photolysis of **2** in 5 hr led to 21% of **5**[6] (mp 257–259°; nmr ($CDCl_3$) δ 3.36 (s, NMe, 3 H), 3.67 (s, NMe, 3 H), 7.18–7.96 (m, aromatic H, 8 H); mass spectrum *m/e* 306 (M^+)) and 3% of **6** (mp 257–259°; nmr ($CDCl_3$) δ 3.40 (s, 2NMe), 7.22 (s, aromatic H), 7.15–7.92 (m, aromatic H); mass spectrum *m/e* 306 (M^+)).

In the case of photolysis of **2**, the results are consistent with a mechanism where the initial photochemical step is a homolytic cleavage of C-1 to give an aromatic radical. The radical may then undergo cyclization in the position 6′ and 8′ of the biphenoxy group to give the observed **6** and **5**, respectively.

To further investigate the mechanism for the formation of the tetracyclic **4**, 6-(2-iodophenoxy)-1,3-dimethyluracil (**7**) (mp 179–181°; nmr ($CDCl_3$) δ 3.32 (s, NMe, 3 H), 3.59 (s, NMe, 3 H), 4.65 (s, C_5H, 1 H), 7.05–8.15 (m, aromatic H, 4 H); mass spectrum *m/e* 358 (M^+)) was synthesized by the same procedure as for **1**, using sodium 2-iodophenoxide as replacing agent and irradiated under similar conditions for 3 hr to give **1**, **4**, and **7**. On continuation for another 8 hr, substance **1** disappeared in favor of **4**.

To show that **4** is not obtained from the reaction of 1,3-dimethyl-6-uracil radical, a possible intermediate due to cleavage of the C–O bond in **1** and **7** and the solvent benzene, the irradiation of **1** and **7** was carried out in hexadeuterated benzene. The base peak in the mass spectrum of the isolated **4** from **1** was at *m/e* 290 (M^+) and from **7** at *m/e* 294 (M^+) and the base peak of the isolated **1** from **7** was at *m/e* 313 (M^+), indicating the inclusion of the solvent only in the latter case. It is thus feasible to consider the intermediates **8** and **9** as the precursor to **4** which is a rather unique process.

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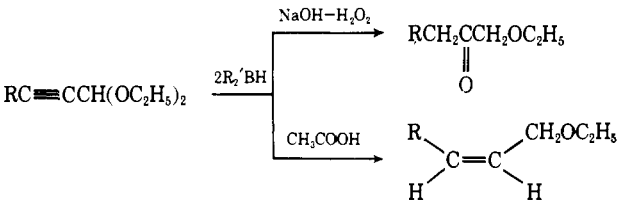
Received September 5, 1973

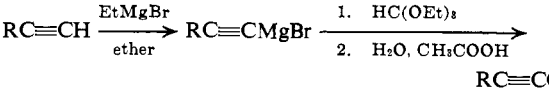
Novel Syntheses of α-Keto Ethers and *cis*-Allylic Ethers *via* the Hydroboration of Acetylenic Acetals[1]

Sir:

We wish to report operationally simple, high yield, stereoselective procedures for preparing α-keto ethers or *cis*-allylic ethers *via* the hydroboration of acetylenic acetals with dialkylboranes. This is followed by treatment of the intermediate organoborane with alkaline hydrogen peroxide or with acetic acid, respectively.



The acetylenic acetals themselves are readily obtained from terminal alkynes in greater than 80% yields by the following procedure.[2]



Hydroboration of 1,1-diethoxy-2-heptyne with 1 equiv of disiamylborane [bis(3-methyl-2-butyl)borane] in tetrahydrofuran solvent, followed by oxidation of the resultant organoborane with alkaline hydrogen peroxide, yielded 40% of a mixture of 1-ethoxy-2-heptanone and 1,1-diethoxy-3-heptanone along with 50% of the unreacted starting material. Complete utilization of the acetylenic acetal was achieved by employing 2 equiv of the hydroborating agent. Oxidation of the intermediate organoborane in this case afforded a 76 to 24% mixture of keto ether and keto acetal in a 90% yield, as evidenced by glpc analysis.

Although mixtures of keto ether and keto acetal were obtained when the alkyl group of the acetylenic acetal was primary, substitution by a secondary or tertiary alkyl group resulted in formation of essentially pure α-keto ethers. For example, sequential treatment of 1,1-diethoxy-4,4-dimethyl-2-pentyne with 2 equiv of disiamylborane, then with alkaline hydrogen peroxide, produced an 85% isolated yield of 1-ethoxy-4,4-dimethyl-2-pentanone containing less than 1% of the corresponding keto acetal. Furthermore, treatment of the hydroboration product with glacial acetic acid afforded 1-ethoxy-*cis*-4,4-dimethyl-2-pentene in a 79% yield.[3]

Some representative conversions of various acetylenic acetals into the corresponding keto ethers and *cis*-allylic ethers are shown in Table I.

Table I. Isolated Yields of α-Keto Ethers and *cis*-Allylic Ether Derived from Acetylenic Acetals

$RC{\equiv}CCH(OC_2H_5)_2$	Yield of α-keto ether, %[a]	Yield of *cis*-allylic ether, %[a]
R = *n*-C_4H_9–	61[b]	65
i-C_3H_7–	85	83
t-C_4H_9–	85	79[c]
	80	81
	81	81
	81	86

[a] The spectral and microanalytical data for all new compounds reported are consistent with the structures proposed. [b] No difficulties were encountered in distilling the α-keto ether from the by-product, 1,1-diethoxy-3-heptanone. [c] Glpc analysis revealed a 95 to 5 mixture of the cis and trans ethers.

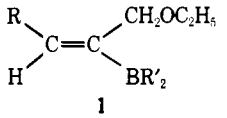
The following experimental procedures are representative. To a solution of disiamylborane[4] (105 mmol) in THF (150 ml) was added at 0–5° a solution of 1,1-diethoxy-3-cyclopentyl-2-propyne (50 mmol) in THF (15 ml), precooled to −25°. The reaction mixture was stirred at 0° for 30 min, then at 25° for 1 hr. The resultant organoborane was oxidized by the addition of 30 ml of 6 *N* sodium hydroxide and 30 ml of 30%

(1) This research was supported by the National Science Foundation through Grant No. GP-26360.
(2) A. L. Kranzfelder and R. R. Voget, *J. Amer. Chem. Soc.*, **60**, 1714 (1938).
(3) In the case of 1,1-diethoxy-2-heptyne, protonolysis of the hydroboration product should afford besides the allylic ether, 1,1-diethoxy-*cis*-3-heptene. However, isolation of this compound has thus far eluded us.
(4) G. Zweifel, G. M. Clark and N. L. Polston, *J. Amer. Chem. Soc.*, **93**, 3395 (1971).

hydrogen peroxide at 25–35°. After stirring at 25° for 30 min, the product was extracted into ether. The ether extract was concentrated and distilled to give 7.0 g (80%) of 1-ethoxy-3-cyclopentyl-2-propanone: bp 56° (0.2 mm); n^{24}D 1.4465; nmr (CCl_4) δ 3.83 (s, 2, $COCH_2O$), 3.51 (q, 2, OCH_2CH_3), 1.85–2.6 (m, 3, $CHCH_2C{=}O$), 1.6 (m, 8, CH_2), and 1.2 ppm (t, 3, OCH_2CH_3).

For preparation of the corresponding allylic ethers, the hydroboration product was treated with 12 ml of glacial acetic acid,[5] refluxed at 70–75° for 30 min, and then oxidized with 50 ml of 6 *N* sodium hydroxide and 30 ml of 30% hydrogen peroxide. After stirring at room temperature for 30 min, the mixture was saturated with sodium chloride. The organic layer formed was separated, and the aqueous phase was extracted with ether. The combined organic phases were washed with a saturated solution of sodium chloride, dried over magnesium sulfate, and distilled through a short Vigreux column to yield 6.2 g (81%) of 1-ethoxy-3-cyclopentyl-*cis*-2-propene: bp 76–78° (8 mm); n^{24}D 1.4532; nmr (CCl_4) δ 5.40 (m, 2, CH=CH), 3.96 (d, 2, $CH_2OCH_2CH_3$), 3.40 (q, 2, $-OCH_2CH_3$), 2.74 (m, 1, CH), 1.68 (m, 8, CH_2), and 1.20 ppm (t, 3, CH_3).

A likely organoborane intermediate which would afford both the α-keto ether on oxidation and the *cis*-allylic ether on protonolysis is **1**. That this is actually



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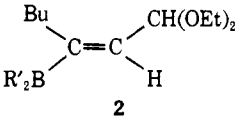
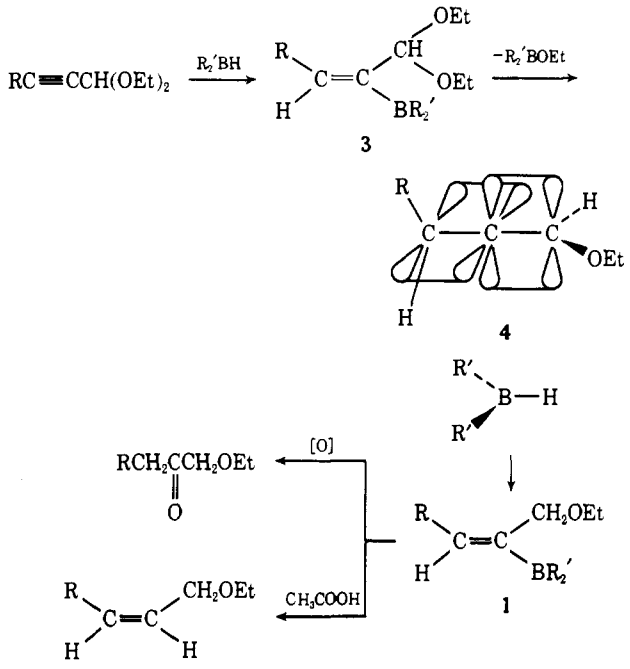


2

the case was borne out by nmr examination of the organoborane obtained by the addition of 2 equiv of disiamylborane to 1,1-diethoxy-4,4-dimethyl-2-pentyne. Thus besides an OCH_2CH_3 quartet (δ 3.99), the spectrum exhibited a doublet at δ 4.42 (J = 1.5 Hz) and a triplet at δ 5.26 (J = 1.5 Hz), pointing to the presence of an allyl ethyl ether moiety, $-CH{=}CCH_2OCH_2CH_3$. The formation of **1** can be rationalized as follows. The electron-withdrawing acetal group directs the boron primarily to the α-carbon, especially when the β-carbon contains a secondary or tertiary alkyl group.[6] The resulting vinylborane **3** then undergoes a fast, spontaneous elimination[7] of $R'_2BOC_2H_5$ to give the allenic ether **4**. Hydroboration of **4** then proceeds to place the boron preferentially at the central carbon and the hydride at the ethoxy substituted carbon of the double bond, owing to electron delocalization by the ethoxy group.

It is important to note here that the observed cis stereochemistry of the allylic ethers obtained must result from a stereoselective addition of B–H to the allenic double bond. In order to minimize nonbonded



interactions between the bulky disiamylborane and the alkyl group of the allenic ether, the hydroborating agent approaches the double bond from the less hindered side remote from the alkyl group (**4**).

On the other hand, the precursor for the β-keto acetal obtained from oxidation of the hydroboration product derived from 1,1-diethoxy-2-heptyne must be organoborane **2**, resulting from addition of boron to the 3 position of the triple bond. In agreement with this proposal is the observation that hydroboration of the acetylenic acetal with 2 equiv of R_2BH resulted in the uptake of only 1.80 equiv of the reagent. If a *gem*-3,3-diboryl intermediate was the precursor for the β-keto acetal, complete utilization of the available hydride would have occurred.

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(5) In cases where the by-product, 3-methyl-2-butanol, might interfere with isolation of the allylic ether, the product was isolated without prior oxidation of the R'_2BH moiety.

(6) A similar regiospecificity was observed in hydroborations of disubstituted alkynes with disiamylborane, ref 4.

(7) It has been shown that *cis*-alkoxyboranes undergo spontaneous elimination.[8,9] The presence of a second ethoxy group in **3** should assist cis elimination of $R'_2BOC_2H_5$ by stabilizing the incipient positive charge which develops on coordination of the boron with the departing ethoxy group.

(8) H. C. Brown and E. F. Knight, *J. Amer. Chem. Soc.*, **90**, 4439 (1968).

(9) D. J. Pasto and J. Hickman, *J. Amer. Chem. Soc.*, **90**, 4445 (1968).

Formation and Fragmentation of a Three-Membered Ring Containing Phosphorane[1]

Sir:

The preparation and chemistry of pentasubstituted phosphorus compounds has been a subject of considerable study in the past few years.[2] Despite this activity there has been no report of a pentacoordinate phosphorus compound in which the phosphorus atom is in a three-membered ring. The ready availability of the relatively unstable phenylphosphiran (**1**) established it as a potential precursor to such compounds.[3] Previous attempts to convert **1** into pentacoordinate phosphorus compounds, *i.e.*, reaction with diethyl peroxide

(1) This research has been supported by the National Science Foundation and by Public Health Service Research Grant No. CA-10737 from the National Cancer Institute.

(2) D. Hellwinkel, "Organic Phosphorus Compounds," Vol. 3, G. M. Kosolapoff and L. Maier, Ed., Wiley-Interscience, New York, N. Y., 1972, Chapter 5b, and references therein.

(3) S. Chan, H. Goldwhite, H. Keyzer, D. G. Rowsell, and R. Tang, *Tetrahedron*, **25**, 1097 (1969).