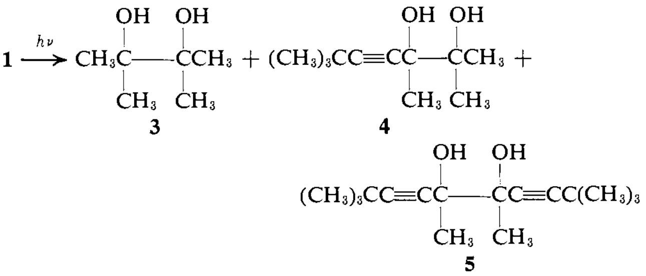
[4] R. C. Henson, J. L. W. Jones, and E. D. Owen, *J. Chem. Soc.*, *A*, 116 (1967).

[5] M. J. Jorgenson, *Tetrahedron Letters*, 5811 (1966).

[6] D. A. Ben-Efraim, *ibid.*, 957 (1967).

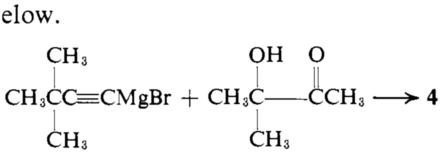
[7] J. C. D. Brand, J. H. Callomon, and J. K. G. Watson, *Discussions Faraday Soc.*, **35**, 175 (1963).

butylacetylene and acetaldehyde. It was irradiated in isopropyl alcohol with a quartz-jacketed Hanovia 450-W lamp. Vapor phase chromatography of the crude product showed four major volatile products which were isolated by preparative vpc: pinacol (**3**), 2,3,6,6-tetramethyl-4-heptyn-2,3-diol (**4**), and *meso*- and *dl*-2,2,5,6,9,9-hexamethyldeca-3,7-diyn-5,6-diol (**5**). These



$$\mathbf{1} \xrightarrow{h\nu} \underset{\mathbf{3}}{CH_3\overset{OH}{\underset{CH_3}{C}}-\overset{OH}{\underset{CH_3}{C}}CH_3} + \underset{\mathbf{4}}{(CH_3)_3CC\equiv C\overset{OH}{\underset{CH_3}{C}}-\overset{OH}{\underset{CH_3}{C}}CH_3} + \underset{\mathbf{5}}{(CH_3)_3CC\equiv C\overset{OH}{\underset{CH_3}{C}}-\overset{OH}{\underset{CH_3}{C}}C\equiv CC(CH_3)_3}$$

products accounted for most of the starting material which disappeared (see Experimental Section). Pinacol (**3**) was identified by vpc and infrared comparison with an authentic sample. The structure of the unsymmetrical pinacol **4** was established by the synthesis shown below.



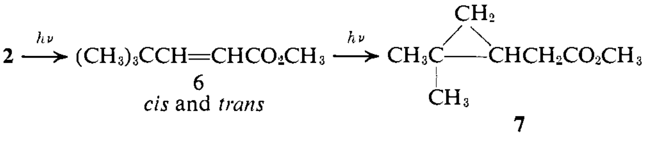
$$CH_3\overset{CH_3}{\underset{CH_3}{C}}C\equiv CMgBr + CH_3\overset{OH}{\underset{CH_3}{C}}-\overset{O}{\overset{\|}{C}}CH_3 \longrightarrow \mathbf{4}$$

The symmetrical pinacols **5** were observed as two barely resolved peaks and were collected together. The combined symmetrical pinacols were cleaved by sodium periodate to the starting ketone **1**. Final proof of the structure was provided by the synthesis shown below.

$$CH_3COCOCH_3 + 2(CH_3)_3CC\equiv CMgBr \longrightarrow \mathbf{5}$$

The nmr spectra (see Experimental Section) of **4** and **5** were consistent with the postulated structures.

Methyl 4,4-dimethyl-2-pentynoate (**2**) was irradiated in methanol with the same unfiltered lamp. The reaction was followed by vpc. About 60% of the reaction product was not eluted from the vpc column in 0.5 hr at 120°. The nonvolatile material was presumably composed of polymers and products resulting from the addition of solvent molecules. The photoreduction of Ben-Efraim[6] was also accompanied by considerable amounts of similar products (60–100%). The sequence of formation of the volatile products is shown below.

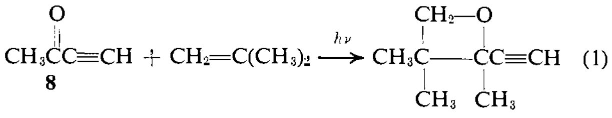


$$\mathbf{2} \xrightarrow{h\nu} \underset{\substack{\mathbf{6}\\ cis \text{ and } trans}}{(CH_3)_3CCH=CHCO_2CH_3} \xrightarrow{h\nu} \underset{\mathbf{7}}{CH_3\overset{CH_2}{\underset{CH_3}{C}}-CHCH_2CO_2CH_3}$$

Chromatography showed that as starting material diminished, *cis*- and *trans*-methyl 4,4-dimethyl-2-pentenoates (**6**) were formed. The olefinic esters were converted on continued irradiation to cyclopropyl ester **7** as reported by Jorgenson.[8] The olefinic esters were isolated by preparative vpc and compared with the *trans* ester prepared by the Wittig reaction between pivalaldehyde and the ylide derived from triethyl phosphite and ethyl α-bromoacetate. The nmr spectra of *cis* and *trans* esters **6** differed mainly in the magnitude of the coupling constants of the two vinyl protons. To obtain an authentic sample of cyclopropyl ester **7**, *trans* **6** from the Wittig reaction was irradiated in methanol.[8]

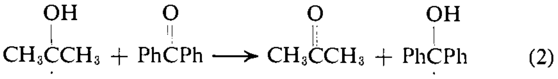
Discussion

The formation of pinacols from the acetylenic ketone **1** is analogous to the photochemical production of pinacols from many ketones and suggests an n,π* triplet state as the source of products. Jorgenson[5] has observed that acetylenic ketones undergo photochemical addition to olefins, *e.g.*, reaction 1, and has commented on the similarity of this behavior to that of saturated ketones and aromatic ketones with a lowest n,π* state. Although the irradiation of **8** in non-



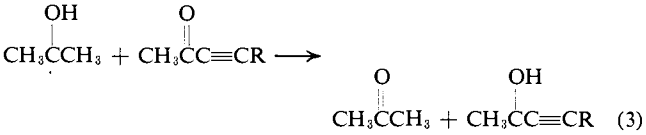
$$\underset{\mathbf{8}}{CH_3\overset{O}{\overset{\|}{C}}C\equiv CH} + CH_2=C(CH_3)_2 \xrightarrow{h\nu} CH_3\overset{CH_2-}{\underset{CH_3}{C}}-\overset{O}{\underset{CH_3}{C}}C\equiv CH \quad (1)$$

hydroxylic solvents yielded only intractable high molecular weight products in the absence of olefins,[5] an n,π* state in which the excitation energy is localized at the carbonyl group[9] is indicated for both **1** and **8**. The appearance of the mixed pinacol **4** is somewhat unusual. The probable reason[10] for the absence of such mixed coupling products in the photoreduction of benzophenone and other aromatic ketones in isopropyl alcohol is the destruction of the radicals derived from isopropyl alcohol by reaction 2. The reaction is



$$CH_3\overset{OH}{\underset{\cdot}{C}}CH_3 + Ph\overset{O}{\overset{\|}{C}}Ph \longrightarrow CH_3\overset{O}{\overset{\|}{C}}CH_3 + Ph\overset{OH}{\underset{\cdot}{C}}Ph \quad (2)$$

favored in the direction shown because of the replacement of the 2-hydroxy-2-propyl radical by the more stable hydroxybenzhydryl radical. In the present case it is probable that the propargyl radical is little stabilized by delocalization[11] and that reaction 3 does not contribute significantly to the destruction of 2-hydroxy-2-propyl radicals. For this reason these radicals survive long enough to combine with acetylenic radicals and to dimerize.



$$CH_3\overset{OH}{\underset{\cdot}{C}}CH_3 + CH_3\overset{O}{\overset{\|}{C}}C\equiv CR \longrightarrow CH_3\overset{O}{\overset{\|}{C}}CH_3 + CH_3\overset{OH}{\underset{\cdot}{C}}C\equiv CR \quad (3)$$

The photochemical reduction of the acetylenic ester **2** to the olefinic esters **6** is in striking contrast to the behavior of the corresponding acetylenic ketone **1**. Ben-Efraim[6] has very recently reported a similar reduction of a conjugated diacetylene to a vinylacetylene.

$$C_4H_9C\equiv CC\equiv CC_4H_9 \xrightarrow{h\nu} C_4H_9CH=CHC\equiv CC_4H_9 + \text{solvent adducts and polymers} \quad (4)$$

Reaction 4 is sensitized by benzene and very probably proceeds through a π,π* triplet state. By analogy we

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[8] M. J. Jorgenson, *Chem. Commun.*, 137 (1965).

[9] The analogy with propynal (see above) suggested a delocalized, planar n,π* state.[7] The propynal spectral analysis, however, was for the singlet state. The geometry and electronic structure of the triplet may be different from those of the singlet.

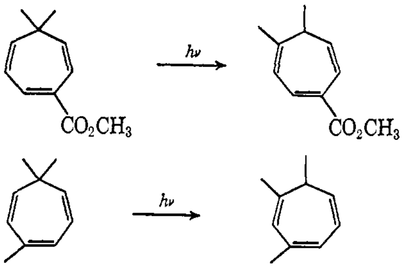
[10] D. C. Neckers, "Mechanistic Organic Photochemistry," Reinhold Publishing Corp., New York, N. Y., 1967, p 165.

[11] M. C. Caserio and R. E. Pratt, *Tetrahedron Letters*, 91 (1967).

postulate that the acetylenic ester is also reduced *via* a π,π* triplet.[12] The assignment of a lowest π,π* triplet state for esters is in accord with simple molecular orbital theory.[13] Closson and coworkers[14] have shown that the π,π* absorption maximum of α,β-unsaturated esters is only slightly shifted toward higher energy (5–10 mμ) relative to the same band of α,β-unsaturated ketones, whereas the n,π* band is shifted by about 70 mμ toward higher energy in going from α,β-unsaturated ketones to α,β-unsaturated esters. Although the situation for conjugated acetylenic esters is somewhat uncertain because the π,π* band maximum lies below 200 mμ, the same compression of n,π* and π,π* singlet states relative to the corresponding ketones probably still occurs. Our absorption spectra show at least that the n,π* band of ester **2** (shoulder at about 240 mμ (ϵ 47)) occurs at a significantly lower wavelength than the n,π* band of ketone **1** (λ_{max} 290 mμ (ϵ 36)). The π,π* band of ketone **1** lies at 220 mμ (ϵ 8 × 10^3), whereas the intense end absorption of ester **2** has not reached a maximum at 210 mμ (ϵ at 210 mμ is approximately 6200). Since the singlet–triplet spacing is greater for π,π* transitions than for n,π* transitions,[15] the assumption that the π,π* triplet state is lowest in the ester whereas the n,π* triplet is lowest in the ketone is a reasonable working hypothesis.[16]

Other explanations for the difference in reactivity between the ester and ketone are not excluded by the present evidence. Among these are the following: (1) both products arise from n,π* states and result from the same first step, hydrogen atom abstraction by oxygen, but different second steps, dimerization in the ketone case (unlikely for esters) and hydrogen abstraction by carbon in the ester case; (2) the two products arise from states of different multiplicity;[17] and (3) at least one of the products arises from a triplet state which is not the lowest triplet.[18] Our preference for an explanation using two different lowest triplets is based mainly on the close analogies between our products and those obtained from other systems in which the reactive excited states have been identified.[19]

It may be that the photochemical reactions of most conjugated unsaturated esters arise from a lowest π,π* triplet state. Although Jorgenson[8] has observed that a series of unsaturated esters undergo an intromolecular hydrogen abstraction which might be explained by an n,π* state, there are several unexpected features of these reactions. Unusual aspects are: the order of ease with which different types of hydrogen are abstracted, the observed solvent effects, and the lack of parallels in some cases with the reactivity of the analogous ketones. Another example may be found in the correspondence between the photochemical reactivity of methyl thujate[20] and 3,7,7-trimethylcycloheptatriene,[21] the excited state of which necessarily must be π,π*.[22]



Experimental Section

The instruments used were: nmr, Varian HA-60-IL; ir, Beckman IR 8; uv, Cary 14; vpc, Aerograph Autoprep, A-700.

***t*-Butylacetylene** was prepared from either 2,2-dichloro-3,3-dimethylbutane[23] or 1,1-dichloro-3,3-dimethylbutane[24] by the method of Puterbaugh and Newman.[25]

5,5-Dimethyl-3-hexyn-2-ol was prepared by a Grignard reaction modeled after the procedure of Bartlett and Rosen.[23] Ethylmagnesium bromide was prepared in 125 ml of ether from 8.8 g (0.367 g-atom) of magnesium and 45 g (0.413 mol) of ethyl bromide. To this solution was added 29 g (0.354 mol) of *t*-butylacetylene in 30 ml of ether. The reaction mixture was stirred overnight to form *t*-butylethynylmagnesium bromide as a white solid. Freshly distilled acetaldehyde (20 g, 0.455 mol) in 40 ml of ether was added over 1 hr, and the reaction mixture was stirred overnight. Saturated ammonium chloride solution (about 50 ml) was added, and the magnesium salt was removed by filtration and washed with ether. The ether was removed at reduced pressure leaving 41 g (92%) of a light yellow liquid which was consistent with the expected structure (strong OH bands at 3620 and 3450 cm^{-1} and medium C≡C bands at 2220 and 2250 cm^{-1}). Vpc (SE 30, 8 ft × 0.25 in., 95°) showed one major component plus very small amounts of low boiling materials.

5,5-Dimethyl-3-hexyn-2-one was prepared by the Jones oxidation[26] of the alcohol. The crude 5,5-dimethyl-3-hexyn-2-ol (41 g, 0.325 mol) described above was dissolved in 63 ml of acetone and cooled in methanol–Dry Ice. A solution of 21.9 g (0.219 mol) of CrO_3 in 19 ml of concentrated H_2SO_4 and 63 ml of water was added slowly

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(12) Photochemical reductions of α,β-olefinic ketones to saturated ketones and of certain cycloalkenes to cycloalkanes are known: (a) H. Köller, G. P. Rabold, K. Weiss, and T. K. Mukherjee, *Proc. Chem. Soc.*, 332 (1964); (b) I. A. Williams and P. Bladon, *Tetrahedron Letters*, 257 (1964); (c) G. W. Griffin and E. J. O'Connel, *J. Am. Chem. Soc.*, **84**, 4148 (1962); (d) B. Nann, D. Gravel, R. Schorta, H. Wehrli, K. Schaffner, and O. Jeger, *Helv. Chim. Acta*, **46**, 2473 (1963); (e) P. J. Kropp, *J. Am. Chem. Soc.*, **89**, 3650 (1967); (f) R. L. Cargill, J. R. Damewood, and M. M. Cooper, *ibid.*, **88**, 1330 (1966).

(13) H. H. Jaffé, D. L. Beveridge, and M. Orchin, *J. Chem. Educ.*, **44**, 383 (1967).

(14) W. D. Closson, S. F. Brady, and P. J. Orenski, *J. Org. Chem.*, **30**, 4026 (1965).

(15) N. J. Turro, "Molecular Photochemistry," W. A. Benjamin, Inc., New York, N. Y., 1965, p 85.

(16) The association of a change in reactivity with a change from a lowest n,π* triplet to a lowest π,π* triplet when a small structural change is introduced has been made frequently. See, for example, (a) G. Porter and P. Suppan, *Trans. Faraday Soc.*, **61**, 1664 (1965); (b) N. C. Yang, M. Nussim, M. J. Jorgenson, and S. Murov, *Tetrahedron Letters*, 3657 (1964); (c) L. A. Singer and P. D. Bartlett, *ibid.*, 1887 (1964); (d) N. C. Yang and M. J. Jorgenson, *ibid.*, 1203 (1964); (e) P. J. Wagner and G. S. Hammond, *J. Am. Chem. Soc.*, **88**, 1245 (1966); (f) E. J. Baum, J. K. S. Wan and J. N. Pitts, Jr., *ibid.*, **88**, 2652 (1966); (g) D. R. Kearns and W. A. Case, *ibid.*, **88**, 5087 (1966); (h) S. G. Cohen, R. Thomas, and M. N. Siddiqui, *ibid.*, **89**, 5845 (1967).

(17) For precedents see, for example, (a) G. W. Griffin and E. J. O'Connel, *ibid.*, **84**, 4148 (1962); (b) H. E. Zimmerman, H. G. Durr, R. S. Givens, and R. G. Lewis, *ibid.*, **89**, 1863 (1967); (c) H. Kristinsson and G. S. Hammond, *ibid.*, **89**, 5968 (1967).

(18) For precedents see, for example, (a) N. C. Yang, M. Nussim, M. J. Jorgenson, and S. Murov, *Tetrahedron Letters*, 3657 (1964); (b) P. de Mayo, J. P. Pete, and M. Tchir, *J. Am. Chem. Soc.*, **89**, 5712 (1967); (c) N. C. Yang, T. Loeschen, and D. Mitchell, *ibid.*, **89**, 5465 (1967).

(19) Although **1** and **2** were irradiated in different alcohols, it is most unlikely that this difference would account for the difference in product types. Ben-Efraim's finding that reaction 4 was unaffected by a change from methanol to isopropyl alcohol may be cited in support of our assumption that the products from the irradiation of ester **2** would be unaffected by a similar solvent change.

(20) O. L. Chapman and S. L. Smith, *J. Org. Chem.*, **27**, 2291 (1962).

(21) L. B. Jones and V. K. Jones, *J. Am. Chem. Soc.*, **89**, 1880 (1967).

(22) We note, however, that product analogies alone are an insufficient basis on which to draw conclusions about the mechanism. See, for example, H. E. Zimmerman and G. E. Samuelson, *ibid.*, **89**, 5971 (1967).

(23) P. D. Bartlett and L. J. Rosen, *ibid.*, **64**, 543 (1942).

(24) J. H. van Boom, P. P. Montijn, L. Brandsma, and J. F. Arens, *Rec. Trav. Chim.*, **84**, 31 (1965).

(25) W. H. Puterbaugh and M. S. Newman, *J. Am. Chem. Soc.*, **81**, 1611 (1959).

(26) R. A. Raphael, "Acetylenic Compounds in Organic Synthesis," Butterworth & Co. (Publishers), Ltd., London, 1955, p 206.

with stirring while keeping the reaction mixture at about 0°. After stirring for an additional 0.5 hr, 400 ml of cold water was added, and the reaction mixture was extracted with four 100-ml portions of ether. The ethereal solution was dried and evaporated at reduced pressure. The residual ketone contained ether and a contaminant with a retention time (vpc on SF 96, 10 ft × 0.25 in., 130°) very close to that of the ketone. This material was distilled twice at reduced pressure through an 18-in. Nester-Faust spinning-band column. Material boiling at 77° (56 mm) and weighing about 15 g (40%) was homogeneous to vpc (SF 96). Its infrared spectrum showed intense absorption at 2220 and 2180 ($C\equiv C$), 1670 ($C{=}O$), and 1360 cm^{-1}. Its nmr spectrum showed two singlets with area ratios of 1:3 at δ 2.20 (CH_3CO) and 1.27 (*t*-butyl). The mass spectrum (70 eV) showed the expected parent peak at *m/e* 124.

The 2,4-dinitrophenylhydrazone[27] was prepared in and recrystallized from 95% ethanol, mp 165–167°. Its infrared spectrum ($C\equiv C$ stretching) and nmr spectrum (one N—H) showed that it was the 1,2- and not the 1,4-addition product. The mass spectrum (70 eV) showed the expected parent at *m/e* 304 and the expected carbon analysis, C_{14}.

Anal. Calcd for $C_{14}H_{16}N_4O_4$: C, 54.97; H, 5.30; N, 18.54. Found: C, 54.43; H, 5.34; N, 18.28.

Irradiation of Ketone 1. 5,5-Dimethyl-3-hexyn-2-one, 2.48 g, was dissolved in 145 ml of reagent isopropyl alcohol. The solution was stirred magnetically and oxygen-free nitrogen (bubbled through ketyl solution)[28] was slowly bubbled in during the reaction. A high-pressure Hanovia, 450-W, Type L lamp in a water-cooled quartz well was immersed in the solution. The reaction was followed by vpc (SF 96, 10 ft × 0.25 in., 195°). The reaction apparently was finished after 2 hr, although the lamp was left on for a total of 12. Confusion about the extent of ketone disappearance resulted from the coincidence of the retention times of ketone **1** and pinacol. The major difference between the 2-hr vpc trace and the 12-hr trace was a small increase in the ketone–pinacol peak just mentioned. Isopropyl alcohol was removed by distillation at atmospheric pressure. Vpc of the pot residue showed five major peaks which were later identified as: isopropyl alcohol, pinacol, **4**, and **5** (*meso* and *dl*). Minor peaks which were not investigated further were observed between isopropyl alcohol and **4**, one just before and one after **5**.

Separation of the photoproducts was accomplished by vpc on a 10 ft × $^3/_8$ in. SF 96 column at 145°. In an experiment to test recovery of injected material, a 46-mg sample was injected and collected in a helix-packed spiral condenser at Dry Ice temperature. After 40 min, 40 mg (87% recovery) of material was collected. The pen had returned to the base line after about 30 min (acetylenic pinacols off at 20 min). It is assumed that most of the photoproducts are accounted for by this method. For product identification, 4.2 g in 30 150-μl portions was injected. Five collectors were used as indicated in Table I. Isopropyl alcohol was not collected. Although a mass balance is not possible with these data, it is assumed that the difference between collected and injected weights is due to uncollected isopropyl alcohol, to uncondensed aerosol spray which was evident especially in the higher boilers, and to some of the minor products which were not collected in the initial injections. The percentages in the last column depend on this assumption.

Table I. Products from Irradiation of Ketone **1**

Fraction	Identity	Wt, mg	Photoproducts, %
A	**3**	865	45
B	**4**	286	15
C	*a*	49	3
D	**5**	530	28
E	*b*	187	10

[a] Minor peaks between B and D. [b] Minor peaks after D.

Characterization of Fraction B (Pinacol 4). This fraction was repurified by gas chromatography. It was a clear oil which could not be crystallized. Its infrared and nmr spectra and vpc retention time were identical with those of an authentic sample described below.

2,3,6,6-Tetramethyl-4-heptyn-2,3-diol (4). 3-Hydroxy-3-methyl-2-butanone[29] (10 g, 0.1 mol) in 25 ml of ether was added to *t*-butylethynylmagnesium (see above) in 140 ml of ether prepared from 4.7 g (0.2 g-atom) of Mg. After having been stirred for several hours, the reaction mixture was worked up with saturated ammonium chloride as above. The ether was evaporated and the residue was distilled in a "Bantamware" short-path distillation apparatus. Fractions boiling at 58–60° (95 mm) and weighing 8.0 g (45%) were collected. Vpc showed two minor contaminants in addition to the product. This material eventually crystallized, mp 40–44°; ir max ($CHCl_3$) 3570, 3450 (OH) and 2210, 2240 cm^{-1} (weak, $C\equiv C$). The nmr spectrum revealed five singlets with relative areas of 2:3:3:9:3 only with a 100-cps sweep width (at the 500-cps sweep there were only four): OH at δ 2.65, the three methyls attached to carbons 2 and 3 at δ 1.35, 1.29, and 1.18, and *t*-butyl at 1.21. Small impurity peaks were also present.

Anal. Calcd for $C_{11}H_{20}O_2$: C, 71.74; H, 10.87. Found: C, 71.91; H, 10.80.

Characterization of Fraction D (Pinacol 5). This fraction was purified by sublimation at 50° (1 mm). The sublimate was an oily, crystalline solid which melted over a broad range somewhat above room temperature. Vpc (SF 96, 10 ft × 0.25 in., 170°) showed several minor impurities with very close retention times. The infrared and nmr spectra and vpc retention times were very close to those of an authentic sample of **5** (which was purified by column chromatography) described below.

A 300-mg (1.2 mmol) sample dissolved in 6 ml of ethanol was mixed with 400 mg (1.9 mmol) of sodium metaperiodate in 5 ml of water and allowed to stand until crystals of sodium iodate appeared. Water was added (10 ml) and the solution was extracted with four 5-ml portions of ether. Vpc showed only ether and one other peak which corresponded to 5,5-dimethyl-3-hexyn-2-one. After drying and evaporation a clear oil weighing 153 mg remained. Vpc showed two minor impurities in addition to the main constituent. The infrared and nmr spectra of this material were similar (several minor additional peaks were present) to the spectra of acetylenic ketone **1** (see above). The 2,4-dinitrophenylhydrazone had spectral properties and melting point (163–164°) identical with those of an authentic sample (see above).

2,2,5,6,9,9-Hexamethyl-3,7-decadiyn-5,6-diol was prepared by the addition of biacetyl (9.6 g, 0.12 mol) in 100 ml of ether to *t*-butyl ethynylmagnesium bromide (see above) in 150 ml of ether prepared from 5.8 g (0.24 g-atom) of Mg. After work-up in the manner described above, a dark oil remained. It was charged to a sublimation apparatus which was evacuated to 5 mm and heated at 80°. A yellow-white oily solid was removed from the cold finger at intervals over 3 days. This material (10.2 g, 37% yield) was chromatographed on silica gel (3 × 73 cm column). White crystals (mp 50–65°) were eluted with 7 l. of 10% ether in hexane after the following solvents had been passed through the column (1000 ml of hexane, 500 ml of 1% ether–hexane, 500 ml of 2% ether–hexane, and 1500 ml of 5% ether–hexane). The infrared spectrum ($CHCl_3$) showed bands at 3560 cm^{-1} (medium, OH) and at 2220 and 2250 cm^{-1} (weak $C\equiv C$). The nmr spectrum ($CDCl_3$) showed a broad peak at δ 2.54 (1 H, OH) and a singlet at δ 1.20 (9 H, *t*-butyl) and peaks at δ 1.51 and 1.45 (total area, 3 H; peak ratios 1.25:1.0). The peaks near δ 1.5 are assigned to the methyl group on the carbinol carbon, slightly different in *meso* and *dl* isomers.

Anal. Calcd for $C_{16}H_{26}O_2$: C, 76.80; H, 10.40. Found: C, 76.63; H, 10.41.

Methyl 4,4-Dimethyl-2-pentynoate (2). 4,4-Dimethyl-2-pentynoic acid was prepared by bubbling carbon dioxide through *t*-butylethynylmagnesium bromide (0.43 mol) in ether (see above). The reaction mixture was acidified with 5% aqueous sulfuric acid and extracted with ether. After drying, the ethereal solution was evaporated, and the liquid residue was distilled through a short Vigreux column at 106° (10 mm) (lit.[30] 110° (10 mm)) to yield 21.7 g (40%) of the acid. Its infrared spectrum showed typical broad carboxylic acid O-H absorption with a maximum at about 2900, a strong $C\equiv C$ band at 2210, and a strong $C{=}O$ band at 1670 cm^{-1}. The acid was esterified by heating it for 4 hr in 75 ml of methanol containing 3 ml of concentrated H_2SO_4. Methylene chloride (60 ml) was added, and the organic layer was extracted with water

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[27] R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," 3rd ed, John Wiley and Sons, Inc., New York, N. Y., 1948, p 171.

[28] L. F. Fieser, "Experiments in Organic Chemistry," 3rd ed, D. C. Heath and Co., Boston, Mass., 1955, p 299.

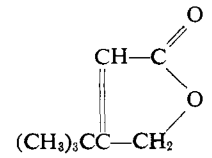
[29] F. Moulin, *Helv. Chim. Acta*, **34**, 2416 (1951).

[30] C. Moureu and R. Delange, *Compt. Rend.*, **136**, 552 (1903).

and aqueous Na_2CO_3. The CH_2Cl_2 was evaporated and the residue was distilled giving 16.3 g (68% yield from the acid) of the methyl ester boiling at 65° (15 mm) (lit.[30] 66° (13 mm)). The infrared spectrum showed strong absorption at 2220 ($C\equiv C$) and 1705 ($C=O$) cm^{-1}. The nmr spectrum ($CDCl_3$) showed two singlets with areas in the ratio of 3:10 at δ 1.26 (*t*-butyl) and δ 3.60 (CH_3O).

Irradiation of Ester 2. Three separate runs are described: run A provided the identification of the *cis* and *trans* olefinic esters and ethylene glycol, run B showed that these esters were changed to the cyclopropyl ester **7**, and run C provided quantitative information on the relative amounts of volatile and high-boiling products.

Run A. A solution of 20 g of ester **2** in 120 ml of reagent methanol was irradiated as described above for ketone **1** except that a Hanovia 200-W, Type S lamp was used. At the end of 114 hr of irradiation (without filter) the methanol was removed by distillation at atmospheric pressure. The residue was distilled at 15 mm through a spinning-band column. The temperature rose continuously from 50 to 110°, so fractions were collected at arbitrary intervals: fraction 1, 50–60°; fraction 2, 60–75°; fraction 3, 75–80°; fraction 4, 89–95°; fraction 5, 95–110°. Each fraction weighed roughly 1.5 g. The large amount of material remaining in the pot cooled to a dark, polymeric glass. Its infrared spectrum was uninformative, and the material was not investigated further. Fractions 1–3 contained three unseparated components according to vpc (SF-96, 10 ft × 0.25 in., 150°) and were combined for separation by preparative-scale vpc (30% Carbowax on Chromosorb W, 10 ft × $^3/_8$ in., 150°). In this run only the first and third peaks (roughly equal intensities) were collected. The infrared spectrum of the first material showed strong absorption bands at 1710 ($C=O$) and 1635 cm^{-1} ($C=C$). Its nmr spectrum (CCl_4) showed two singlets at δ 1.16 (*t*-butyl) and 3.65 (CH_3O) as well as a pair of coupled (J = 13 cps) doublets centered at δ 5.55 and 6.15 which were assigned as *cis*-vinyl protons. The relative areas were in the expected ratios of 9:3:1:1. The infrared spectrum of the other compound also showed strong absorption bands due to the carbonyl group (1705 cm^{-1}) and the conjugated double bond (1647 cm^{-1}). The nmr spectrum was very similar to that of the *cis* isomer with singlets (area ratio, 9:3) at δ 1.07 (*t*-butyl) and 3.69 (CH_3O). The pair of doublets (area ratio 1:1) at δ 5.69 and 6.95 were assigned as *trans*-vinyl protons on the basis of the large coupling constant of 16 cps. Fraction 4 separated into two layers, the lower of which was identified as ethylene glycol by its solubility in water, the coincidence of its vpc retention time with that of an authentic sample, and the identity of its infrared spectrum with that of an authentic sample. Fraction 5 and the upper layer of fraction 4 were combined, weighing approximately 2 g. Vpc showed at least five overlapping, high-boiling components. One that was slightly separated from the others was collected by preparative-scale vpc. This material, weighing about 100 mg, was never obtained in a completely pure state, but its infrared and nmr spectra were consistent with structure **9**.



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Run B. A solution of 4.3 g of ester **2** in 90 ml of methanol (0.33 M) was irradiated with the Type L, 450-W Hanovia immersion lamp as described above. The progress of the reaction was followed by vpc (20% SF 96, 10 ft × 0.25 in., 150°). As the starting material peak diminished, two peaks on either side of it began to appear (*cis* and *trans* **6**). After several hours the center peak (cyclopropyl ester **7** and starting material, the retention times of which were coincident) began to rise again. At the end of 6 hr the two side peaks had almost disappeared. It was noted that the area under this curve was about 25% of the area of the starting material peak at the beginning of the run (sample volumes were the same). The lamp was turned off and the methanol was removed by distillation at atmospheric pressure. The volatile product was separated from the remaining methanol and the high-boiling products by preparative-scale vpc (20% SF 96, 10 ft × $^3/_8$ in., 150°). The infrared and nmr spectra of the pure product were identical with those described below for **7** obtained from irradiation of methyl 4,4-dimethyl-2-pentenoate.

Run C. A solution of 2.9 g (0.02 mol) of ester **2** in 200 ml of methanol was irradiated with the Type L, 450-W Hanovia immersion lamp as described above. When a Pyrex filter sleeve was used, there was no evidence of reaction after 6 hr. When the filter was removed the reaction commenced. At the end of 2 hr the lamp was turned off. The methanol was removed by distillation. Vpc indicated that the residue had three volatile products in addition to a small amount of methanol. The following procedure was performed twice to determine the percentage of vpc volatile material in the sample. A weighed sample was injected (20% SF 96, 10 ft × $^3/_8$ in., 150°) and exited through a weighed collector cooled in liquid nitrogen. At the end of about 30 min the collector was warmed and weighed again. The two runs indicated 40 and 54% recovery of injected material.

Methyl 4,4-dimethyl-2-pentenoate[8] was prepared using the procedure of Wadsworth and Emmons.[31] The reaction of 17 g (0.075 mol) of triethyl phosphonacetate, 6.45 g (0.075 mol) of pivalaldehyde, and 3.6 g (0.075 mol) of 50% sodium hydride in 150 ml of dimethoxyethane gave, after distillation through a short Vigreux column, 6.28 g (55% yield) of a clear liquid, bp 72–75° (15 mm). The ethyl ester was hydrolyzed in aqueous NaOH and converted to the methyl ester by isolation of the acid and reesterification in acidic methanol. The crude ester was distilled to provide 3 g of the methyl ester. The vpc retention time and the infrared and nmr spectra were identical with those of the photoproduct (see above) which had been assigned the structure: methyl *trans*-4,4-dimethyl-2-pentenoate.

Methyl (2,2-Dimethylcyclopropyl)acetate (7).[8] Methyl *trans*-4,4-dimethyl-2-pentenoate (4.4 g) in 90 ml of methanol was irradiated as in run B described above. At the end of 1 hr there were roughly equal amounts of *cis* and *trans* esters. At the end of 1 hr 40 min the peak heights of cyclopropyl ester **7** and *cis* and *trans* esters **6** were in the ratio of 17:36:28. At the end of 5.5 hr only the cyclopropyl compound, the center peak, remained. It was isolated by vpc. Its infrared spectrum ($CHCl_3$) showed a strong carbonyl band at 1725 cm^{-1}. Its nmr spectrum ($CDCl_3$) showed two barely separated singlets (6 H) centered at δ 0.98 (*gem*-dimethyl), singlet (3 H) at 3.60 (CH_3O), a doublet (2 H) at 2.30 and 2.18 (CH_2CO_2R), and a multiplet (3 H) at 0.80 to −0.03 (cyclopropyl hydrogens). Because of the cyclopropyl hydrogen absorption near the TMS signal, no TMS was added. Instead, a small amount of $CHCl_3$ was used as internal reference and lock signal, with the assumption that the $CHCl_3$ absorbs at 435 cps downfield from TMS.

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(31) W. S. Wadsworth, Jr., and W. D. Emmons, *J. Am. Chem. Soc.*, **83**, 1733 (1961).