Irradiation of Benzaldehyde in 1-Hexyne[1,2]

Jerald S. Bradshaw,* Ronald D. Knudsen, and Wesley W. Parish

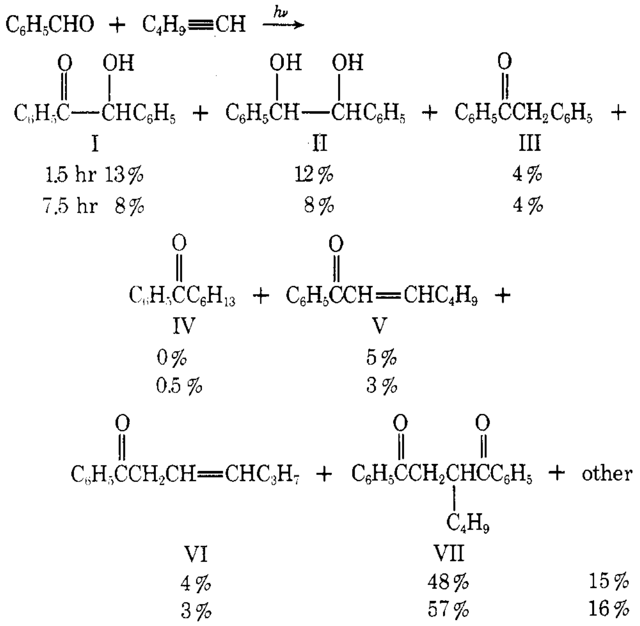
Chemistry Department, Brigham Young University, Provo, Utah 84602

Received June 27, 1974

The photoreactions of benzaldehyde have been reported extensively. Some of these include photooxidations,[3] photoreductions,[4] cycloadditions to form oxetanes[5] and suspected oxetene intermediates,[6] and mechanistic studies using chemically induced dynamic nuclear polarization (CIDNP) techniques.[7] We wish to report on the products of the ultraviolet irradiation of benzaldehyde and 1-hexyne.

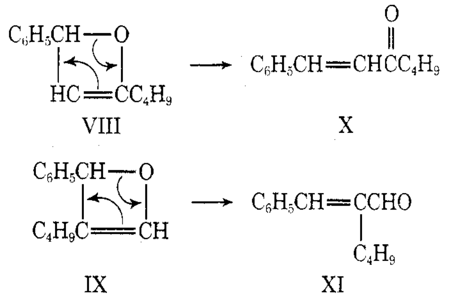
Mixtures of 1-hexyne and benzaldehyde were irradiated through Pyrex under a nitrogen atmosphere. The reaction mixture was separated by vapor phase chromatography (vpc) and the products (Scheme I) were analyzed by comparisons with authentic samples some of which were prepared in our laboratory. Products V and VI were both isolated in the course of preparing V. The structures are consistent with their nmr spectra. The aliphatic portion of the nmr spectrum for V is the same as that for 1-hexene while the aliphatic portion of the nmr spectrum for VI is the same as that for 1-pentene. We believe that compound V has the trans form because the infrared spectrum has two carbonyl bands.[8] Six per cent of the benzaldehyde was converted in 1.5 hr and 17% in 7.5 hr. The listed yields are based on the actual conversion of the benzaldehyde.

Scheme I



Products I, II, and III were formed from benzaldehyde-benzaldehyde reactions as previously reported.[2] As shown by the products, radical addition to 1-hexyne to form IV–VII dominates, but radical pair formation[7a] and hydrogen abstraction[4] mechanisms are also in evidence. We believe that benzoyl radicals formed by hydrogen abstraction from benzaldehyde add to the first carbon of 1-hexyne as has been observed for the addition of free radicals to 1-alkynes.[9] The resulting hexenyl radical ($C_6H_5C(=O)$-$CH{=}\dot{C}C_4H_9$) would abstract a hydrogen from another benzaldehyde or from a 1-hexyne molecule to form 2-heptenophenone (V). This reaction is similar to that reported by Wiley and Harrell for the cobalt-60 induced addition of various aldehydes to the esters of maleic and acetylenedicarboxylic acids.[10] Product IV is formed by a photochemical reduction of V. Indeed, irradiation of V gave IV probably in a similar manner as that reported by Griffin and O'Connell for the reduction of *cis*-dibenzoylethylene.[11] Product VII is formed by further addition of benzaldehyde to V as shown by the fact that irradiation of V in benzaldehyde gave a high yield of VII in a very short period of time. It is instructive to note that product VII was the major product of the overall reaction. This is probably a result of the high reactivity of V toward radical reactions. The second benzoyl radical added to the second carbon of the original 1-hexyne, giving the more stable radical α to the benzoyl group. This reaction has possible value as a preparative method for γ-diketones although we made no attempt to study the preparative aspects.[12] Product VI probably resulted from a simple photochemical isomerization of V as first shown by Yang and Jorgenson.[13] In our case, mixtures of V and VI, when irradiated, gave products which contained 95% or more of compound VI.

We do not believe that the addition of benzaldehyde to 1-hexyne involves the cycloaddition of triplet state benzaldehyde to the unsaturated system to form an oxetene as reported by Buchi and coworkers.[6] They obtained 6-benzylidene-5-decanone when benzaldehyde was irradiated in 5-decyne. They proposed an oxetene intermediate which opened to give the observed product.[6] In our reaction of benzaldehyde with 1-hexyne, two different oxetene intermediates (VIII and IX) would be possible. Ring opening of these intermediates would lead to 1-phenyl-1-hepten-3-one (X) and α-*n*-butylcinnamaldehyde (XI). Neither X nor XI was found in our reaction indicating that an oxetene intermediate is not involved.



Experimental Section

Materials and Apparatus. Spectra were obtained as follows: ir, Perkin-Elmer Model 457 spectrophotometer; nmr, Varian A60-A; uv, Cary Model 15 spectrophotometer; mass spectra, Varian MAT-111 gc–ms system using a 4 ft × ⅛ in. column packed with 3% SE-30 on Chromosorb W. A Varian Aerograph 202-B temperature programming vapor phase chromotograph (vpc) was used to analyze and separate all reaction mixtures. Accurate analytic analyses were carried out using a 4 ft × 0.25 in. stainless steel column packed with 4% Carbowax 20M on Chromosorb G/AW, 80–100 mesh. Quantitative yields were obtained by calibrating the columns with a mixture of weighed amounts of the compounds to be analyzed.[14] A Hanovia 450-W medium-pressure lamp was used for all irradiations. Benzaldehyde (J. T. Baker) and 1-hexyne (Chemical Samples Co.) were distilled prior to use.

Preparation of 2-Heptenophenone (V).[15] Phenacyltriphenylphosphonium bromide (0.65 g, 14.1 mmol), prepared from triphenylphosphine and 2-bromoacetophenone, was dissolved in 25 ml of ethanol containing about 0.1 g of potassium hydroxide. To this solution was added 0.23 g (2.68 mmol) of pentanal in 25 ml of tetrahydrofuran. This mixture was refluxed for 25 hr and evaporated leaving a yellow liquid and a white solid. The liquid was separated on the vpc to give compounds V (65%) and VI (35%). Compound V exhibited the following spectra: nmr δ 7.85 (m, 2), 7.40 (m, 3), 6.80 (m, 2), 2.20 (m, 2), 1.40 (m, 4), 0.95 (m, 3); uv λ_{max} (ethanol) 258 nm (ϵ 18,000); ir 1673 and 1625 cm^{-1}. Compound VI exhibited the following spectra: nmr δ 7.85 (m, 2), 7.40 (m, 3), 5.55 (m, 2), 3.60

(m, 2), 2.0 (m, 2), 1.40 (m, 2), 0.90 (m, 3); uv λ_{max} (ethanol) 244 nm (ϵ 9700); ir 1690 cm^{-1}.

Anal. (for a mixed V and VI sample). Calcd for $C_{13}H_{16}O$: C, 82.93; H, 8.57. Found: C, 82.78; H, 8.67.

Irradiation of Benzaldehyde and 1-Hexyne. A solution of 8.09 g (75 mmol) of benzaldehyde and 3.1 g (38 mmol) of 1-hexyne was placed in a Pyrex tube and purged with nitrogen for 10 min. The tube was then stoppered and irradiated at a distance of 8 in. from the light source. Aliquots were removed from the irradiated mixture at various times and analyzed by vpc. The results for 1.5 and 7.5 hr are listed in Scheme I. The vpc fractions (at 7.5 hr) were collected and the structures determined as follows. Fraction 1 proved to be 1-hexyne. Fraction 2 was benzaldehyde (83% recovered). Fraction 3 (0.5%) exhibited an ir spectrum identical with that of authentic heptanophenone (IV) (Pfaltz-Bauer Inc.). Fraction 4 (3%) exhibited ir and mass spectra identical with that of an authentic sample of 3-heptenophenone (VI). Fraction 5 (3%) exhibited ir and mass spectra identical with that of an authentic sample of 2-heptenophenone (V). Fraction 6 (4%) exhibited an ir spectrum identical with that of deoxybenzoin (III) prepared by the method of Allen and Barker.[16] Fraction 7 (8%) showed ir spectrum identical with that of an authentic sample of benzoin (I) (Heyden Chemical Co.). Fraction 8 (8%) exhibited an ir spectrum identical with that of hydrobenzoin (II) (Sadtler spectrum no. 37,405). Fraction 9 (57%) showed ir, nmr, and mass spectra identical with that of 2-*n*-butyl-1,4-diphenyl-1,4-butanedione (VI) prepared by the procedure of Sawa and coworkers.[17]

Other fractions were observed but could not be isolated in a large enough yield to characterize.

Irradiation of a Mixture of V and VI in Benzaldehyde. A mixture of V and VI (0.069, 0.32 mmol) and 10 g of benzaldehyde was irradiated as above to yield VII (67%) along with compounds I, II, and III. Compound VI was recovered.

Irradiation of V and VI Mixtures in Benzene. In two experiments a mixture of 78% VI and 22% V and a mixture of 89% V and 11% VI were irradiated in benzene through a 310–410-nm filter. Both irradiations resulted in a mixture greater than 95% VI and 5% V. Small amounts of compound IV were also formed in these reactions.

Acknowledgment. The authors wish to thank the Research Division, Brigham Young University, and Mr. Paul Parish for their generous financial support and Dr. Richard T. Hawkins for his many helpful discussions. R. D. Knudsen expresses thanks to the graduate school, Brigham Young University, for a graduate internship for 1971–1972.

Registry No.—V, 5595-63-1; VI, 53403-90-0; benzaldehyde, 100-52-7; 1-hexyne, 693-02-7; phenacyltriphenylphosphonium bromide, 6048-29-9; pentanal, 110-62-3.

References and Notes

(1) Presented at the 167th National Meeting of the American Chemical Society, Los Angeles, Calif., April, 1974.

(2) For a preliminary communication of part of this work see J. S. Bradshaw, R. D. Knudsen, and W. W. Parish, *J. Chem. Soc., Chem. Commun.*, 1321 (1972).

(3) See H. L. J. Backstrom and U. Runer, *Acta Chem. Scand.*, **20,** 630 (1966).

(4) (a) J. H. Stocker and D. H. Kern, *J. Org. Chem.*, **33,** 291 (1968); (b) T. Matsuura and Y. Kitaura, *Bull. Chem. Soc., Jap.*, **41,** 2483 (1968).

(5) (a) D. R. Arnold, R. L. Hinmon, and A. H. Glick, *Tetrahedron Lett.*, 1425 (1964); (b) N. C. Yang, J. I. Cohen, and A. Shani, *J. Amer. Chem. Soc.*, **90,** 3264 (1968); (c) J. S. Bradshaw, *J. Org. Chem.*, **31,** 237 (1966).

(6) G. Buchi, J. T. Kofron, E. Koller, and D. Rosenthal, *J. Amer. Chem. Soc.*, **78,** 876 (1956).

(7) (a) M. Cocivera and M. Trozzolo, *J. Amer. Chem. Soc.*, **92,** 1772 (1970); (b) G. L. Closs and D. R. Paulsen, *ibid.*, **92,** 7229 (1970).

(8) See R. M. Silverstein and G. C. Bassler, "Spectrometric Identification of Organic Compounds," Wiley, New York, N.Y., 1968, p 87.

(9) (a) R. M. Kpochik and J. A. Kampmeier, *J. Amer. Chem. Soc.*, **90,** 6773 (1968); Y. Amiel, *Tetrahedron Lett.*, 661 (1971).

(10) R. H. Wiley and J. R. Harrell, *J. Org. Chem.*, **25,** 903 (1960).

(11) G. W. Griffin and E. J. O'Connell, *J. Amer. Chem. Soc.*, **84,** 4148 (1962).

(12) A similar reaction has been reported for acetaldehyde; V. H. H. Schulbach, V. Frouzen, and E. Duhl, *Justus Liebigs Ann. Chem.*, **587,** 124 (1954).

(13) N. C. Yang and M. J. Jorgenson, *Tetrahedron Lett.*, 1203 (1964).

(14) F. D. Lewis and J. G. Mahyar, *J. Org. Chem.*, **37,** 2101 (1972).

(15) The method was taken from that of C. F. Hauser, T. W. Brooks, M. S. Miles, M. A. Raymond, and G. B. Butler, *J. Org. Chem.*, **28,** 372 (1963).

(16) C. H. F. Allen and W. E. Barker, "Organic Syntheses," Collect. Vol. II, Wiley, New York, N.Y., 1967, p 156.

(17) Y. Sawa, I. Hashimoto, M. Ryaug, and S. Tstusumi, *J. Org. Chem.*, **33,** 2159 (1968).

Reaction of 2-Butynal Diethyl Acetal with Lithium Aluminum Hydride

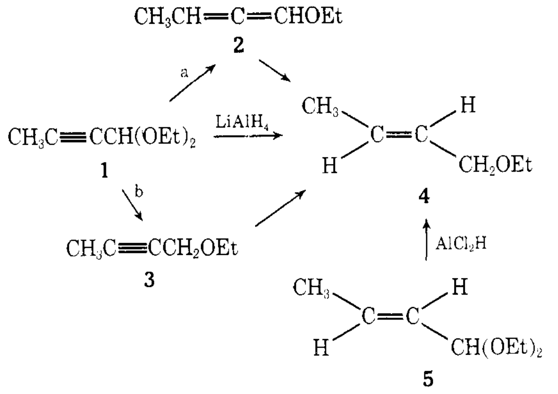
Walter W. Zajac, Jr.* and Kevin J. Byrne[1]

Department of Chemistry, Villanova University,
Villanova, Pennsylvania 19085

Received August 12, 1974

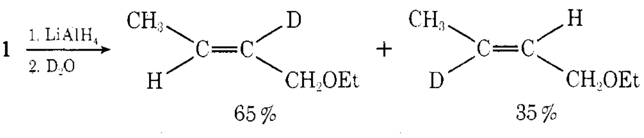
The hydrogenolysis of cyclic and acyclic acetals and ketals to the corresponding ethers can be effected by alane,[2] chloroalane,[2] dichloroalane,[2] alkoxyalanes,[3] and alkoxychloroalanes.[3] Hydrogenolysis of acetals or ketals by lithium aluminum hydride (LAH) is rare. However certain allylic acetals can be reductively rearranged to vinyl ethers by $LiAlH_4$ alone. For example, hex-2-enopyranosides led to 3-deoxyglycals[4] and certain vinyl-substituted 2-vinyl-1,3-dioxolanes led to 1-propenyl 2-hydroxyethyl ethers.[5] In the light of these results and because of our continuing interest[3,6] in the hydrogenolysis of acetals and ketals, we chose to study the reactions of an acetylenic acetal, 2-butynal diethyl acetal **1**. If hydrogenolysis by LAH alone were analogous to the allylic acetal reaction, then C–O bond cleavage of the acetylenic acetal with bond migration would yield an allenic ether[7] **2** (Scheme I, path *a*). Otherwise C–O bond cleavage without bond migration would simply lead to the acetylenic ether **3** (Scheme I, path *b*).

Scheme I



In this work the reaction of **1** with LAH led to *trans*-crotyl ethyl ether **4**. To determine if the observed product resulted from reduction of allenic ether **2**, reduction of **1** with LAH was repeated and the reaction quenched with D_2O (Scheme II). There was found a 65% deuterium incorporation at C-2 and 35% at C-3.[8] For the allenic ether to be an intermediate 100% of the hydrogen at C-3 must come from LAH. When the reduction of **1** was repeated using $LiAlD_4$ followed by quenching with H_2O, the crotyl ethyl ether **4** was found to have 65% deuterium at C-3, 35% at C-2, and 100% at C-1[8] (Scheme III). For the allenic ether to be an intermediate, there would have to be 100% incorporation of deuterium at C-3 and C-1.

Scheme II



2-Butynyl ethyl ether **3** was ruled out as a possible intermediate by allowing it to react with LAH in refluxing ether for 48 hr. While **3** gave crotyl ethyl ether **4** in 65% yield, 35% of **3** remained unreacted. On the contrary no trace of