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A NEW SYNTHESIS OF KETONES FROM 1,2-DIMETHOXYETHENYLLITHIUM, ORGANOBORANES, AND ALKYL FLUOROSULFONATES

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The reaction of alkyl fluorosulfonates with lithium 1,2-dimethoxyethenyltrialkylborates readily prepared from organoboranes gives corresponding ketones in good yields.

Recently we have reported on the reaction of Brönsted acids with lithium 1,2-dimethoxyethenyltrialkylborates obtainable from 1-bromo-1,2-dimethoxyethene and trialkylboranes, which provides a convenient synthesis of 1,1-dialkylethenes.[1] In this Letter, we wish to report that such an ate-complex (I) reacts smoothly with alkyl fluorosulfonates to afford corresponding ketones in good yields (eqs. 1 and 2).

$$\mathrm{MeOCBr{=}CHOMe} \xrightarrow{\mathrm{BuLi}} \mathrm{MeO\bar{C}{=}CHOMe} \xrightarrow{\mathrm{R_3B}} \mathrm{MeOC(BR_3^-){=}CHOMe} \quad (1)$$

I

$$\mathrm{I} \xrightarrow[\text{2) aq. HCl}]{\text{1) } \mathrm{R'OSO_2F}} \mathrm{RCCH_2R'} \quad (2)$$

O

In an attempt to develop the synthetic utility of lithium 1,2-dimethoxyethenyltrialkylborates (I), the reaction of I with dimethyl sulfate as an alkylating agent was first examined. When 1,2-dimethoxyethenyltrihexylborate was treated with dimethyl sulfate followed by hydrochloric acid, 3-nonanone was obtained in a 56% yield. Several methylating agents were examined for the alkylation of I. The yield of 3-nonanone was found to be increased in the following order; methyl iodide, methyl p-toluenesulfonate, dimethyl sulfate, and methyl fluorosulfonate. The best yield of 3-nonanone was given under the conditions by using methyl fluorosulfonate at -78 °C.

The following procedure for the preparation of 3-nonanone is representative. To a solution of 1,2-dimethoxyethenyllithium[2] prepared from 1-bromo-1,2-dimethoxyethene (323 mg, 1.93 mmol) and butyllithium (1.5 ml of a 1.3 M solution in ether) in 6 ml of ether, trihexylborane (0.60 ml of a 3.2 M solution in THF, 1.93 mmol) was added at -78 °C. After stirring for 10 min at -78 °C, methyl fluorosulfonate (0.17 ml, 2.12 mmol) was added to the mixture and then stirred for 30 min at -78 °C. The reaction mixture thus obtained was allowed to warm to room temperature and then stirred overnight. Finally 4 ml of 3M hydrochloric acid was added at 0 °C, followed by stirring for 6 h at room temperature. Glpc analysis of the organic layer showed that 1.75 mmol of 3-nonanone had formed in a yield of 91%. The representative results are summarized in Table 1.

The reaction is considered to proceed through the following pathways. The borate (I) reacts with an alkylating agent to give the adduct (II) by one alkyl group migration from boron to carbon. Dialkylmethoxyborane is eliminated from II to give a vinylic ether derivative (III), which undergoes

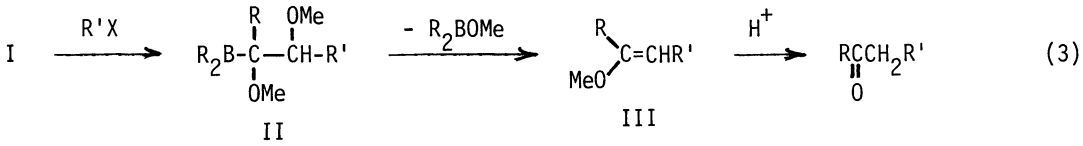
Table 1. Synthesis of Ketones

Organoborane R_3B, R=	Alkyl fluorosulfonate $R'OSO_2F$, R'=	Yield of ketone, $RCOCH_2R'$ (%)[a]
Butyl	Methyl	83
	Ethyl	89
Isobutyl	Methyl	69
	Ethyl	48
Pentyl	Methyl	85
	Ethyl	84
Hexyl	Methyl	91
	Ethyl	87
Cyclopentyl	Methyl	37
	Ethyl	17

[a]Glpc yield based on the organoborane used.

hydrolysis to form the corresponding ketone (eq. 3). The vinylic ether derivative is isolated by distillation of the reaction mixture. For example, in the reaction of 1,2-dimethoxyethenyltrihexylborate with methyl fluorosulfonate, a mixture of (Z)- and (E)-3-methoxy-2-nonene was obtained, the structure of which was determined by NMR, IR and mass spectra.[3] Furthermore, the structure was confirmed by hydrolysis with hydrochloric acid to 3-nonanone.

Whereas the reaction of borate complexes (I) with Brönsted acids gives 1,1-dialkylethenes by two alkyl group migration from boron to carbon,[1] the treatment with alkyl fluorosulfonates brings about one alkyl group migration to afford III after elimination of dialkylmethoxyborane.



(3)

Although there have been other published procedures for the preparation of ketones from organoboranes,[4] the present reaction provides a new synthesis of ketones by using readily available 1,2-dimethoxyethenyllithium and organoboranes.

References

1. T. Yogo and A. Suzuki, Chem. Lett., 1980, 591.
2. C. N. Skold, Synthetic Commun., 6, 119 (1976).
3. ^{1}H NMR (CCl_4); δ 4.1-4.4 (m, olefinic), 3.44 (d, J=1.5 Hz, OCH_3). IR (film); 1670 and 1107 cm^{-1}. MS (m/e); 156.
4. For eamples, see (a) H. C. Brown, Organic Synthesis via Boranes," John Wiley & Sons, New York (1975); (b) J. Weill-Raynal, Synthesis, 1976, 633; (c) G. M. L. Cragg and K. R. Koch, Chem. Soc. Rev., 6, 393 (1977).

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