^{13}C NMR (ppm from Me_4Si, C_6D_6, +10 °C, 67.89 MHz): 36.9 (t, J_{CH} = 128 Hz, CH_2CH_3), 36.4 (tt, J_{CH} = 150, J_{CP} = 7.3 Hz, C_2H_4), 14.1 (qt, J_{CH} = 128, J_{CP} = 9.5 Hz, PMe_3), −2.3 (q, J_{CH} = 123 Hz, CH_2CH_3). ^1H NMR (τ, C_6D_6, 270 MHz): 8.85 (t, 18, J_{PH} = 2.4 Hz, PMe_3), 9.13 (qt, CH_2CH_3, J_{PH} = 23.8, J_{HH} = 8.0 Hz), 9.48 (m, $C_2H_2H_2'$), 10.29 (m, $C_2H_2H_2'$), 11.00 (t, CH_2CH_3, J_{HH} = 8.0 Hz). Mol wt (cyclohexane): calcd, 418; found, 372.

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(11) $Ta(C_2H_4)_2(n\text{-butyl})(PMe_3)_2$ ^{13}C NMR (ppm from Me_4Si, toluene-d_8, −20 °C, 67.89 MHz): 52.6 (tt, J_{CH} = 118, J_{CP} = 4.4 Hz, $CH_2CH_2CH_2CH_3$), 39.4 (tt, J_{CH} = 145, J_{PC} = 7.3 Hz, C_2H_4), 33.5 (t, J_{CH} = 124 Hz, $CH_2CH_2CH_2CH_3$), 28.2 (t, J_{CH} = 124 Hz, $CH_2CH_2CH_2CH_3$), 14.7 (qt, J_{CH} = 128, $J_{CP} \approx$ 11 Hz, PMe_3), 12.7 (q, J_{CH} = 124 Hz, $CH_2CH_2CH_2CH_3$).

(12) $Ta(C_2H_4)(C_4H_6)Cl(PMe_3)_2$ ^{13}C NMR (ppm from Me_4Si, toluene-d_8, −30 °C, 67.89 MHz): 94.9 (d, J_{CH} = 160 Hz, $CH_2{=}CHCH{=}CH_2$), 92.6 (d, J_{CH} = 163 Hz, $CH_2{=}CHCH{=}CH_2$), 51.8 (tt, J_{CH} = 147, J_{CP} = 5.6 Hz, $CH_2{=}CH_2$), 43.4 (ddd, J_{CH} = 156, $J_{CH'}$ = 148, J_{CP} = 5.7 Hz, $CH_2{=}CHCH{=}CH_2$), 34.8 (ddd, J_{CH} = 141, $J_{CH'}$ = 149, J_{CP} = 7.8 Hz, $CH_2{=}CHCH{=}CH_2$), 30.2 (td, $J_{CH} \approx$ 150, J_{CP} = 8.2 Hz, $CH_2{=}CH_2$), 14.9 (qd, $J_{CH} \approx$ 130, J_{CP} = 21.6 Hz, PMe_3), 13.5 (qd, $J_{CH} \approx$ 130, J_{CP} = 23.3 Hz, PMe_3).

(13) $Nb(C_2H_4)_2(PMe_3)_2(C_2H_5)$ can be prepared in low yield by reacting $MgEt_2$ (dioxane) (2.5 equiv) with $NbCl_5$ (1 equiv) and PMe_3 (2.1 equiv) in Et_2O at −78 °C. A better yield is obtained when $Nb(CH_2CMe_3)_2(C_2H_5)_3$ decomposes in ether in the presence of 2.1 equiv of PMe_3. ^{13}C NMR (ppm from Me_4Si, toluene-d_8, −10 °C, 15 MHz): 35.1 (tt, J_{CH} = 149, J_{CP} = 7.3 Hz, C_2H_4), 30.8 (br t, J_{CH} = 134 Hz, CH_2CH_3), 14.2 (qt, J_{CH} = 127, J_{CP} = 7.3 Hz, PMe_3), −0.97 (q, J_{CH} = 121 Hz, CH_2CH_3).

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(16) Heating $(\eta^5\text{-}C_5Me_5)Me_2TaCH_2CH_2CH_2CH_2$[15] in pentane under C_2H_4 to 50 °C for 6 h yields $(\eta^5\text{-}C_5Me_5)$(butadiene)$TaCH_2CH_2CH_2CH_2$: S. J. McLain, unpublished results.

(17) We have shown that free L exchanges with coordinated L at 25–100 °C on the NMR scale in all such five-coordinate molecules (bisneopentylidene-tantalum complexes included) and that the rate is fastest in more crowded molecules of a given type. In relatively uncrowded $Ta(C_2H_4)_2L_2Et$, however, the exchange rate is fast at 25 °C. We are presently investigating these exchange reactions in more detail.

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(19) Green $Ta(C_2H_4)(PMe_3)_2(C_2H_5)Cl$ (probably trans,trans) can be prepared readily from *trans,mer*-$Ta(C_2H_4)(PMe_3)_2Cl_3$ and 2 mol of EtMgCl at −78 °C in ether. So far this complex has not been obtained pure; it is mixed with 5–10% of the monoethyl analogue.

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(22) It is almost certainly true that ethylene can rapidly insert into a Ti–alkyl bond[2f] (the Cossee mechanism[23]) and probably into other metal–alkyl bonds (V and Cr). (It is interesting, however, to note that V and Cr catalysts are believed to be most active in the +2 oxidation state.[24]) Variations of this metallacyclopentane proposal are possible. For example, the crucial intermediate in Cramer's ethylene dimerization system[2c] could well be $[Cl_3(C_2H_4)RhCH_2CH_2CH_2CH_2]^{2-}$ and $[Rh(butyl)Cl_3(C_2H_4)(solvent)]^-$ the result of protonating the metallacycle at C_α.

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(25) Camille and Henry Dreyfus Teacher–Scholar Grant Recipient, 1978–1983.

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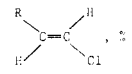
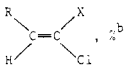
Received April 12, 1979

α-Chloroalkenylalanates. Their Preparation and Conversion into (*E*)-1-Chloro-1-alkenes and Mixed 1,1-Dihalo-1-alkenes

Sir:

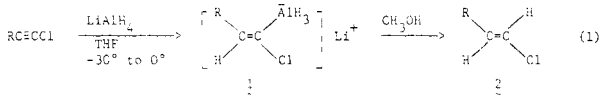
A number of years ago we revealed that preparation of the synthetically valuable α-haloalkenylboranes may be readily achieved through hydroboration of 1-halo-1-alkynes with dialkylboranes.[1] Unfortunately, attempts to synthesize the corresponding α-haloalkenylalanates via the reaction of 1-halo-1-alkynes with diisobutylaluminum hydride were unsuccessful.[2] However, since the trifunctional α-halovinylalanyl moiety represents a uniquely constituted synthon for substituted olefins, we continued to search for suitable approaches for its preparation.

Table I. Yields of (*E*)-1-Chloro-1-alkenes and (*Z*)-1-Halo-1-chloro-1-alkenes from 1-Chloro-1-alkynes[a]

RC≡CCl	 , %	 , %[b]
R=		X=
$n\text{-}C_4H_9$	(96)	Br 78
		I 85
$n\text{-}C_6H_{13}$	80	Br 80
		I 86
	(93)	Br 87
		I 89
$t\text{-}C_4H_9$	(76)	Br 61
$THPO(CH_2)_3$	(95)	Br 86[c]

[a] The numbers in parentheses are GLC yields. [b] The NMR and mass spectral data are consistent with the assigned structures. [c] The structural assignment follows from the stereochemical results observed with the other 1-chloro-1-alkynes.

We now disclose that the lithium [(*E*)-1-chloro-1-alkenyl]-alanates **1** (eq 1) may be prepared by the highly stereo- and



(1)

regioselective trans addition in tetrahydrofuran solvent of the Al-H moiety of lithium aluminum hydride to the triple bond of the readily available 1-chloro-1-alkynes.[3-5] These α-halovinylalanates represent a novel class of compounds which possess moderate stability at 0 °C and provide upon methanolysis excellent yields of the corresponding (*E*)-1-chloro-1-alkenes **2** (Table I).

The lower GLC yield of **2** (R = $t\text{-}C_4H_9$) realized in the case of *t*-butylchloroacetylene (Table I) results from the fact that its hydroalumination produces besides **1** an appreciable amount of *tert*-butylacetylene (23%). On the other hand, 1-chloro-1-alkynes containing primary or secondary alkyl substituents on reaction with $LiAlH_4$ give, after workup, <6% of the corresponding 1-alkynes. The formation of 1-alkynes can be rationalized in terms of an α-elimination of $LiAlH_3Cl$ (or LiCl) from the hydroalumination product **1** with concomitant 1,2 shift of hydrogen (Fritz–Buttenberg–Wiechell rearrangement).[6]

In exploring the further scope of the α-chlorovinylalanates **1** as intermediates for organic synthesis, we next directed our attention toward their conversion into mixed 1,1-dihalo-1-alkenes of defined stereochemistry. In contrast to the 1-halo-1-alkenes whose usefulness as synthons for preparing olefins and diene has been clearly demonstrated, the 1,1-dihalo-1-ethenyl moiety has not yet played a major role in synthetic methodology. This is probably because most of the currently available methods for its synthesis are limited to the preparation of homo 1,1-dihalo olefins.[7,8] Thus, we were gratified to observe that conversion of the trihydridoalumino moiety of **1** into the triisopropoxyalumino moiety in **3** by treatment with acetone followed by addition of bromine at −78 °C and hydrolytic workup affords (*Z*)-1-bromo-1-chloro-1-alkenes (**4**, eq 2) in >97% isomeric purities and in good yields (Table I).[9] In a similar manner, treatment of **3** with a solution of iodine monochloride (1.1 equiv) in methylene chloride at −30 °C, followed by stirring of the reaction mixture at this temperature for 1 h and at ambient temperature for 2 h, produces, after hydrolytic workup, the corresponding (*Z*)-1-chloro-1-iodo-1-alkenes **5** (Table I).[10]

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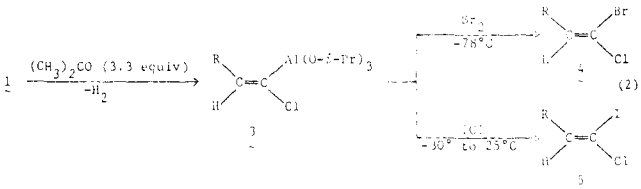
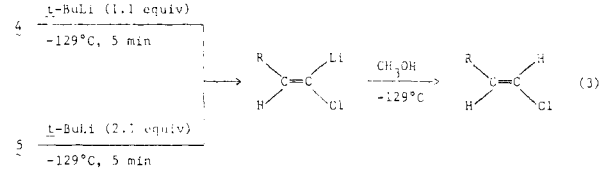


The configurations of the 1,1-dihalo olefins obtained were established through their conversion into the known *trans*-1-chloro-1-alkenes. This was accomplished by sequential treatment of **4** or **5** dissolved in a mixture of THF–ether–*n*-pentane (4:4:1)[6] and cooled to −129 °C (*n*-pentane–liquid N_2 bath) with precooled solutions of *tert*-butyllithium in *n*-pentane and methanol in ether. After workup, GLC analysis revealed the nearly exclusive formation of the *trans*-chloro-1-alkenes in >85% yields (eq 3).



A typical procedure for the preparation of **4** (R = *n*-C_4H_9) is as follows. To a solution of $LiAlH_4$ (1 M, 20 mmol) in THF cooled to −30 °C ($CaCl_2$–H_2O–dry ice)[11] was added 1-chloro-1-hexyne (20 mmol)[5] while the temperature was maintained below −25 °C during the addition. After the mixture was stirred for an additional 15 min, it was brought to 0 °C (ice bath) and stirred for 90 min. Dry acetone (66 mmol) was then added dropwise over a 20-min period while the temperature was maintained below 10 °C. After 1 hr, the reaction mixture was cooled to −78 °C and then treated dropwise with a solution of bromine (22 mmol) in methylene chloride (10 mL). The mixture was allowed to warm to room temperature in the dark and then was slowly poured into a mixture of 10% HCl (80 mL), 10% aqueous $NaHSO_3$ (10 mL), *n*-pentane (20 mL), and ice (50 g). After extraction with *n*-pentane, the combined organic extract was washed with 10% HCl and saturated aqueous sodium bicarbonate and then treated with a few crystals of 2,6-di-*tert*-butyl-*p*-cresol (BHT). Drying ($MgSO_4$) and distillation from a small amount of $CaCO_3$ afforded a 78% yield of (*Z*)-1-bromo-1-chloro-1-hexene. GLC examination on a glass capillary column (SE-30, 90 m, 80 °C)[12] revealed that the compound was 97% isomerically pure. To prevent isomerization from occurring, it is important to treat the pure 1,1-dihalo olefins distillate immediately with a few crystals of BHT.

Acknowledgment. The authors thank the National Science Foundation for support of this investigation.

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(2) For example, hydroalumination of 1-chloro-1-octyne with diisobutylaluminum hydride resulted, after hydrolysis, in a complex mixture of products. It is noteworthy that the reaction of 1-bromo-2-phenylethyne with diisobutylaluminum hydride afforded nearly exclusively phenylacetylene (Eisch, J. J.; Foxton, M. W. *J. Org. Chem.* **1971,** *36,* 3520), whereas its reaction with $LiAlH_4$ in the presence of $AlCl_3$ led to the formation of *trans*-styryl bromide in 40–60% yields after a hydrolytic workup (Kruglikova, R. I.; Kravets, L. P.; Unkovskii, B. V. *Zh. Org. Khim.* **1975,** *11,* 263).
(3) It has been reported that the reactions of 1-chloroalk-1-yn-3-ols with $LiAlH_4$ lead, after workup, to 1-chloroalk-1-en-3-ols. The trans structure has been tentatively assigned to these. Julia, M.; Surzur, J.-M. *Bull. Soc. Chim. Fr.* **1956,** 1615.
(4) Hydroalumination of the 1-chloro-1-alkynes was done using 1.0 equiv of $LiAlH_4$. Use of 0.5 equiv of $LiAlH_4$ resulted in somewhat lower yields of the α-chloroalkenylaluminum compounds.
(5) The 1-chloro-1-alkynes were prepared as follows. The hexane was stripped from a solution of *n*-butyllithium in hexane (0.21 mol, 1.72 M) under reduced pressure at 25 °C and then was replaced with THF (200 mL) at −78 °C. To dissolve the *n*-butyllithium, the reaction mixture was brought to −25 °C. Then it was cooled to −78 °C and treated sequentially with the 1-alkyne (0.20 mol) and *N*-chlorosuccinimide (0.23 mol) at −25 °C. The resulting mixture was maintained for 2 h at −25 °C and then was stirred for an additional 4 h at room temperature (Zweifel, G.; Murray, R. E., unpublished results).
(6) Köbrich, G. *Angew. Chem., Int. Ed. Engl.* **1972,** *11,* 473.
(7) For the preparation of homo 1,1-dihaloalkenes, see: Corey, E. J.; Fuchs, P. L. *Tetrahedron Lett.* **1972,** 3769. Salmond, W. G. *Ibid.* **1977,** 1239. Mendoza, A.; Matteson, D. S. *J. Organomet. Chem.* **1978,** *152,* 1. For nonstereospecific preparations of mixed 1,1-dihaloalkenes, see: Köbrich, G.; Trapp, H. *Chem. Ber.* **1966,** *99,* 670.
(8) A stereoselective synthesis of mixed 1,1-dihalo-1-alkenes has been achieved via metalation–halogenation of *trans*-styryl chloride: Schlosser, M.; Landenberger, V. *Chem. Ber.* **1967,** *100,* 3893. Schlosser, M.; Heinz, G., *Ibid.* **1969,** *102,* 1944.
(9) Direct treatment of **1** with 2.5 equiv of bromine in methylene chloride at −78 °C also gave high yields of the simple 1-bromo-1-chloro-1-alkenes **4**. However, with α-chloroalkenylalanates containing functional groups, prior treatment with acetone was necessary to obtain high yields of **4**.
(10) Interestingly, direct iodination of **1** (R = *n*-C_4H_9) with 2.5 equiv of iodine did not produce the anticipated 1-chloro-1-iodo-1-hexene but yielded after workup a mixture of iodo-1-hexene and 1-hexyne. Also, treatment of **3** with 1 equiv of iodine afforded **5** in only modest yields.
(11) Bryan, W. P.; Byrne, R. H. *J. Chem. Educ.* **1970,** *47,* 361.
(12) GLC analyses were performed on J & W glass capillary columns.

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Received December 14, 1978

Biosynthesis of Vitamin B_1 in Yeast. Origin of the Thiazole Unit

Sir:

More than forty years after the elucidation of the structure of vitamin B_1 (thiamin),[1,2] the primary precursors of its thiazole unit (**5**) are still in dispute[3] and a chemically rational hypothesis of the biosynthesis of this unit has not yet been formulated. We now advance such a hypothesis and present some evidence which is consistent with it.

It is our view that, in yeast, the thiazole unit of vitamin B_1 is derived from one of the stereoisomers of the Schiff base **3**, which is generated by condensation of glycine (**1**) with a phosphoketopentose (**2**). The Schiff base **3** is converted into the thiazole derivative **4**[5] in a multistep sequence (Scheme I) comprising dehydration (or elimination of phosphate) (A), dehydration and tautomerization (B and C), and addition of sulfur (D), followed by ring closure (E) and concerted decarboxylation and dehydration. Several variants of this route are shown in Scheme I.

In support of this scheme, we now present experimental evidence which demonstrates the participation of a C_5 unit (**2**) derived from glucose in the biosynthesis of the thiazole unit of thiamin in yeast. The incorporation of C-2 and N of glycine (**1**) into the thiazole unit of thiamin in yeast, in accord with Scheme I, has been documented.[4,10]

Origin of the C_5 Unit 2. Yeast (*Saccharomyces cerevisiae*) does not utilize ribose or other pentoses[11] when these are supplied to the culture medium. Evidence for the participation of a pentose in thiamin biosynthesis was therefore obtained indirectly, by testing the mode of incorporation of glucose and fructose. These hexoses are known to be utilized and to yield pentoses in vivo. In separate experiments,[12] D-[1-^{14}C]-, D-[2-^{14}C]-, and D-[6-^{14}C]glucose and D-[1-^{14}C]fructose were administered to growing yeast cultures (*S. cerevisiae* A.T.C.C. 24903)[13] at the onset of logarithmic growth. The cells were collected when logarithmic growth had ceased and radioactive thiamin was isolated[4] by carrier dilution. Bisulfite cleavage[9] yielded the thiazole moiety (5-(β-hydroxyethyl)-4-methylthiazole) (**5**) as an oil, some of which was oxidized[14] to 5-formyl-4-methylthiazole[15] (isolated as the semicarbazone[15]) and some of which was converted, via the 5-(β-chloroethyl) derivative,[16,17] into the 5-(-β-phthalimidoethyl) derivative.[18] This

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