(m, 2), 2.0 (m, 2), 1.40 (m, 2), 0.90 (m, 3); uv $\lambda_{max}$ (ethanol) 244 nm ($\epsilon$ 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

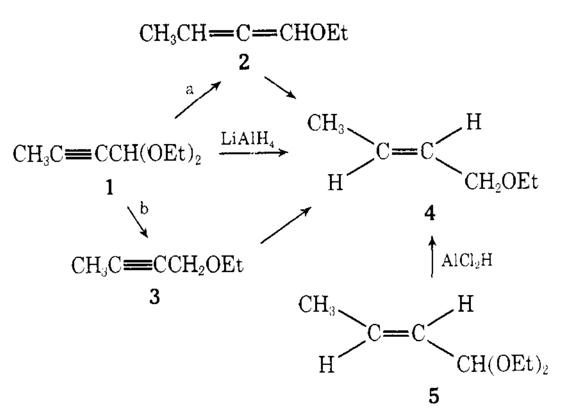
Walter W. Zajac, Jr.* and Kevin J. Byrne[1]

*Department of Chemistry, Villanova University, Villanova, Pennsylvania 19085*

*Received August 12, 1974*

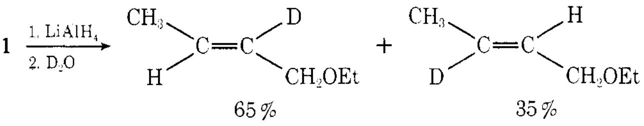
The hydrogenolysis of cyclic and acyclic acetals and ketals to the corresponding ethers can be effected by alane,[2] chloroalane,[2] dichloroalane,[2] alkoxyalanes,[3] and alkoxychloroalanes.[3] Hydrogenolysis of acetals or ketals by lithium aluminum hydride (LAH) is rare. However certain allylic acetals 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**



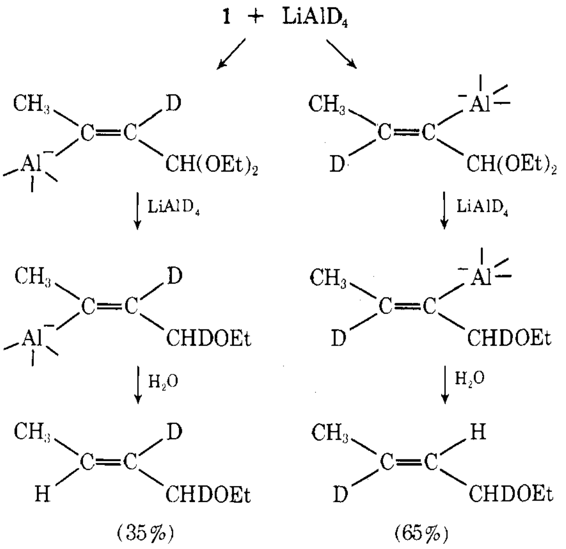
In this work the reaction of **1** with LAH led to *trans*-crotyl ethyl ether **4**. To determine if the observed product resulted from reduction of allenic ether **2**, reduction of **1** with LAH was repeated and the reaction quenched with $D_2O$ (Scheme II). There was found a 65% deuterium incorporation 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

**Scheme III**



2-butynyl ethyl ether was found from the reaction of 1 with LAH after 24 hr. Therefore it appears that 2-butynyl ethyl ether **3** is too unreactive to be considered an intermediate in the reaction of 1 with LAH.

Based upon the results from the above experiments, the formation of the observed product *trans*-crotyl ethyl ether 4 from the reaction of 2-butynal diethyl acetal 1 with LAH can be explained by a pathway involving the nonregiospecific addition of LAH or LAD to the triple bond followed by hydrogenolysis of the acetal linkage (see Scheme III).

A number of the other experiments were also carried out. 2-Butynal diethyl acetal 1 was smoothly hydrogenolyzed by dichloroalane in ether to 2-butynyl ethyl ether **3**.

*trans*-Crotyl ethyl ether **4** can be obtained by the dichloroalane hydrogenolysis of *trans*-crotonaldehyde diethyl acetal **5** and is identical with the product of the LAH reduction of 2-butynal diethyl acetal **1**.

It was also determined that crotonaldehyde diethyl acetal **5** is 8 times more reactive than 2-butynal diethyl acetal **1**. Since the carbon–carbon double bond can stabilize a positive charge better than the carbon–carbon triple bond, the preceding result is consistent with the accepted mechanism of acetal hydrogenolysis which predicts the acetal producing the more stable carbonium ion to be more reactive, other factors, such as steric, being the same.[6]

## Experimental Section

An F&M Model 700 gas chromatograph was used for glpc analyses. Nmr spectra were obtained with a Varian A-60 spectrometer on $CDCl_3$ solutions with TMS as an internal standard.

2-Butynal diethyl acetal 1 and 2-butynyl ethyl ether 3 were obtained from Farchan Laboratories, Willoughby, Ohio.

*Trans*-Crotonaldehyde diethyl acetal[9] 5 was prepared from *trans*-cortonaldehyde and triethyl orthoformate by a method previously described.[6]

*trans*-Crotyl ethyl ether[10] 4 was prepared by the dichloralane hydrogenolysis of *trans*-crotonaldehyde diethyl acetal by a method previously described.[5]

Competitive hydrogenolyses of 1 and 5 with alane were carried out according to the procedure of Davis and Brown.[5]

**Reaction of 2-Butynal Diethyl Acetal 1 with $LiAlH_4$.** This reaction was carried out by the procedure of Davis and Brown.[5] The reaction was repeated using $LiAlH_4$ but quenched with $D_2O$. The reaction was also carried out with $LiAlD_4$ and quenched with $H_2O$. In each there was obtained an 83% yield of *trans*-cortyl ethyl ether 4 and 12% of starting material. In each case the crotyl ethyl ether was subjected to nmr analysis in the following manner. In a glove bag with a nitrogen atmosphere, 63 mg of $Eu(fod)_3$ was weighed into an nmr tube and dissolved in 30 $\mu$l of $CDCl_3$. The glpc-purified crotyl ethyl ether was added to the nmr tube and the spectra were run. From the initial amount of 30 $\mu$l, the amount of crotyl ethyl ether was successively increased to 40, 50, 60, and finally 85 $\mu$l. The nmr spectra were run and analyzed as described.[8]

**Registry No.**—1, 2806-97-5; 4, 1476-06-8; $LiAlH_4$, 16853,85-3.

## References and Notes

(1) Taken from the Ph.D. thesis of K. J. Byrne, Villanova University, May 1973.

(2) M. N. Rerick, "Reduction," R. L. Augustine, Ed., Marcel Dekker, New York, N.Y. 1968, pp 46–50.

(3) W. W. Zajac, Jr. and K. J. Byrne, *J. Org. Chem.*, **38**, 384 (1973).

(4) S. Y-K. Tam and B. Fraser-Reid, *Tetrahedron Lett.*, 4897 (1973); B. Fraser-Reid and B. Radatus, *J. Amer. Chem. Soc.*, **92**, 6661 (1970); B. Radatus, M. Yunker, and B. Fraser-Reid, *ibid.*, **93**, 3086 (1971); B. Fraser-Reid and B. Radatus, **93**, 6342 (1971); I. Achmatowicz and B. Szechner, *Tetrahedron Lett.*, 1205 (1972).

(5) H. A. Davis and R. K. Brown, *Can. J. Chem.*, **49**, 2563 (1971).

(6) W. W. Zajac, Jr., and K. J. Byrne, *J. Org. Chem.* **35**, 3375 (1970); **37**, 521 (1972).

(7) The intermediacy of an allenic ether has been postulated in the production of *cis*-allylic ethers *via* the hydroboration of acetylenic acetals with disiamylborane followed by protonolysis of the resulting organoborane: G. Zweifel, A. Horng, and J. E. Plamondon, *J. Amer. Chem. Soc.*, **96**, 316 (1974).

(8) The analysis was carried out by nmr. Integration of the nmr spectra of the product **4** shows the multiplet at $\delta$ 5.64 due to the vinyl protons decreasing from 2 to 1. Addition of the shift reagent $Eu(fod)_3$ shifts the C-2 hydrogen downfield relative to the C-3 hydrogen. Integration of the shifted spectra gives the relative proportion of incorporation at C-2 and C-3.

(9) J. A. Van Allen, "Organic Syntheses," Collect. Vol. IV, Wiley, New York, N.Y., 1963.

(10) H. C. Brown and R. M. Gallivan, *J. Amer. Chem. Soc.*, **90**, 2906 (1968).

---

# Reduction of Quaternary Ammonium Salts with Lithium Triethylborohydride. A Convenient Method for the Demethylation of Substituted Trimethylammonium Salts

Manning P. Cooke, Jr.*, and Robert M. Parlman

*Department of Chemistry, Washington State University, Pullman, Washington 99163*

*Received July 27, 1973*

Lithium triethylborohydride has recently been reported to be a source of remarkably nucleophilic hydride ion as demonstrated by its ability to rapidly reduce organic halides susceptable to $S_N2$ displacement.[1] In light of the apparent high nucleophilicity of this reagent it seemed that lithium triethylborohydride might serve as a source of hydride ion for the displacement of groups which are much poorer leaving groups than halide ions. We now wish to report that this reagent readily effects the displacement of tertiary amines from quaternary ammonium iodides in THF.[2] Results are shown in Table I.

As can be seen from the results in Table I, aromatic trialkylammonium iodides readily react with lithium triethylborohydride at room temperature to give the tertiary amine resulting from the displacement on an alkyl group by hydride ion. It is also evident that displacement occurs predominately on a methyl group in salts containing at least two methyl groups while an appreciable amount of deethylation is observed with phenyldiethylmethylammonium iodide which contains but one methyl group. The surprising increase in deethylation in this case may be due to an increased steric hindrance to the attack on the remaining methyl group.

It is worthy of note that while the above mentioned salts are readily demethylated at 25°, these displacements are considerably slower than those involving the displacement of halide ion. Under conditions in which *n*-octyl bromide is said to be completely reduced to *n*-octane (2 min, 25°),[1] *n*-