Carbon vs. Oxygen Abstraction in the Photochemical Reduction of an Acetylenic Ester

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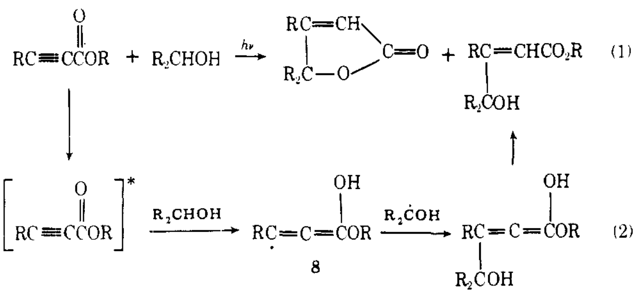
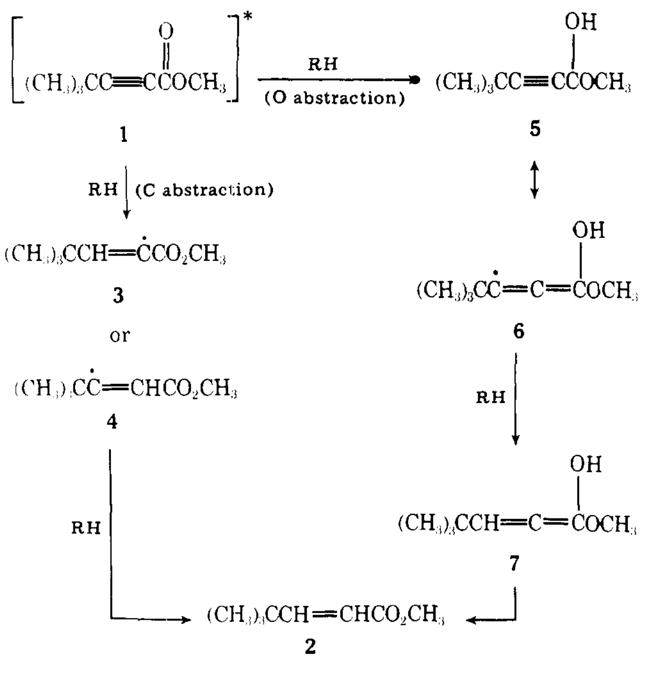
The irradiation of methyl 4,4-dimethyl-2-pentynoate (1) in methanol-*O-d* yields *cis*- and *trans*-methyl 4,4-dimethyl-2-pentenoate (2) containing no deuterium and methyl (2,2-dimethylcyclopropyl)acetate (9) containing one deuterium on the α carbon. The irradiation of 1 in CD_3OH yields 2 and 9 containing two atoms of deuterium per molecule. The irradiation of 2-ethoxyethyl 4,4-dimethyl-2-pentynoate in methanol yields the ethoxyethyl esters (and some acidic material) corresponding to 2 and 9 instead of the type II cleavage product, 4,4-dimethyl-2-pentynoic acid. These observations are consistent with a mechanism that involves abstraction of hydrogen from solvent by the carbons of the triple bond rather than abstraction by carbonyl oxygen.

It was argued earlier[1] that the photochemical reduction of 1 to 2 in methanol involved hydrogen abstraction at carbon by the π, π^* triplet excited state of the ester. However, the initial site of hydrogen abstraction can be either oxygen or carbon as shown in Chart I. Support for an oxygen abstraction mechanism may be found in the fact that other acetylenic esters[2,3] (and 1 to a small extent[1]) undergo photochemical addition of solvent to the β carbon (reaction 1). A simple rationale for the formation of these products includes intermediate radical 8, the product of hydrogen abstraction by oxygen (reaction 2).



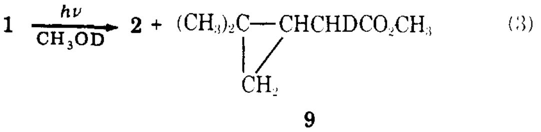
Several experiments were designed to resolve this question about the initial site of hydrogen abstraction in the formation of 2: (a) methyl ester 1 was irradiated in CH_3OD and in CD_3OH and (b) ethoxyethyl ester 10 was prepared and irradiated in methanol. The results of these experiments are consistent with the carbon abstraction mechanism.

Chart I



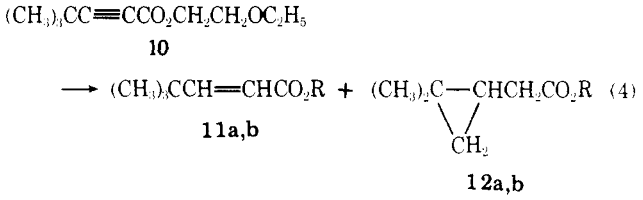
Results

When 1 was irradiated in methanol-*O-d*, three volatile products were formed:[1] *cis*- and *trans*-2 and the cyclopropyl ester 9 (reaction 3). The mixture of *cis*- and *trans*-2 contained no deuterium. One atom of deuterium was found in 9 on the carbon α to the carbonyl group. When 1 was irradiated in CD_3OH, the same three products contained two atoms of deuterium per molecule according to the mass spectrum and NMR spectrum of the product mixture.



9

When ethoxyethyl ester 10 was irradiated in methanol, the same three types of products, *cis*- and *trans*-11a and 12a, and their corresponding acids, 11b and 12b, were formed (reaction 4). The yield of acidic material was about 35%. Its NMR spectrum showed at most a trace of the acetylenic acid $(CH_3)_3CC{\equiv}CCO_2H$ (15) and was very similar to the spectrum of the acidic material obtained from the irradiation of 11a. The *irradiation of the acetylenic acid* 15 *in methanol* produced a similar mixture, but too slowly to be the source of these products in the irradiation of 10.



12a,b

a, R = $CH_2CH_2OC_2H_5$; b, R = H

When 1 was irradiated in benzene–methanol (with benzene absorbing most of the incident light), the same products, 2 and 9, were formed as in methanol alone.

Discussion

The fact that no deuterium was incorporated into 2 during its formation from 1 is evidence that 2 was formed by the carbon abstraction mechanism of Chart I. The oxygen abstraction mechanism would have produced enol 7, which would have yielded 13 on ketonization in the deuterated solvent.

$$1 \xrightarrow{h\nu} 7 \xrightarrow{CH_3OD} (CH_3)_3CCH{=}CDCO_2CH_3$$

13

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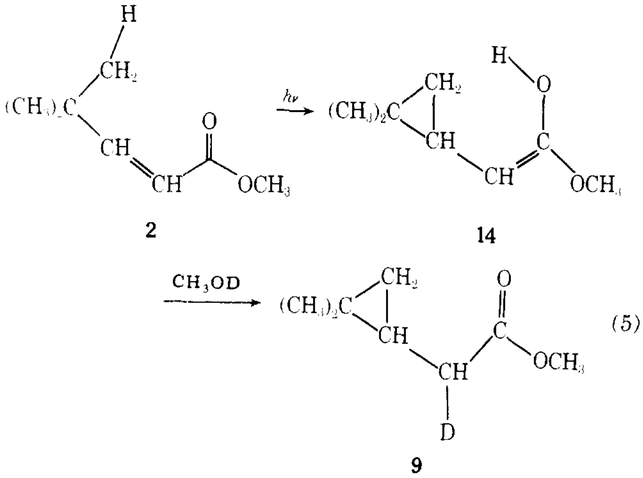
That photochemical formation of an enol does lead to deuterium incorporation under these conditions was shown by the fact that one atom of deuterium was incorporated into **9** during its formation from **2** by way of enol **14**. The oxygen abstraction mechanism of reaction 5 was originally suggested by Jorgenson and Gundel.[4]

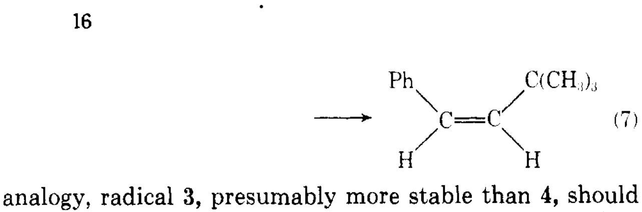


Further evidence for the carbon abstraction mechanism for the formation of **2** is provided by the finding that the irradiation of ethoxyethyl ester **10** yielded at most only a trace of **15**, the product expected from intramolecular oxygen abstraction (reaction 6).[5] The products are instead analogous to those formed from **1**. It is unlikely that **11a** and **12a** are formed by initial intermolecular hydrogen abstraction by oxygen since intramolecular abstraction by oxygen is not observed.[6] The acidic material formed in the irradiation of **10** apparently came from the subsequent irradiation of products **11a** and **12a**.

$$\mathbf{10} \nrightarrow \underset{\mathbf{15}}{(CH_3)_3CC{\equiv}CCO_2H} + CH_2{=}CHOC_2H_5 \qquad (6)$$

That the reaction is sensitized by benzene suggests, but does not prove,[7] a triplet mechanism for the reduction. Ben-Efraim[9] and Zimmerman and Pincock[10] have provided evidence that triplet excited states are responsible for similar reductions.

A choice between abstraction by the carbon β to the carbonyl (yielding **3**) and abstraction by the α carbon (yielding **4**) cannot be made on the basis of evidence reported here. However, Zimmerman and Pincock[10] have argued that the initial point of hydrogen abstraction in **16** is at the carbon β to the conjugated phenyl group (reaction 7). According to this analogy, radical **3**, presumably more stable than **4**, should precede the formation of **2**.[11] If both oxygen abstraction, yielding **6** (ruled out by the evidence above), and α-carbon abstraction, yielding **4** (ruled out by the analogy), are untenable, then another mechanism for the formation of products resulting from the addition of solvent molecules (see reaction 1) is required. A radical chain mechanism, initiated by excited state hydrogen abstraction and involving subsequent attack by solvent-derived radicals on the ground state acetylenic molecule, is a reasonable choice. This mechanism has been suggested in several other studies of photochemically initiated addition of solvent molecules to unsaturated esters.[2,13-15]



Experimental Section

The instruments used were the following: IR, Beckman IR-8; NMR, Varian T-60 or CFT-20; mass spectroscopy, Perkin-Elmer RMU-7; gas chromatography (GC), Varian 90P. Unless otherwise noted for GC analyses, a 10% Carbowax 4000, 19 ft × 0.25 in. column at 160 °C was used. Chemical shifts (δ values) are given in parts per million from Me_4Si as an internal standard. Irradiations were conducted with either (1) a Rayonet reactor (Model RPR-100) with 16 low-pressure mercury lamps (~35 W) using a quartz tube (13 × 300 mm) closed with a polyethylene stopper or (2) a 450-W Hanovia immersion lamp in a quartz cooling well.

Irradiation of Methyl 4,4-Dimethyl-2-pentynoate (1) in Methanol-*O-d*. A solution of 3.0 g of **1** (prepared according to ref 1) in 50 mL of methanol-*O-d* (Diaprep Inc., minimum isotopic purity 99%) was irradiated with the Hanovia lamp for 3 h 40 min. The solvent was removed by distillation, and the volatile products were collected by flash distillation at 1 mm. They were separated by gas chromatography (20% Carbowax 4000, 20 ft × 0.375 in, 150 °C) into three fractions: *cis*- and *trans*-**2** and **9**. The mass spectra and NMR spectra of the cis and trans esters formed in CH_3OD were similar to the spectra of these esters formed in CH_3OH. However, the area of the pair of triplets (J = 2 Hz) assigned to the α proton in the NMR spectrum of **9** formed in CH_3OD was half that of the doublet assigned to the α protons of **9** formed in CH_3OH. The parent regions in the mass spectra of **9** formed in the two solvents were also different. In CH_3OD, the relative intensities of M, M + 1, and M + 2 were 100 (*m/e* 143), 14 (*m/e* 144), and 2 (*m/e* 145) (average values of two runs). In CH_3OH they were 100 (*m/e* 142), 14 (*m/e* 143), and 3 (*m/e* 144).

Irradiation of 1 in Benzene–Methanol. A solution of 112 mg of **1** in 10 g of methanol and 1 mL of benzene was irradiated in the Rayonet reactor. Under these conditions the benzene absorbed greater than 95% of the incident light at 254 nm. At intervals a sample was withdrawn and mixed with a measured sample of reference compound [bis(2-ethoxyethyl) ether]. A sample of this mixture was analyzed by gas chromatography. The relative instrument responses of the products were assumed to be the same as that of **1**. Listed below for each sample are the (1) time, (2) percentage of **1** remaining, and (3) percentage of the original area of **1** that is accounted for by the areas of remaining **1** and the three volatile products: 31 min, 71%, 82%; 63 min, 49%, 65%; 99 min, 36%, 63%; 209 min, 11%, 49%. For the purpose of comparison with an unsensitized run, the same values are recorded below for a sample of 102.2 mg of **1** in 10 g of methanol without benzene: 30 min, 85%, 106%; 65 min, 57%, 88%; 95 min, 42%, 75%; 215 min, 15%, 67%.

Irradiation of 1 in CD_3OH. A solution of 110 mg of **1** in 9.99 g of CD_3OH (Aldrich, 99.5 atom % D) was irradiated for 5 h in the Rayonet reactor. Most of the solvent was removed by distillation at atmospheric pressure. The residue was purified by gas chromatography. Products **2** and **9** were collected together. The mass spectrum of this material showed a parent at *m/e* 144 with minor peaks at *m/e* 143 and 142 representing a maximum of 7% mono- and 4% nondeuterated **2** and **9**. The NMR spectrum of the mixture showed no vinyl protons and alterations in the multiplets assigned to the methylene and cyclopropyl hydrogens.

2-Ethoxyethyl 4,4-Dimethyl-2-pentynoate (10). A mixture of 8.0 g (0.064 mol) of 4,4-dimethyl-2-pentynoic acid,[1] 28.6 g of 2-ethoxyethanol, and 2 mL of concentrated sulfuric acid was refluxed for 3 h. Ether and water were added. The ether layer was washed with sodium bicarbonate and water, dried, and concentrated. Distillation gave 5.4 g (43%) of **10**: bp 131–132 °C (20 mm); IR ($CHCl_3$) 2970, 2220 (C≡C), 1700 (C=O), 1270, 1230, 1125, and 1040 cm^{-1}; NMR ($CDCl_3$) δ 1.27 (s, 9 H, *tert*-butyl), 1.20 (t, 3 H, J = 7 Hz, OCH_2CH_3), 3.53 (q, 2 H, J = 7 Hz, OCH_2CH_3), and 3.63 and 4.28 (A_2B_2, 4 H, OCH_2CH_2O). The mass spectrum at 70 eV showed no molecular ion at *m/e* 198, but showed instead an ion at $(M - 15)^+$ = 183. Anal. Calcd for $C_{11}H_{12}O_3$: C, 66.64; H, 9.15. Found: C, 66.53; H, 9.14.

2-Ethoxyethyl 4,4-Dimethyl-2-pentenoate (11a). A solution of 1.38 g of **2**, prepared from pivalaldehyde and trimethyl phosphonoacetate,[1] and 3 drops of concentrated sulfuric acid in 20 mL of 2-ethoxyethanol was refluxed for 3 h. The solvent was removed by distillation at about 35 mm. Ester **11a** was isolated by distillation through a short-path still, bp 63 °C (0.1 mm), and contained a little higher boiling material according to gas chromatography: NMR ($CDCl_3$) δ 7.00 (d, 1 H, J = 16 Hz, vinyl), 5.75 (d, 1 H, J = 16 Hz, vinyl), 4.38–4.22 (m, 2 H, CH_2O), 3.75–3.40 (m, 4+ H, CH_2O), 1.23 (t, 3 H, J = 7 Hz, CH_3CH_2), and 1.12 (s, 9 H, *tert*-butyl). An analytical sample was obtained by gas chromatography and flash distillation at 0.2 mm. Anal. Calcd for $C_{11}H_{20}O_3$: C, 65.96; H, 10.06. Found: C, 65.74; H, 10.10.

Irradiation of 4,4-Dimethylpentynoic Acid (15) in Methanol. A solution of 111 mg of **15** in 10 g of methanol was irradiated in the Rayonet reactor for 196 min. Samples removed during this period and analyzed by gas chromatography showed that no volatile products were being formed. Most of the methanol was removed on the rotary evaporator, 10 mL of ether was added, and the solution was extracted with 2 × 5 mL of saturated $NaHCO_3$. The aqueous layers were acidified and extracted with 20 mL of ether in three portions. After drying and evaporation, 94 mg of an oil remained. Its NMR spectrum showed two doublets centered at δ 7.03 and 5.68 ($J = 16$ Hz) for *trans*-**11b** and two doublets centered at δ 6.11 and 5.61 ($J = 13$ Hz) for *cis*-**11b.** There were three *tert*-butyl singlets of roughly equal areas at δ 1.30 (**15**) and at δ 1.22 and 1.10 (*cis*- and *trans*-**11b**). Minor peaks extending from δ 2.42 to 0 indicated the presence of **12b** also. An OH peak was present at δ 8.83.

Irradiation of 10 in Methanol. A solution of 108 mg of **10** in 10 g of methanol was irradiated in the Rayonet reactor. The analytical procedure and the time–percentage list that follows are described above for the irradiation of **1** in benzene–methanol except that benzyl acetate was used as a standard: 31 min, 59%, 80%; 62 min, 34%, 68%; 93 min, 24%, 51%; 153 min, 5%, 40%; 212 min, 0%, 37%. After 212 min the sample was worked up as described above for the irradiation of **15**; the residue weighed 26 mg. The NMR spectrum was not as well resolved as that of the product from **15**, but it showed the same pair of AB quartets in the region from δ 7.0 to 5.6 as well as a broadened OH peak at δ 6.85. In addition to the two *tert*-butyl singlets at δ 1.1 and 1.2, there was weak, ill-resolved absorption in the region of δ 1.30, possibly due to a small amount of **15**, and other small peaks between δ 2.5 and 0 that may have been due to **12b.**

In an earlier run, 4.0 g of **10** in 90 mL of methanol was irradiated with the Hanovia lamp (Vycor filter sleeve) for 4 h in order to isolate samples of **11a** and **12a.** The methanol was removed by distillation, and the residue, 4.86 g, was separated into acidic (212 mg) and neutral portions (2.96 g) by extraction. The neutral material was distilled in a short-path apparatus at 1 mm to yield 1.65 g of material which showed only three peaks by gas chromatography. The material was separated on a 20% Carbowax 4000 column (20 ft × 0.375 in, 160 °C).

The first fraction (317 mg) was identified as *cis*-2-ethoxyethyl 4,4-dimethyl-2-pentenoate (**11a**): IR ($CHCl_3$) 1710 (C=O) and 1645 (C=C) cm^{-1}; NMR ($CDCl_3$) δ 6.07 (d, 1 H, $J = 13$ Hz, vinyl), 5.34 (d, 1 H, $J = 13$ Hz, vinyl), 4.32–4.15 (m, 2 H, CH_2O), 3.73–3.35 (m, 4 H, CH_2O), 1.20 (t, 3 H, CH_3CH_2), and 1.20 (s, 9 H, *tert*-butyl); mass spectrum (70 eV), highest mass fragment at *m/e* 185 (M − 15). Anal. Calcd for $C_{11}H_{20}O_3$: C, 65.96; H, 10.06. Found: C, 66.19; H, 10.31.

The middle fraction (144 mg) was identified as 2-ethoxyethyl (2,2-dimethylcyclopropyl)acetate (**12a**): IR ($CHCl_3$) 1725 cm^{-1} (C=O); NMR ($CDCl_3$) δ 4.28–4.12 (m, 2 H, CH_2O), 3.65–3.30 (m, 4 H, CH_2O), 2.32 (d, 2 H, $CHCH_2CO_2R$), 1.13 (t, 3 H, CH_3CH_2), 1.02 and 1.00 (two s, 6 H total, $(CH_3)_2C$), and 0.97 to −0.10 (m, 3 H, cyclopropyl); mass spectrum (70 eV), *m/e* 200 (molecular ion).

The final fraction (268 mg) was identified as *trans*-2-ethoxyethyl 4,4-dimethyl-2-pentenoate (**11a**): IR ($CHCl_3$) 1710 (C=O) and 1645 (C=C) cm^{-1}; the NMR spectrum was identical with that described above for this compound.

To obtain a sample of **12a** for analysis, a 511-mg sample of **11a** was irradiated for 100 min in 125 mL of ether with the Hanovia lamp (Vycor filter). The residue remaining after the ether had been removed (556 mg) was purified by gas chromatography and flash distillation at 0.2 mm. Anal. Calcd for $C_{11}H_{20}O_3$: C, 65.96; H, 10.06. Found: C, 65.60; H, 10.50.

Irradiation of 11a in Methanol. A solution of 114 mg of *trans*-**11a** in 10 g of methanol was irradiated for 218 min in the Rayonet reactor. After removal of solvent and extraction as above, 20 mg of acidic material remained. Its NMR spectrum was very similar to that of the acidic material from **10** except that there was additional weak unresolved absorption at about δ 3.6, there was no OH peak at δ 6.8, and the weak absorbtion apparently due to **12b** seemed to be missing.

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Registry No.—**1,** 20607-85-6; *cis*-**2,** 57539-96-5; *trans*-**2,** 20664-51-1; **9,** 68258-15-1; **10,** 68258-16-2; *cis*-**11a,** 68258-17-3; *trans*-**11a,** 68258-18-4; *cis*-**11b,** 1577-94-2; *trans*-**11b,** 16666-45-8; **12a,** 68258-19-5; **12b,** 68258-20-8; **15,** 52418-50-5; CH_3OD, 1455-13-6; benzene, 71-43-2; methanol, 67-56-1; CD_3OH, 1849-29-2; 2-ethoxyethanol, 110-80-5.

References and Notes

(1) J. W. Wilson and V. S. Stubblefield, *J. Am. Chem. Soc.*, **90,** 3423 (1968).

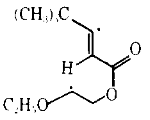
(2) S. Majeti, *J. Org. Chem.*, **37,** 2914 (1972).

(3) G. Büchi and S. H. Feairheller, *J. Org. Chem.*, **34,** 609 (1969).

(4) M. J. Jorgenson and L. Gundel, *Tetrahedron Lett.*, 4991 (1968).

(5) H. Morrison, R. Brainard, and D. Richardson, *Chem. Commun.*, 1653 (1968); R. Brainard and H. Morrison, *J. Am. Chem. Soc.*, **93,** 2685 (1971).

(6) Intramolecular hydrogen transfers to either the α or β carbons are formally possible (structures i and ii are the intermediate biradicals that would be



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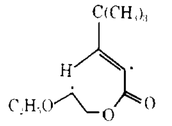

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formed by hydrogen atom transfer to these two carbons) but are without precedent and would probably lead to products isomeric with starting material only in the absence of solvents able to donate hydrogen atoms. Intermediates i and ii are not ruled out as precursors to **2.**

(7) Singlet–singlet energy transfer from benzene to esters has been observed, however.[5,8]

(8) J. E. Gano, *Mol. Photochem.*, **3,** 79 (1971).

(9) D. A. Ben-Efraim, *Tetrahedron Lett.*, 957 (1967).

(10) H. E. Zimmerman and J. A. Pincock, *J. Am. Chem. Soc.*, **95,** 3246 (1973).

(11) Though we isolated no products resulting from the coupling of **3** with solvent-derived radicals, there are precedents[12] for this type of product.

(12) (a) S. Majeti and T. W. Gibson, *Tetrahedron Lett.*, 4889 (1973); (b) S. Wolff, W. L. Schreider, A. B. Smith, III, and W. C. Agosta, *J. Am. Chem. Soc.*, **94,** 7797 (1972).

(13) P. Singh, *J. Org. Chem.*, **37,** 836 (1972).

(14) G. Ahlgren, *J. Org. Chem.*, **38,** 1369 (1973).

(15) M. Pfau and R. Dolou, *Bull. Soc. Chim. Fr.*, 3336 (1967).