for many discussions and to Dr. D. Dolphin for the preparation of d_{20}-ZnTPP.

A. Forman, D. C. Borg
Medical Research Center, Brookhaven National Laboratory
Upton, New York 11973

R. H. Felton
Department of Chemistry, Georgia Institute of Technology
Atlanta, Georgia 30332

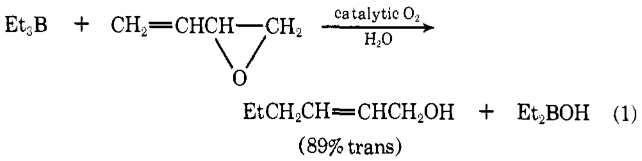
J. Fajer*
Department of Applied Science
Brookhaven National Laboratory, Upton, New York 11973

Received February 20, 1971

A New Four-Carbon-Atom Homologation Involving the Free-Radical Chain Reaction of 1,3-Butadiene Monoxide with Organoboranes. Synthesis of 4-Alkyl-2-buten-1-ols from Olefins *via* Hydroboration

Sir:

1,3-Butadiene monoxide, which fails to react spontaneously with trialkylboranes, readily reacts in the presence of catalytic amounts of oxygen or other free-radical initiators. This provides a new four-carbon-atom homologation leading to the corresponding 4-alkyl-2-buten-1-ols in relatively high stereochemical purity (eq 1).

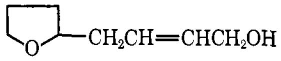


$$Et_3B + CH_2{=}CH\underset{\diagdown\,O\,\diagup}{CH{-}CH_2} \xrightarrow[H_2O]{\text{catalytic } O_2} \underset{(89\%\ \text{trans})}{EtCH_2CH{=}CHCH_2OH} + Et_2BOH \quad (1)$$

We have previously reported that trialkylboranes, readily available *via* hydroboration, undergo a "spontaneous" 1,4 addition to numerous α,β-unsaturated carbonyl compounds including methyl vinyl ketone,[1a] isopropenyl methyl ketone,[1b] acrolein,[1c] α-methylenecyclanones,[1d] and 2-methyl- and 2-bromoacrolein.[1e] Other derivatives, such as *trans*-crotonaldehyde, *trans*-3-penten-2-one, 2-cyclohexen-1-one, and acetylacetylene, failed to react spontaneously, but reacted quite readily through photochemical sensitization[2a] or by catalysis with typical free-radical initiators, such as acyl peroxides,[2a] azobisisobutyronitrile,[2b] and oxygen.[2b,c] Thus, these 1,4 addition reactions apparently proceed by a free-radical chain mechanism since they are promoted by typical free-radical initiators and are inhibited by free-radical scavengers, such as galvinoxyl.[1b]

No reaction occurs between 1,3-butadiene monoxide and triethylborane in the absence of oxygen. However, the reaction proceeds nicely with the introduction of small quantities of air.

Since trialkylboranes are generally prepared as tetrahydrofuran (THF) solutions, THF has normally been the solvent of choice for such 1,4 addition reactions. Unfortunately, in the present case we observed in this solvent the formation of considerable quantities of 4-(2′-tetrahydrofuryl)-2-buten-1-ol[3] (**1**) accompanying the formation of the desired product. The reaction evidently involves free-radical intermediates and the free-radical addition of THF to the epoxide takes place competitively. This side reaction could be avoided with benzene as the solvent.



1

Under these conditions, the yield of 2-hexen-1-ol was 44% with equal molar amounts of monoxide and triethylborane, but improved significantly with increasing molar ratios of monoxide to borane (see Table I). Indeed, quite satisfactory yields could be realized with excess monoxide (Table I). The 2-hexen-1-ol[4] was predominantly the trans isomer, 89% trans, 11% cis. This ratio was insensitive to both the temperature and the monoxide concentration.

Table I. Oxygen-Induced Addition of Organoboranes to 1,3-Butadiene Monoxide[a]

Borane	Molar ratio (epoxide/borane)	4-Alkyl-2-buten-1-ol[b] yield,[c] % Benzene (trans/cis)	Diethyl ether	n^{20}D, deg
Triethyl	1	44 (89/11)		1.4363
Triethyl	1.5	58 (89/11)		
Triethyl	2	68 (88/12)		
Triethyl	3	75 (89/11)	65	
Tri-*n*-butyl	3	73[d]	66[d]	1.4465
Triisobutyl	3	44	53	1.4433
Tricyclopentyl	3	46	56	1.4777
Tricyclohexyl	3	45	61	1.4811

[a] The reactions were conducted at 25° using 5 mmol of organoborane in 5 ml of solvent and adding air at the rate of 1 ml/min. [b] All alcohols were characterized by nmr and ir spectra, refractive index, and elemental analysis. [c] Based on 5 mmol of organoborane. [d] The product was composed of a 93:7 mixture of straight and branched chain isomers, respectively. [e] These values are in good agreement with those reported by E. S. Huyser and L. R. Munson, *J. Org. Chem.*, **30**, 1436 (1965).

Typical free-radical initiators, such as di-*tert*-butyl peroxide and azobisisobutyronitrile, as well as oxygen, are also effective in promoting the reaction. Moreover, a typical free-radical scavenger, galvinoxyl, inhibits the reaction. Thus, this reaction must involve a free-radical chain mechanism.

Trialkylboranes react with oxygen[5] and *tert*-butoxy radicals[6] to generate alkyl radicals (eq 2). In the presence of 1,3-butadiene monoxide, these alkyl radicals must add to the double bond of the epoxide to yield an

---

(1) (a) A. Suzuki, A. Arase, H. Matsumoto, H. C. Brown, M. M. Rogić, and M. W. Rathke, *J. Amer. Chem. Soc.*, **89**, 5708 (1967); (b) G. W. Kabalka, H. C. Brown, A. Suzuki, S. Honma, A. Arase, and M. Itoh, *ibid.*, **92**, 710 (1970); (c) H. C. Brown, M. M. Rogić, M. W. Rathke, and G. W. Kabalka, *ibid.*, **89**, 5709 (1967); (d) H. C. Brown, M. M. Rogić, M. W. Rathke, and G. W. Kabalka, *ibid.*, **90**, 4166 (1968); (e) H. C. Brown, M. M. Rogić, M. W. Rathke, and G. W. Kabalka, *ibid.*, **90**, 4165 (1968).

(2) (a) H. C. Brown and G. W. Kabalka, *ibid.*, **92**, 712 (1970); (b) A. Suzuki, S. Nozawa, M. Itoh, H. C. Brown, G. W. Kabalka, and G. W. Holland, *ibid.*, **92** 3503 (1970); (c) H. C. Brown and G. W. Kabalka, *ibid.*, **92**, 714 (1970).

(3) All products were isolated and characterized by nmr, ir, and elemental analysis.

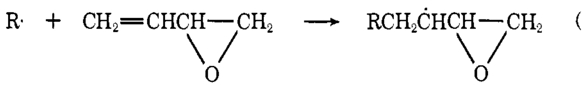
(4) The infrared spectrum of each 4-alkyl-2-buten-1-ol prepared in the present study exhibits a strong band at ~980 cm^{-1} indicating that the trans isomer is the predominant component. The cis/trans ratio of 2-hexen-1-ol was determined by comparison of the glpc trace obtained on a 12-ft 5% Quadrol column with those of authentic mixtures of the cis and trans alcohols.

(5) (a) A. G. Davies and B. P. Roberts, *J. Chem. Soc. B*, 311 (1969); (b) P. G. Allies and P. B. Brindley, *ibid.*, 1126 (1969); (c) H. C. Brown, M. M. Midland, and G. W. Kabalka, *J. Amer. Chem. Soc.*, **93**, 1024 (1971).

(6) A. G. Davies and P. B. Roberts, *Chem. Commun.*, 699 (1969).

intermediate radical **2** (eq 3) which then rearranges with opening of the epoxide ring to **3** (eq 4). The alkoxy radical **3** reacts with the trialkylborane (eq 5) to form a borinate **4**, displacing an alkyl radical[1b,6] which continues the chain. Hydrolysis of the intermediate borinate produces the 4-alkyl-2-buten-1-ol **5** (eq 6).

$$R_3B + O_2 \longrightarrow R\cdot + R_2BO_2 \qquad (2)$$



$$R\cdot + CH_2{=}CHCH{-}CH_2(O) \longrightarrow RCH_2\dot{C}HCH{-}CH_2(O) \qquad (3)$$

2

$$2 \longrightarrow \underset{3}{RCH_2CH{=}CHCH_2O\cdot} \qquad (4)$$

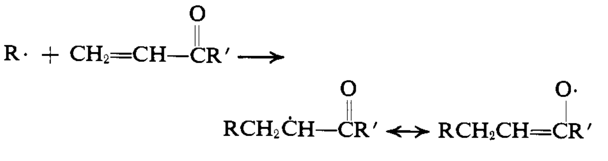
$$3 + R_3B \longrightarrow \underset{4}{RCH_2CH{=}CHCH_2OBR_2} + R\cdot \qquad (5)$$

$$4 + H_2O \longrightarrow \underset{5}{RCH_2CH{=}CHCH_2OH} + R_2BOH \qquad (6)$$

Thus, this new reaction appears to be one of wide generality and provides a convenient, one-step four-carbon-atom homologation, leading to a variety of 4-alkyl-2-buten-1-ols. Both primary and secondary trialkylboranes react satisfactorily. Although the yields realized with secondary trialkylboranes are somewhat lower, they can be improved by the use of diethyl ether as the solvent (Table I), in spite of the competitive reaction with the solvent (**5**, R = 1-ethoxyethyl), analogous to that observed in THF.

The following procedure is representative. A 25-ml flask equipped with a side-arm inlet containing a rubber septum was fitted with a condenser and magnetic stirring bar and flushed with nitrogen. To the flask was added 5 ml of benzene, followed by 0.71 ml (5 mmol) of triethylborane, and finally 1.2 ml (15 mmol) of 1,3-butadiene monoxide (Aldrich). The mixture was vigorously stirred at 25° as air was passed into the flask at the rate of 1 ml/min through a syringe needle placed through the rubber septum to a point just above the reaction mixture. Samples were removed periodically and analyzed by glpc on a Dow 710 column. Analysis after 1.5 hr indicated that all of the borane had reacted. At this point 1.6 ml of 3 *N* sodium hydroxide was added followed by the gradual addition of 1.6 ml of 30% hydrogen peroxide. The mixture was stirred for an additional hour at room temperature. Potassium carbonate was added until the aqueous layer was saturated. Analysis of the organic layer by glpc indicated that 3.75 mmol (75%) of 2-hexen-1-ol had formed. Distillation of the organic layer from a reaction conducted on a 25-mmol scale yielded 1.7 g (68%) of 2-hexen-1-ol, bp 69–72° (20 mm); $n^{20}\mathrm{D}$ 1.4363.

In our earlier reports[1,2] of the synthetic potential of organoboranes *via* free-radical processes, the substrates employed all contained an "activated" double bond in that it was conjugated with a carbonyl function and produced an intermediate radical which was resonance stabilized (eq 7). Even though the reaction with 1,3-butadiene monoxide requires that the alkyl radical add to a relatively "unactivated" double bond that does not produce a resonance-stabilized intermediate, its addition is quite facile and produces good yields of 4-alkyl-2-buten-1-ols. This suggests that compounds containing double bonds that are not in direct conjugation with a carbonyl function, such as dehydronorcamphor, are possible substrates for this reaction.[7]



$$R\cdot + CH_2{=}CH{-}\overset{O}{\overset{\|}{C}}R' \longrightarrow RCH_2\dot{C}H{-}\overset{O}{\overset{\|}{C}}R' \longleftrightarrow RCH_2CH{=}\overset{O\cdot}{\overset{|}{C}}R' \qquad (7)$$

Our observations with the oxygen-induced addition of organoboranes to acetylacetylene[2b] suggests that trialkylboranes may also react with 3,4-epoxy-1-butynes to yield allenic alcohols. This reaction is currently under investigation.

---

(7) Experiments with dehydronorcamphor and other homoconjugated compounds are currently in progress.

(8) National Institutes of Health Postdoctorate Fellow at Purdue University, 1969–1971.

(9) Postdoctorate research associate on a research grant (DA 31-124 ARO(D) 453) supported by the U. S. Army Research Office (Durham).

Akira Suzuki, Norio Miyaura, Mitsuomi Itoh
Department of Chemical Process Engineering
Hokkaido University, Sapporo, Japan

Herbert C. Brown,* George W. Holland,[8] Ei-ichi Negishi[9]
Richard B. Wetherill Laboratory, Purdue University
Lafayette, Indiana 47907

Received February 20, 1971

Photolysis of α-*N*-Alkylamidoacetophenones, a Direct Route to 3-Azetidinols[1]

Sir:

To our knowledge there are only three synthetic routes to 3 functionally substituted azetidines,[2] all of which have inherent limitations. Our attempts to repeat a reported fourth rather general procedure, involving the photolysis of α-*N*,*N*-dialkylamino ketones (eq 1, **a**–**c**),[3] were unsuccessful. In the photolysis of **1c** for example, a 95% yield of acetophenone (*i.e.*, Norrish type II cleavage) was obtained and glc analysis of the distilled basic fraction revealed a minimum of seven components. The ability of α-phenacylamines to undergo virtually exclusive type II photoelimination,[4] albeit with low quantum efficiency,[5] renders our results unexceptional.

We now wish to report that the photolysis of α-*N*-alkylamidoacetophenones (**1d**–**g**), especially when Z = tosyl, results in very high yields (74 to >95%) of the corresponding N-substituted 3-azetidinols (**2d**–**g**),[6] which can readily be converted into the corresponding amines **2a**–**c**. Furthermore, the azetidines **2a**–**c** prepared in this manner have physical properties fully consistent with their assigned structures, but very different from

---

(1) E. H. Gold, Abstracts, 2nd Northeast Regional Meeting of the American Chemical Society, Providence, R. I., Oct 1970, p 53.

(2) (a) V. R. Gaertner, *J. Org. Chem.*, **32**, 2972 (1967); V. R. Gaertner, *Tetrahedron Lett.*, 4691 (1966); (b) B. J. Gaj and D. R. Moore, *ibid.*, 2155 (1967); (c) J. L. Kurz, B. K. Gillard, D. A. Robertson, and A. G. Hortmann, *J. Amer. Chem. Soc.*, **92**, 5008 (1970).

(3) (a) R. A. Clasen, Ph.D. Thesis, Kansas State University, Manhattan, Kan., 1966; (b) R. A. Clasen and S. Searles, Jr., *Chem. Commun.*, 289 (1966).

(4) A. Padwa, W. A. Eisenhardt, R. Gruber, and D. Pashayan, *J. Amer. Chem. Soc.*, **91**, 1857 (1969).

(5) P. Wagner, personal communication on type II photoelimination of **1a**.

(6) The only analogous reaction that we are aware of involves the photocyclization of 2-oxoamides to 3-hydroxy-β-lactams (B. Akermark and N-G. Johansson, *Tetrahedron Lett.*, 371 (1969)).