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**Preliminary communication**

# SYNTHETIC METHODS

# IX*. HYDROBORATION OF SILYLACETYLENES. A NEW SYNTHESIS OF α-SILAKETONES

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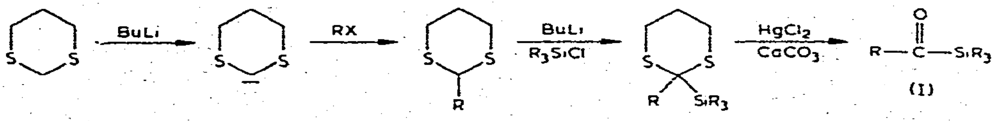
## Summary

The first example of monohydroboration of silylacetylenes with dichloroborane is described. The reaction occurs regio- and stereo-specifically and leads after methanolysis to isolable vinylboronic esters (III). The latter undergo photo $Z \rightleftharpoons E$ isomerization. Oxidation of III to the corresponding α-silaketone was accomplished in high yield using trimethylamine-*N*-oxide dihydrate. The overall method represents a useful conversion of acetylenes to α-silaketones.

Acylsilanes, I (α-silaketones)**, have been the subject of many interesting studies in recent years [1, 2]. Because of the sensitivity of I to acids and bases, synthetic pathways to this important class of compounds have been somewhat limited. The most general synthetic routes involve the use of dithiane [3] (see below) and of vinyl methyl ethers [4].



Other methods, such as oxidation of α-hydroxy silanes [5a], halogenation of benzylsilanes [5b] or silylation of imidoyl chlorides [5b] are often limited by the availability of proper starting materials or by the choice of substituents.

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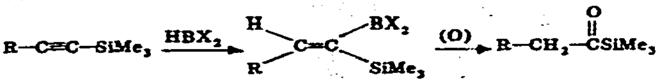
*For part VIII see ref. 12.

**To stress the generality of these structures and to make naming more congruent with that applied to cyclic silaketones, we prefer the designation of α-silaketones rather than that of acylsilanes.

We wish to report the use of dichloroborane in hydroboration of silyl acetylenes II and a new convenient synthetic route to α-silaketones I from II according to Scheme 1.

SCHEME 1



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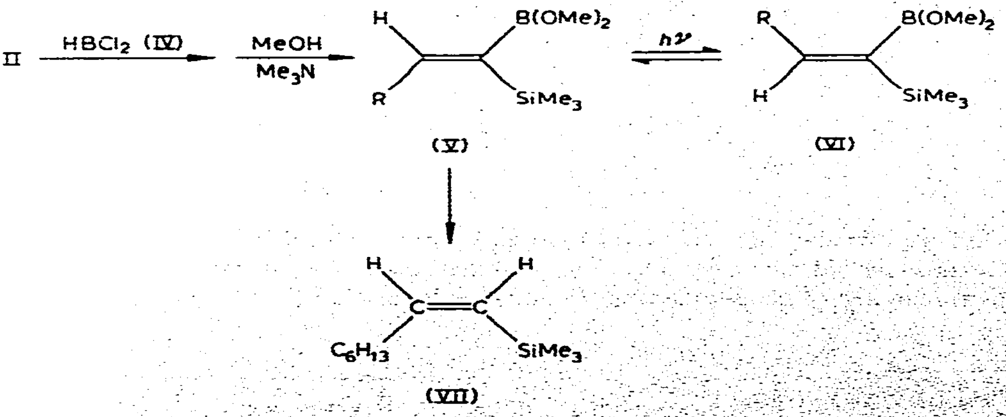
|---|---|---|
| (IIa) R = $C_6H_5$ | (IIIa) (46%) | (Ia) (88%) |
| (IIb) R = $CH_2{=}C(CH_3)$ | (IIIb) (48%) | (Ib) (79%) |
| (IIc) R = n-$C_6H_{13}$ | (IIIc) (30%) | (Ic) (80%) |
| (IId) R = $SiMe_3$ | (IIId) (45%) | (Id) (65%)* |

Since silylacetylenes II are readily accessible from monosubstituted alkynes this represents an example of an alkyne as an acyl anion equivalent in the synthesis of I.

The success of the above scheme depends on several critical factors; the correct regiochemistry of hydroboration, the choice of X in the hydroborating reagent to permit separation of the product I from other species present and the choice of oxidizing agent for the vinylboron species III to avoid destruction of the product.

While hydroboration of silylacetylenes has been reported [6], the subsequent oxidation of the expected vinylboranes has not been described. Further, in order to simplify the conversion III→I, it was considered important to choose a hydroborating reagent such that the group X need not be oxidized (i.e., X = OR, Cl). Catecholborane had been shown to be a reagent of choice in monoaddition to acetylenes [7] yet we found that with allylacetylenes II addition of catecholborane and oxidation led to a mixture of products. Dichloroborane (IV) proved to be a suitable reagent since it not only led to regiospecific monohydroboration but the adducts could also be converted to the isolable vinylboronates V and ultimately this reagent allowed ready separation of the final products.



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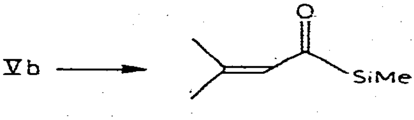
*A 50/50 mixture of Id and bis(trimethylsilyl)ethanal.

The isolation of vinylboronic esters Va—Vc as the sole products* (in 30—50% yield) on methanolysis of the initial adducts III (X = Cl), as well as their conversion to I, VI and VII, were indicative of the regiospecificity and stereospecificity of the hydroboration process. Thus the NMR spectrum of Vc showed a triplet ($J$ 6.7 Hz) at $\delta$ 6.27 ppm for the vinylic proton requiring placement of the boron $\alpha$ to silicon. Photolysis of Va in benzene-$d_6$ led to $Z \rightleftharpoons E$ isomerization with formation of an 80/20 mixture of Va/VIa. During the photoisomerization Va$\rightleftharpoons$VIa the vinylic proton experienced an upfield shift (from 7.37 to ~7.0 ppm), as expected, based on related studies [8]. Protonolysis of Vc in acetic acid to authentic *cis*-1-hexyl-2-trimethylsilylethene (VII) further verifies the $Z$-configuration of V**.

The regiospecificity observed in II→V, with formation of the C—B bond $\alpha$ to Si, is in agreement with similar directive effects observed in hydralumination of II [9], in hydroboration with dicyclohexylborane*** and in certain hydroborations of vinylsilanes [10]. It is interesting to note that selective hydroboration of the silylacetylene can be achieved in the presence of an alkene functional group (cf. IIb).

The usual oxidation of boranes employs alkaline hydrogen peroxide. Use of this reagent with the vinylboronic esters V did not lead to ketones I. Indeed, we found that silaketones I rapidly decomposed in the presence of alkaline peroxide. On the other hand, trimethylamine oxide as the commercially available dihydrate led to silaketones I in excellent yield. This oxidizing agent for vinyl boranes offers a definite advantage over hydrogen peroxide and no special pretreatment is required as in the case of anhydrous trimethylamine oxide [11]. In the case of Vb, oxidation was accompanied by isomerization to the conjugated ketone VIII.

$$\text{Va, Vc} \xrightarrow[C_6H_6]{Me_3\overset{+}{N}-\overset{-}{O}\cdot 2H_2O} \text{Ia, Ic}$$



(VIII)

With bistrimethylsilylacetylene (IId), hydroboration/oxidation led to a 50/50 mixture of Id and bis(trimethylsilyl)ethanal*. The thermal and photochemistry of these compounds is currently under investigation.

The following procedure for the preparation of Ia is representative**. To 0.1 mole of silylacetylene (IIa) in pentane (100 ml) at –78°C was added dichloro-

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*Although dihydroboration of II with dichloroborane is possible [13], the presence of only small amounts (<5%) of unreacted II after the hydroboration step suggests that this reaction pathway is not solely responsible for the low yields of III. The low stability of III is also suggested by attempts to extend this procedure to the synthesis of germanium or tin analogues of Vb, which led only to dark mixtures from which the corresponding vinylboronic ester could not be isolated.

**Protonolysis of Va, Vb and Vd led to mixtures of *cis* and *trans* isomers and this interesting phenomenon will be discussed in a later paper.

***After the present study had been concluded a report appeared on hydroboration of 1-trimethylsilyloctyne with dicyclohexylborane in which the boron added regiospecifically to Si [6d].

*The interpretation of this unusual result will be discussed in detail in the full paper.

**When the hydroboration/oxidation of II was carried out without isolation of III, yields of 20—45% for I were obtained, indicating that isolation of III did not significantly reduce the overall yield of the ketone. Since the product I was more difficult to purify using this procedure, it is recommended that III be isolated as described prior to the oxidation step.

borane etherate IV (0.1 mol) and boron trichloride (50 ml 2.0 *M* in $C_5H_{12}$) under an argon atmosphere. After 12 h at room temperature, the supernatant liquid at 0°C was treated with an equimolar mixture of trimethylamine/methanol (20 g solution; 10% excess). After addition of 100 ml of pentane, the mixture was filtered and distilled to give 11.3 g of IIIa (46%), b.p. 96—98°C (1.0 torr)*.

Oxidation of IIIa (46 mmol) was accomplished by heating in benzene (100 ml) and trimethylamine-*N*-oxide dihydride (40 mmol) for 1 h under reflux. After washing and drying, distillation gave 7.8 g (88%) of Ia, b.p. 78°C (1 torr) (lit. [2] 50°C (0.08 torr)).

## Acknowledgement

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## References

1 A.G. Brook, Accounts Chem. Res., 7 (1974) 77.
2 (a) A.R. Bassindale, A.G. Brook and J. Harris, J. Organometal. Chem., 90 (1975) C6; (b) A.G. Brook, J.W. Harris and A.R. Bassindale, ibid., 99 (1975) 379.
3 (a) A.G. Brook, J.M. Duff, P.F. Jones and N.R. Davis, J. Amer. Chem. Soc., 89 (1967) 431; (b) E.J. Corey, D. Seebach and R. Freedman, ibid., 89 (1967) 434.
4 (a) E.M. Dexheimer and L. Spialter, J. Organometal. Chem., 107 (1976) 229; (b) J.A. Soderquist and A. Hassner, in preparation.
5 (a) A.G. Brook, Advan. Organometal. Chem., 7 (1968) 95; (b) A.G. Brook, G.E. LeGrow and R. Kivisikk, Can. J. Chem., 43 (1965) 1175; (c) P. Bourgeois, J. Organometal. Chem., 76 (1974) C1.
6 (a) J. Cudlin, J. Schraml and V. Chvalovsky, Collect. Czech. Chem. Commun., 29 (1964) 1476; (b) R.B. Miller and T. Reichenbach, Tetrahedron Lett., (1974) 543; (c) P.R. Hudrlik, P. Peterson and R.J. Rona, J. Org. Chem., 40 (1975) 2263; (d) K. Uchida, K. Utimota and H. Nozaki, ibid., 41 (1976) 2941.
7 H.C. Brown and S.K. Gupta, J. Amer. Chem. Soc., 94 (1972) 4370.
8 (a) D.S. Matteson and R.A. Bowie, J. Amer. Chem. Soc., 87 (1965) 2587; (b) L.W. Hall, J.D. Odom and P.D. Ellis, J. Organometal. Chem., 97 (1975) 145.
9 (a) J.J. Eisch and M.W. Foxton, J. Org. Chem., 36 (1971) 3520; (b) J.J. Eisch and S.-G. Rhee, J. Amer. Chem. Soc., 97 (1975) 4673.
10 A. Hassner and J.A. Soderquist, J. Org. Chem., in preparation.
11 (a) R. Koster and Y. Morita, Liebigs Ann. Chem., 704 (1967) 70; (b) V. Franzen, Org. Syn. Coll. Vol., V (1973) 782.
12 A. Hassner, R.N. Reuss and H.W. Pinnick, J. Org. Chem., 40 (1975) 3427.
13 H.C. Brown and N. Ravindran, J. Amer. Chem. Soc., 98 (1976) 1798.

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*All new compounds showed proper analysis and/or consistent mass spectra (parent peaks and fragmentation patterns), IR and NMR spectra.