Photochemical Reactions. XIV.[1] Additions to Ethyl Propiolate

G. BÜCHI AND S. H. FEAIRHELLER[2]

Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

Received July 11, 1968

The photolytically initiated additions of cyclohexane, ethanol, and 2-propanol to ethyl propiolate, and of 2-propanol to 1-hexyne are described. 1:1 adducts are formed, along with products of their photorearrangement. Structures have been assigned on the basis of spectral evidence and direct comparison with known substances.

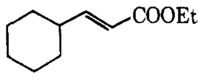
In pursuit of certain synthetic aims we undertook a study of the photolytic reactions of ethyl propiolate in several solvents. Since the completion of this work a number of closely related reactions have been reported and comparison with the present results is made in the concluding section of this paper.

Dilute solutions of ethyl propiolate in cyclohexane, ethanol and 2-propanol were irradiated under a nitrogen atmosphere for periods up to 2 weeks with a quartz-jacketed mercury lamp emitting over a wide wavelength range. Photolyses were continued until the ethyl propiolate was completely consumed either in formation of products or in polymerization. Mild conditions were used in isolating the products and the crude reaction mixtures were examined by gas chromatography.

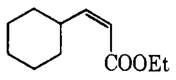
Products.—The irradiation of ethyl propiolate (**1**) in cyclohexane yielded 10.4% (based on the ester) of a mixture of products with boiling point 115–132° (20 mm). The mixture was resolved by gas chromatography into three components—**2**, **3**, and **4**—in proportions 47:41:12. The spectra of **2** quickly identified it as an α,β-unsaturated ester and it was shown to be identical with an authentic sample of ethyl β-cyclohexyl-*trans*-acrylate synthesized from chlorocyclohexane.[3,4] The second product, **3**, was also an α,β-unsaturated ester as evidenced by its infrared (1720, 1630, 1180 and 820 cm^{-1}) and ultraviolet spectra [213 mμ (ϵ 11,600)]. Combustion analysis suggested the formula $C_{11}H_{18}O_2$, confirmed by a mass spectrometric molecular weight of 182, which again represents a monoadduct of ethyl propiolate and cyclohexane. The proton magnetic resonance (pmr) spectrum showed signals due to the protons of the ethoxy group (δ 1.27 triplet; 4.08, quartet, J = 7.0 cps), ten aliphatic protons (0.7–2.0, unresolved), an allylic proton (3.30, broad doublet, J = 9.0 cps), and two olefinic protons (5.93, doublet of doublets, J = 11.5 and 9.0 cps; 5.55, doublet, J = 11.5 cps). Thus **3** was deduced to be ethyl β-cyclohexyl-*cis*-acrylate. This structure was confirmed by hydrogenation of both **2** and **3** over platinum catalysts to the same compound, ethyl β-cyclohexylpropionate (**5**), in almost quantitative yield. The third product was identified as a nonconjugated ester, and proved to be identical with ethyl β-cyclohexylidenepropionate (**4**) prepared by alkali isomerization of ester **2**.[5]

$HC{\equiv}CCOOEt$

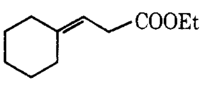
1



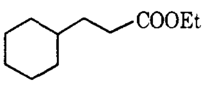
2



3

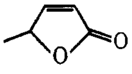


4

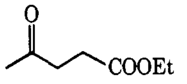


5

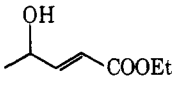
The photoreaction of ethyl propiolate with ethanol also yielded three products (27.7%), and fractional distillation gave fractions boiling at 83–86 and 120° (11 mm). The lower boiling fraction was separated by gas chromarography into two components which were shown to be β-angelica lactone[6,7] (**6**) and ethyl levulinate (**7**). The higher boiling fraction was a single compound having infrared absorptions at 3500, 1715, 1650, 1300, 1265, 1175, 1145, 1045 and 980 cm^{-1} and ultraviolet absorption at 207 mμ (ϵ 12,050). Its microanalysis was consistent with the formula $C_7H_{12}O_3$ and it had a mass spectrometric molecular weight of 144. The pmr spectrum showed signals arising from an ethoxy group (δ 1.38, triplet; 4.15, quartet, J = 7.0 cps), a methyl group (1.83, doublet, J = 6.5 cps), a hydroxyl proton (3.68, broad singlet), a highly coupled proton (4.35, complex) and two olefinic protons (5.91, doublet of doublets, J = 15.5 and 1.5 cps; 6.89, doublet of doublets, J = 15.5 and 4.5 cps). This evidence suggested the presence of ethyl 4-hydroxy-*trans*-2-pentenoate (**8**). Oxidation with activated manganese dioxide gave, almost quantitatively, ethyl β-acetylacrylate (**9**) characterized by its phenylhydrazone and semicarbazone.



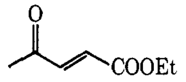
6



7



8



9

Two products were produced by irradiation of ethyl propiolate in 2-propanol, and separated by fractional distillation. The first, obtained in 20.3% yield, showed infrared bands at 1750, 1605, 1275, 1195, 1130, 960, 945 and 820 cm^{-1} and end absorption in the ultraviolet spectrum. Its analysis was consistent with the formula $C_6H_8O_2$ and its molecular weight, determined mass spectrometrically, was 112. The pmr spectrum showed a six-proton singlet at δ 1.47, and one-proton doublets at δ 5.90 and 7.53 (J = 5.5 cps). It was assigned the structure **10** by analogy with the lactone **6**

---

(1) Part XIII: G. Büchi and J. D. White, *J. Amer. Chem. Soc.*, **86**, 2884 (1964).

(2) National Science Foundation Predoctoral Fellow, 1962–1963.

(3) D. Jerchel, H. Fischer, and M. Kracht, *Ann.*, **575**, 162 (1952).

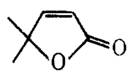
(4) S. S. G. Sircar, *J. Chem. Soc.*, 54 (1928).

(5) R. P. Linstead, A. B. Wang, J. H. Williams, and K. D. Errington, *J. Chem. Soc.*, 1136 (1937).

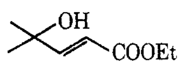
(6) J. H. Helberger, S. Ulubay, and H. Cievelekoglu, *Ann.*, **561**, 215 (1949).

(7) J. Thiele, R. Tischbein, and L. Lossow, *ibid.*, **319**, 180 (1901).

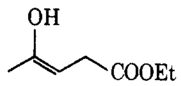
produced from ethanol. The physical properties corresponded with those recorded for the authentic compound;[8] it was readily hydrogenated to the saturated lactone. The second product, obtained in 20.9% yield, showed infrared bands at 3550, 1720, 1660, 1305, 1280, 1190, 1155, 1040 and 960 cm^{-1} and ultraviolet absorption at 207 mμ (ε 13,300). Microanalysis and mass spectrometric molecular weight (158) were consistent with the formula $C_8H_{14}O_3$ and the pmr spectrum showed signals for an ethoxy group (δ 1.30, triplet; 4.15, quartet, $J = 7.0$ cps), two methyl groups β to a hydroxyl (1.32, singlet), a hydroxyl group (3.31, broad singlet), and an AB system of olefinic protons (doublets at 5.92 and 6.96, $J = 15.5$ cps). The ester was thus **11** and its nature was confirmed by hydrolysis to the known 4-hydroxy-4-methyl-*trans*-2-pentenoic acid.[9]



10



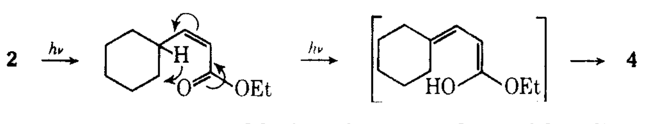
11



12

Discussion.—Examination of the structures of the photoproducts suggests that, in each case, the solvent has essentially been added to the acetylenic bond to form an α,β-unsaturated ester with *trans* double bond (**2**, **8**, and **11**), from which the other products may be derived by means of secondary photochemical reactions. Photoisomerization about a double bond is a well-known process,[10] and that the *cis*-α,β-unsaturated γ-hydroxy esters so formed should cyclize to lactones **6** and **10** is unexceptional. The α,γ-unsaturated ester **4** probably arises from the *cis*-α,β-unsaturated ester **3** by means of a cyclic process which is now well documented (Scheme I).[11] A similar process involving hydroxy ester **8** would give rise to enol **12** of levulinic acid ester. When ethyl β-cyclohexyl-*trans*-acrylate (**2**) was irradiated in cyclohexane under the usual conditions and the reaction monitored by gas chromatography, the concentration of starting material decreased monotonically and the β-cyclohexylidenepropionate (**4**) was formed as the final product. The formation of the *cis*-acrylate (**3**) as an intermediate became clear from its appearance, maximization and subsequent disappearance from the assayed samples. Similar isomerization of **11** is impossible because of the substitution at the γ carbon.

Scheme I

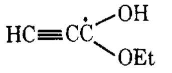


Radical additions to acetylenes have been known for some time,[12] although the radicals are usually preformed chemically (*e.g.*, by means of peroxides), thermally, or photolytically from suitable substrates. In present work, however, the three solvents employed are inert to light of the wavelength used and hence the ultimate source of the radicals must lie in the excitation of the propiolic ester itself.

In following this mechanistic clue, certain further observations are worthy of mention although they do not lead to a detailed mechanistic scheme. First, the increase in yields of 1:1 adducts on going from cyclohexane to ethanol to 2-propanol (and the accompanying rate increase) is probably a reflection of the ease of formation and the stability of the solvent radicals, which increase in that order. Abstraction of a hydrogen atom from the solvent by an excited ethyl propiolate molecule could reasonably lead to radicals **13**, **14**, or **15** of which the former two should be energetically more favorable because of delocalization with the adjacent carbonyl group[13,14] or with the triple bond. Subsequent combination of **13** with the solvent radical would not lead to the products observed. However, pairing of the solvent radical with **14** followed by tautomerization would indeed explain the course of the reaction. Similarly addition of the alkyl radical to the β-carbon atom of ethyl propiolate should lead to a radical which is then able to abstract a hydrogen atom from another solvent molecule and thus sustain a chain reaction. An attempt was thus made to duplicate the photolytic reaction by means of chemically generated radicals. It is known that cyclohexyl radicals are produced when benzoyl peroxide decomposes in boiling cyclohexane.[15] When a solution of ethyl propiolate in cyclohexane containing benzoyl peroxide was heated the acrylic esters **2** and **3** were produced in approximately equal amounts, but none of the unconjugated ester **4** was detected in the reaction mixture. Several recent reports describe the use of peroxides as initiators for free-radical additions to acetylenes[16-18] and olefins.[19] Irradiation of solutions containing acetone as a radical source has also been reported to effect additions to acetylene.[17]

$CH_2{=}\dot{C}COOEt$

13



$HC{\equiv}C\dot{C}(OH)(OEt)$

14

$\dot{C}H{=}CHCOOEt$

15

We have found that conjugation of the triple bond is not essential to the process described although it considerably accelerates it, since irradiation of 1-hexyne in 2-propanol slowly yielded a mixture of products in 15.3% yield. This mixture consisted of two ethers, inseparable by gas chromatography (17 and 27%, respectively), and the two 2-hydroxy-2-methyl-3-octenes **16** (35%) and **17** (21%) which were identified by comparison with authentic samples. The infrared spectrum of the ether mixture suggested a mixture of unconjugated *cis* and *trans* olefins. Its mass spectrometric molecular weight, 184, connoted its formation from 2 mol of 2-propanol and 1 mol of 1-hexyne with loss of a molecule of water, and the fragmentation pattern was consistent with structures **18** and **19**.

---

[8] L. J. Haynes and E. R. H. Jones, *J. Chem. Soc.*, 954 (1946).

[9] D. Lavie and Y. Shvo, *Proc. Chem. Soc.*, 220 (1958).

[10] G. M. Wyman, *Chem. Rev.*, **55**, 625 (1955).

[11] M. Mousseron, *Pure Appl. Chem.*, **9**, 481 (1964).

[12] G. Sosnovsky, "Free Radical Reactions in Preparative Organic Chemistry," The Macmillan Co., New York, N. Y., 1964.

[13] M. S. Kharasch, J. G. McNab, and M. C. McNab, *J. Amer. Chem. Soc.*, **57**, 2463 (1935).

[14] H. Bader, L. C. Cross, I. Heilbron, and E. R. H. Jones, *J. Chem. Soc.*, 619 (1949).

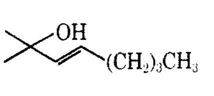
[15] C. G. Swain, L. J. Schaad, and A. J. Kresge, *J. Amer. Chem. Soc.*, **80**, 5313 (1958).

[16] N. I. Shuikin, B. L. Lebedev, and V. G. Nikol'skii, *Neftekhimiya*, **6**, 544 (1966).

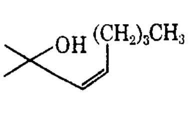
[17] J. K. Hoffman, U. S. Patent 3,304,247 (Cl. 204-158) (Feb 14, 1967) to Cumberland Chemical Corp.

[18] N. F. Cywinski and H. J. Hepp, *J. Org. Chem.*, **30**, 3814 (1965).

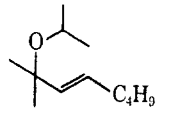
[19] J. I. G. Cadogan, D. H. Hey, and S. H. Ong, *J. Chem. Soc.*, 1939 (1965).



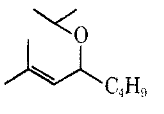
16



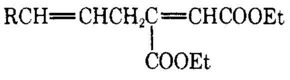
17



18



19



$RCH{=}CHCH_2\underset{\displaystyle COOEt}{C}{=}CHCOOEt$

20

The nmr spectrum was also in agreement with the presence of these two products. Cleavage of the ethers under acidic conditions in the presence of 3,5-dinitrobenzoyl chloride[20] gave only isopropyl 3,5-dinitrobenzoate.

Hydrogenolysis of the ether mixture over a palladium catalyst produced 2-propanol and 2-methyloctane which were identified by gas chromatographic analysis and infrared spectroscopy.

Photoexcitation of conjugated diynes is implied by their photoreduction to enynes in solvents capable of donating hydrogen atoms, but here again the exact nature of the excited state is unknown.[21] Finally we note that merely heating a conjugated acetylene in a suitable solvent can promote addition of a solvent molecule to the triple bond. Thus terminal olefins $RCH_2CH{=}CH_2$ have been added to acetylene dicarboxylic ester to give adducts such as **20**,[22] and 2-propanol has been added to propiolic ester to give **11**.[23]

Experimental Section[24]

Reagents.—Ethyl propiolate was prepared according to the method of Perkin and Simonsen[25] from propiolic acid, which was in turn prepared from propargyl alcohol according to the procedure given by Wolf.[26] It had bp 122° [lit.[25] 119° (745 mm)] and its infrared spectrum (CCl_4) showed bands at 3340, 2120, 1715 and 1225 cm^{-1}. The cyclohexane was Baker reagent grade and was used without further purification as was the Merck reagent grade 2-propanol. Absolute ethanol was used directly. 1-Hexyne was prepared from acetylene and 1-bromobutane as described by Vogel.[27] It boiled at 72° (lit.[27] bp 72°) and showed infrared absorptions at 3300 and 2105 cm^{-1} (CCl_4).

General Procedure and Apparatus.—Solutions (2–5%) of the acetylenic compound in the chosen solvent were irradiated for priods of time ranging from 2 days to 2 weeks in a 500-ml Kjeldahl flask modified with a side arm to which was attached a reflux condenser. For the irradiation, a quartz-contained mercury arc[28] was placed in the main neck of the flask and immersed in the solution which was stirred rapidly with a magnetic stirrer and kept under a slight positive pressure of nitrogen. The flask was immersed in a bath of continuously flowing tap water.

Irradiation of Ethyl Propiolate in Cyclohexane.—A solution of ethyl propiolate (10.0 g, 0.102 mol) in cyclohexane (470 ml) was irradiated for 14 days at an average bath temperature of 27°. The cyclohexane was removed by distillation at atmospheric pressure and the residue was distilled through a spinning-band column to yield 2.93 g of a mixture of **2**, **3**, and **4**, bp 115–132° (20 mm). These products were separated for characterization by gas chromatography. Compound **2** was identical in all respects with ethyl β-cyclohexyl-*trans*-acrylate which was synthesized from chlorocyclohexane.[3,4] Substances **3** and **4** were shown to be ethyl β-cyclohexyl-*cis*-acrylate and ethyl β-cyclohexylidenepropionate, respectively, as described in the text.

Irradiation of Ethyl Propiolate in Ethanol—A solution of ethyl propiolate (19.9 g, 0.203 mol) in absolute ethanol (465 ml) was irradiated for 3 days at an average bath temperature of 12°. The ethanol was removed by distillation at 100-mm pressure, and the residue distilled rapidly at 10-mm pressure to yield 8.1 g of a colorless liquid boiling between 83 and 107°. Gas chromatographic analysis showed that this distillate contained 38% **6**, 25% **7**, and 37% **8**. Careful fractionation through a spinning-band column at 11-mm pressure yielded two main fractions. The first, bp 83–86°, was a mixture of **6** and **7** which was separated by gas chromatography for characterization, while the second, bp 120°, was pure **8**. Lactone **6** was identical in all respects with β-angelica lactone which was synthesized from levulinic acid in two steps.[6,7] Compound **7** was identified as ethyl levulinate. The deduction of the structure of **8** from spectral evidence is described in the text.

Oxidation of Hydroxy Ester 8.—A solution of the hydroxy ester (0.22 g, 1.5 mmol) in chloroform (80 ml) was stirred at room temperature for 40 hr with activated manganese dioxide (4.0 g, 46 mmol). The mixture was filtered and the residue washed thoroughly with ether. The combined filtrate and washings were evaporated under reduced pressure to a yellow oil (0.19 g) which, according to gas chromatographic analyses, was a single compound. Structure **9** was consistent with the infrared spectrum which showed bands at 1725, 1705, 1695, 1645, 1365, 1300, 1260, 1185, 1160, and 983 cm^{-1}. A portion was converted, without further purification, into the semicarbazone, mp 203–205° (lit.[29] mp 205–206°), and a portion to the phenylhydrazone, mp 118–120° (lit.[29] mp 117.5°).

Irradiation of Ethyl Propiolate in 2-Propanol.—A solution of ethyl propiolate (20.8 g, 0.212 mol) in 2-propanol (460 ml) was irradiated for 3 days at an average bath temperature of 12°. The 2-propanol was removed by distillation at 100-mm pressure and the residue was distilled rapidly at 7-mm pressure, yielding 16.7 g of a colorless liquid boiling at 73–104°. Careful fractionation of this liquid through a spinning-band column yielded 6.8 g of pure **10**, bp 81–82° (9 mm) [lit.[8] bp 80° (10 mm)] and 7.0 g of pure **11**, bp 115–116° (9 mm). Identification of these compounds from spectral evidence is described in the text.

Irradiation of Ethyl β-Cyclohexyl-*trans*-acrylate.—A solution of ethyl β-cyclohexyl-*trans*-acrylate (**2**, 3.11 g, 17 mmol) and triethylamine (0.05 g) in cyclohexane (475 ml) was irradiated under the usual conditions for 24 hr. As the reaction proceeded, 0.1-ml aliquots were removed and evaporated under reduced pressure. The residue was then analyzed by gas chromatography with the results given in Table I. Ester **3** was identified only by its gas chromatographic retention time. After 24 hr a 50-ml aliquot was taken and the residue, obtained as above (0.19 g), distilled. The distillate was identical by the usual physical criteria with ethyl β-cyclohexylidenepropionate (**4**).

TABLE I

	Relative percentages		
Time, hr	Ester 2	Ester 3	Ester 4
0	100	0	0
1.75	70	30	Trace
3.5	45	43	12
5.25	40	35	25
7.0	34	32	34
10.0	23	26	51
24.0	0	0	100

Peroxide-Initiated Reaction between Ethyl Propiolate and

---

[20] H. W. Underwood, O. L. Baril, and G. C. Toone, *J. Amer. Chem. Soc.*, **52**, 4087 (1930).

[21] D. A. Ben-Efraim, *Tetrahedron Lett.*, 957 (1957).

[22] K. Alder and H. Von Brachel, *Ann.*, **651**, 141 (1962).

[23] E. Winterfeldt and H. Preuss, *Chem. Ber.*, **99**, 450 (1966).

[24] All temperature measurements are uncorrected. The infrared spectra were determined on a Perkin-Elmer Infracord spectrophotometer. Ultraviolet spectra were measured on a Cary automatic recording spectrophotometer in ethanol solutions. Nuclear magnetic resonance spectra were determined as carbon tetrachloride solutions on a Varian A-60 spectrometer. Microanalyses were by Dr. S. M. Nagy and his associates at MIT. Gas chromatographic analyses were performed on a 15% silicone grease on Chromosorb P column at column temperatures of 150–180° except in the case of the 1-hexyne reaction where a 15% GE XF-1150 on Chromosorb P column was used at temperatures of 55–150°.

[25] W. H. Perkin, Jr., and J. L. Simonsen, *J. Chem. Soc.*, 816 (1907).

[26] V. Wolf, *Ber.*, **86**, 735 (1953).

[27] A. I. Vogel, "Practical Organic Chemistry," Longmans, Green and Co., London, 1959, p 897.

[28] Labortauchelampe S81, Hanovia Lamp Division, Engelhard Hanovia, Inc., Newark, N. J.

[29] I. Heilbron and H. M. Bunbury, "Dictionary of Organic Compounds," Vol. I, Oxford University Press, London, 1943, p 7.

Cyclohexane.—A solution of ethyl propiolate (2.10 g, 20.5 mmol) and recrystallized dibenzoyl peroxide (485 mg, 2.0 mmol) in cyclohexane (30 ml) was refluxed under a slight positive pressure of nitrogen for 24 hr in a glass apparatus which had been dried under nitrogen at 110° prior to use. At the end of this time the solution gave a negative test for peroxides. The cyclohexane and ethyl propiolate were removed by evaporation at reduced pressure and left a residue (705 mg) which comprised 55% **2** and 45% **3** according to gas chromatographic analysis.

A reaction run under the same conditions containing only 0.1 mmol of peroxide for 12 hr gave less than 1% yield of products. A blank reaction, with no peroxide, gave no products.

Irradiation of 1-Hexyne in 2-Propanol.—A solution of 1-hexyne (20.8 g, 0.254 mol) in 2-propanol (460 ml) was irradiated for 3 days at an average bath temperature of 14°. The unreacted starting materials were removed by distillation at 100-mm pressure and the residue was distilled at 30-mm pressure to yield 5.9 g of a colorless liquid boiling at 80–85°. Gas chromatographic analysis of the product showed four components in a ratio 17:27:35:21, later identified as **18**, **19**, **16**, and **17**, respectively. The original distillate was redistilled at atmospheric pressure and yielded 13.3 g of 1-hexyne. Compounds **18** and **19** were readily separated from **16** and **17** by gas chromatography. Compounds **18** and **19** were, however, inseparable and were investigated as a mixture. Alcohol **16** was obtained pure by gas chromatography but the best separation left **17** containing approximately 10% **16**.

Alcohol **16** had a gas chromatographic retention time and an infrared spectrum identical with those of 2-hydroxy-2-methyl-*trans*-3-octene[30] which was prepared from 2-hydroxy-2-methyl-3-octyne[31] in a single step. Compound **17** had a gas chromatographic retention time and an infrared spectrum identical with those of 2-hydroxy-2-methyl-*cis*-3-octene, prepared by hydrogenation of the corresponding alkyne[31] over a Lindlar catalyst.

The mixture of ethers **18** and **19** had infrared absorption maxima at 1670, 1455, 1445 (shoulder), 1370, 1355, 1160 (shoulder), 1150, 1120, 1095, 1035, 1010, 990, 975, 950, 880 and 850 cm^{-1}. The nmr spectrum of the mixture was analyzed carefully considering the relative percentages of the two compounds present, and was fully assignable on this basis.

Cleavage of Ethers 18 and 19.—Following the procedure of Underwood, *et al.*,[20] a 3,5-dinitrobenzoate was isolated which had mp 121.5–122.5° and a mixture melting point with an authentic sample of the 3,5-dinitrobenzoate of 2-propanol of 121–122.5°.

Hydrogenolysis of Ethers 18 and 19.—A solution of the mixture of ethers (0.51 g, 2.8 mmol) in ether (25 ml) was hydrogenated over Pd-C catalyst (50 mg) at 0° and atmospheric pressure. When hydrogen uptake was complete (35 min) the solution was filtered free of catalyst and concentrated to a volume of *ca.* 2 ml by careful distillation. Gas chromatogaphic analysis indicated the presence of two products with retention times corresponding to those of 2-propanol and 2-methyloctane. The latter (0.16 g) was isolated by gas chromatography and shown to be identical with an authentic sample prepared from 2-hydroxy-2-methyl-3-octene[31] by dehydration and hydrogenation.

Registry No.—**1**, 623-47-2; **2**, 17343-88-3; **3**, 18521-02-3; **4**, 18559-89-2; **6**, 591-11-7; **7**, 539-88-8; **8**, 10150-92-2; **9**, 10150-93-3; **11**, 18521-05-6; **16**, 18521-06-7; **17**, 18521-07-8; **18**, 18521-08-9; **19**, 18542-61-5.

Acknowledgments.—The authors are indebted to the National Institutes of Health for financial support and to Dr. I. D. Rae for his help with the preparation of the manuscript.

---

[30] K. N. Campbell and L. T. Eby, *J. Amer. Chem. Soc.*, **63**, 216 (1941).

[31] K. N. Campbell, B. K. Campbell, and L. T. Eby, *ibid.*, **60**, 2882 (1938).

Cycloadditions. XXIII. The Mercury-Sensitized Gas Phase Photodecarbonylation of 3,3-Dideuterio- and *exo*- and *endo*-3-Deuterionorcamphor[1,2]

John E. Baldwin[3] and James E. Gano[4]

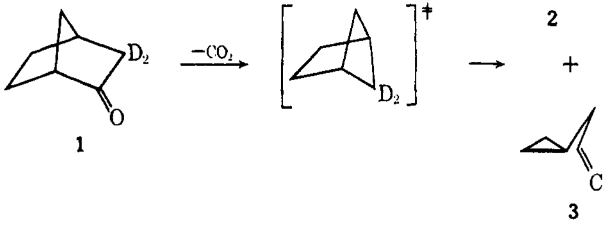
Department of Chemistry and Chemical Engineering, University of Illinois, Urbana, Illinois 61801

Received July 2, 1968

The mercury-sensitized gas phase photodecarbonylation of 3,3-dideuterionorcamphor gave 1,1- and 3,3-dideuteriohexa-1,5-diene in a 90:10 ratio; (3,3-dideuterioallyl)- and (1,1-dideuterioallyl)cyclopropane and allyldideuteriocyclopropane in a 45:45:10 ratio; and 5,5-dideuterio- and 2,2-dideuteriobicyclo[2.1.1]hexane in a 93:7 ratio. Photodecarbonylation of *exo*- and *endo*-3-deuterionorcamphor gave quantitatively analogous data; equal portions of *exo*- and *endo*-5-deuteriobicyclo[2.1.1]hexane and the same ratio of *cis*- and *trans*-1-deuteriohexa-1,5-diene were formed from either labeled ketone. These results are interpreted in terms of the known kinetics of the decarbonylation, diradical intermediates as precursors of the hydrocarbon products, and a Cope rearrangement that competes with collisional deactivation of the 1,5-hexadiene produced through the decarbonylation process.

The mercury-sensitized gas phase photolysis of 3,3-dideuterionorcamphor (**1**) has been reported[5] to give a 1:1 mixture of (3,3-dideuterioallyl)cyclopropane (**3**) and (1,1-dideuterioallyl)cyclopropane (**2**) (Scheme I). This result was taken as necessitating a symmetrical intermediate and was rationalized by postulating the production of allylcyclopropane through decomposition of a vibrationally excited, photochemically generated bicyclo[2.1.1]hexane. The other hydrocarbons reported were 1,1-dideuteriohexa-1,5-diene and 5,5-dideuteriobicyclo[2.1.1]hexane.[5]

Scheme I



---

[1] Papers XXI and XXII in this series: J. A. Kapecki and J. E. Baldwin, *J. Amer. Chem. Soc.*, **91**, 1120 (1969); J. E. Baldwin and S. Y. Hong, *J. Heterocycl. Chem.*, **5**, 565 (1968).

[2] Supported in part by National Science Foundation, Grant GP-5226, and a Du Pont Grant-in-Aid to the Department of Chemistry and Chemical Engineering of the University of Illinois.

[3] Alfred P. Sloan Research Fellow. To whom inquiries should be addressed: Department of Chemistry, University of Oregon, Eugene, Ore. 97403.

[4] Eli Lilly and Co. Fellow, 1964–1965; Allied Chemical Fellow, 1965–1966; Standard Oil of California Fellow, 1966–1967.

[5] R. Srinivasan, *J. Amer. Chem. Soc.*, **83**, 4923 (1961).