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THE REACTION OF 3,3-DICHLOROALLYLTRIMETHYLSILANE WITH n-BUTYLLITHIUM

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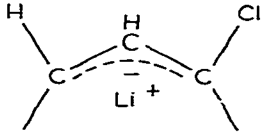
Summary

n-Butyllithium reacts with 3,3-dichloroallyltrimethylsilane to metalate the vinyl proton. Under the reaction conditions the $Me_3SiCH_2C(Li)=CCl_2$ formed undergoes β-elimination of LiCl to give $ClC\equiv CCH_2SiMe_3$ whose subsequent reaction with n-butyllithium produces $LiC\equiv CCH_2SiMe_3$. Addition of trimethylchlorosilane gives $Me_3SiC\equiv CCH_2SiMe_3$. When two molar equivalents of n-butyllithium are used, further metalation of $LiC\equiv CCH_2SiMe_3$ gives $LiC\equiv CCH(Li)SiMe_3$. The action of *N*-bromosuccinimide on $Me_3SiCH_2CH=CCl_2$ resulted in formation of $Me_3SiCH=CHCCl_2Br$.

Introduction

In a recent investigation [1], we prepared the novel ambident allylic lithium reagent *gem*-chloro(trimethylsilyl)allyllithium (I) and studied its reactions with a variety of substrates. Another trimethylsilyl-substituted allyllithium reagent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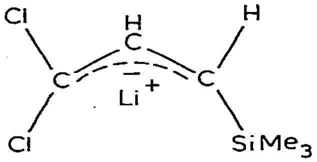
which was of potential interest to us was II, and we report here concerning our



(II)

attempts to prepare this reagent. Although they were unsuccessful, the route examined was of interest since it involved the reaction of n-butyllithium with a molecule which had three different potential sites at which the lithium reagent could attack.

Results and discussion

The organosilicon compound which was chosen as a potential precursor for II was 3,3-dichloroallyltrimethylsilane, $Me_3SiCH_2CH{=}CCl_2$ *. This was readily prepared. The condensation of trichlorosilane with 1,1,3-trichloropropene by the method of Furuya and Sukawa [2] (eq. 1) gave $Cl_3SiCH_2CH{=}CCl_2$ whose methylation with methylmagnesium bromide produced the desired silane.

$$Cl_2C{=}CHCH_2Cl + HSiCl_3 + Et_3N \xrightarrow[Et_2O]{CuCl} Cl_3SiCH_2CH{=}CCl_2 + Et_3NH^+Cl^- \quad (1)$$

The hoped-for reaction of $Me_3SiCH_2CH{=}CCl_2$ with n-butyllithium is the one shown in eq. 2. Metalation α to a silyl group is a favorable process since silicon

$$Me_3SiCH_2CH{=}CCl_2 + n\text{-}C_4H_9Li \rightarrow Li(Me_3SiCHCHCCl_2) + n\text{-}C_4H_{10} \quad (2)$$

stabilizes an adjacent negative charge [3]. In fact, trimethylsilylallyllithium, $Li(Me_3SiCHCHCH_2)$, is readily prepared by reaction of allyltrimethylsilane with n-butyllithium [4,5]. However, the two chlorine atoms in $Me_3SiCH_2CH{=}CCl_2$ also will have activating effects on the attack by n-butyllithium, and these will oppose the desired metalation process. On the one hand, they will enhance the acidity of the vinyl proton, making it more reactive toward a base; on the other hand, the two chlorine substituents will mutually enhance each other's reactivity toward lithium/chlorine exchange with an alkyllithium. Thus $Me_3SiCH_2CH{=}CCl_2$ offers three potential sites for attack by n-butyllithium.

In the initial experiment, a molar equivalent of n-butyllithium in hexane was added to a solution of $Me_3SiCH_2CH{=}CCl_2$ in tetrahydrofuran (THF) which was cooled to −90°C. After 30 min, an excess of trimethylchlorosilane was added to the reaction mixture. The products were an acetylenic silane, 2,2,6,6-tetramethyl-2,6-disila-3-heptyne, $Me_3SiC{\equiv}CCH_2SiMe_3$, in 26% yield, and 2,2,6,6-tetramethyl-2,6-disila-3-chloro-3-heptene, $Me_3SiC(Cl){=}CH\text{-}CH_2SiMe_3$, in 6% yield. A 68% recovery of the starting silane was realized.

Further experiments (Table 1) showed that longer reaction times or higher temperatures increase the yield of the acetylene. The last three experiments

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* The action of n-butyllithium on the isomeric $Me_3SiCCl_2CH{=}CH_2$ was reported in ref. 1.

TABLE 1

REACTIONS OF 3,3-DICHLOROALLYLTRIMETHYLSILANE WITH ONE MOLAR EQUIVALENT OF n-BUTYLLITHIUM. TRIMETHYLCHLOROSILANE QUENCH

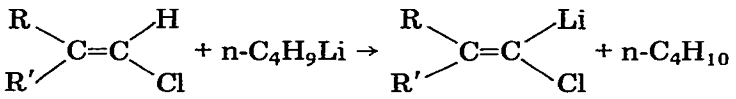
Reaction temperature (°C)	Reaction time (min)	Relative yields [a]	
		$Me_3SiC{\equiv}CCH_2SiMe_3$	$Me_3SiCH_2CH{=}CCl_2$
−90	30	26 [b]	68 [b]
−90	150	59	41
−46	30	55	45
−1	30	53	47

[a] Relative ratio determined by GLC. [b] Absolute yield determined by GLC (internal standard method).

show roughly the same result, that just over one-half of the starting material is converted to the acetylene. Apparently, the conditions of the first experiment did not allow the reaction to go to completion.

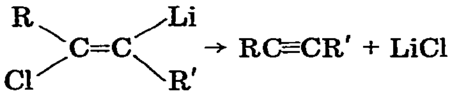
The fact that about one-half of the starting material remains unreacted suggests that two molar equivalents of n-butyllithium are consumed per equivalent of substrate. However, doubling the amount of the lithium reagent caused more deprotonation of the substrate, and on reaction of the organolithium intermediates with trimethylchlorosilane, 1,3,3-tris(trimethylsilyl)propyne, $Me_3SiC{\equiv}CCH(SiMe_3)_2$, was formed in 19% yield, in addition to $Me_3SiC{\equiv}CCH_2SiMe_3$ (37%). Such multiple substitution had been observed by West et al. [6], who obtained the same tris(trimethylsilyl)propyne in a reaction of an excess of n-butyllithium with propyne with subsequent addition of trimethylchlorosilane.

These observations are explicable in terms of initial metalation of the vinyl proton of $Me_3SiCH_2CH{=}CCl_2$. Previous work reported by Köbrich et al. [7—9] is pertinent. Low temperature reactions of n-butyllithium with equimolar quantities of mono-, di- (*cis*- and *trans*-) and tri-chloroethylene were found to result in metalation of the vinylic hydrogens to give α-chlorovinyllithium compounds (eq. 3). The stabilities of these products depended on their configuration. The least stable were those with vicinal chlorine and lithium substitution in *trans* relationship. These decomposed by *trans*-elimination to give an acetylene (eq. 4). In those cases where a chloroacetylene was produced, further reaction with n-butyllithium gave alkynyllithium reagents. Such chemistry is involved in the $Me_3SiCH_2CH{=}CCl_2$/$n\text{-}C_4H_9Li$ interaction.



(3)

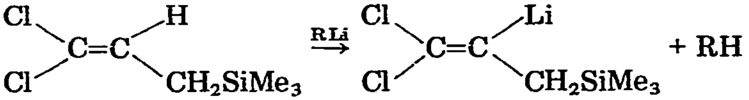
(R, R' = H and/or Cl)



(4)

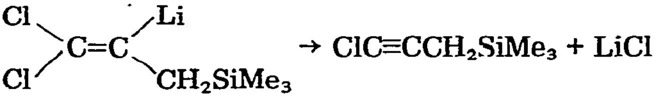
(R, R' = H and/or Cl)

The initial step must be metalation (eq. 5). The product undergoes *trans-β*-



(5)

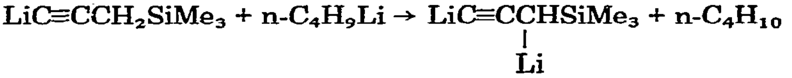
elimination of lithium chloride (eq. 6). The chloroacetylene produced reacts



(6)

with n-butyllithium, giving Li/Cl exchange (eq. 7). The reaction sequence (5,6,7) utilizes two molar equivalents of n-butyllithium per mol of $Me_3SiCH_2CH=CCl_2$. If excess n-butyllithium is present, the alkynyllithium reagent III undergoes further metalation to give the dilithium species IV (eq. 8). Addition of trimethylchlorosilane to such reaction mixtures results in formation of the silylation products of III and IV, $Me_3SiC{\equiv}CCH_2SiMe_3$ and $Me_3SiC{\equiv}CCH(SiMe_3)_2$, respectively. Since the initial lithium reagent produced (eq. 5) is only a transient species which undergoes rapid β-elimination of lithium chloride, it is clear why, as Table 1 shows, low reaction temperatures are not required. The first lithium reagent which persists, III, is stable at room temperature.

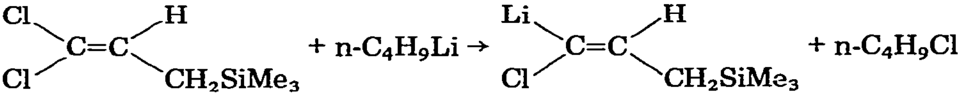
$$ClC{\equiv}CCH_2SiMe_3 + n\text{-}C_4H_9Li \rightarrow \underset{(III)}{LiC{\equiv}CCH_2SiMe_3} + n\text{-}C_4H_9Cl \quad (7)$$



$$LiC{\equiv}CCH_2SiMe_3 + n\text{-}C_4H_9Li \rightarrow LiC{\equiv}C\underset{Li}{\underset{|}{C}}HSiMe_3 + n\text{-}C_4H_{10} \quad (8)$$

(IV)

The small amount of 2,2,6,6-tetramethyl-2,6-disila-3-chloro-3-heptene formed in the $Me_3SiCH_2CH=CCl_2$/n-C_4H_9Li/Me_3SiCl reaction results from competitive Li/Cl exchange as shown in eq. 9. Reagent V, an α-chlorovinyllithium species, is sufficiently stable for reaction with trimethylchlorosilane to take place, giving $Me_3SiC(Cl)=CHCH_2SiMe_3$. It is clear that the β-Cl effect on the acidity of a vinyl proton is greater than the α-Si effect on the acidity of a methylene proton, and thus the desired chemistry (eq. 2) did not develop.



(9)

(V)

Our successful route to *gem*-chloro(trimethylsilyl)allyllithium involved the transmetalation reaction between $Ph_3PbCH_2CH=C(Cl)SiMe_3$ and n-butyllithium. The required organolead precursor was prepared by reaction of $Ph_3PbMgBr$ with $Me_3SiC(Cl)=CHCH_2Cl$ *. A similar route should, in principle, be applicable

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* Such a procedure also served well in the synthesis of *gem*-dichloroallyllithium [10]: $CCl_2=CHCH_2Cl \xrightarrow{Ph_3PbMgBr} CCl_2=CHCH_2PbPh_3 \xrightarrow{n\text{-}BuLi} Li[CCl_2CHCH_2]$. It is apparent that such transmetalation processes occur more readily than vinyl proton metalation β to a vinylic chlorine atom.

to the synthesis of $Ph_3PbCH(SiMe_3)CH{=}CCl_2$, VI, and via reaction of the latter with n-butyllithium, of $Li(Me_3SiCHCHCCl_2)$. This would require a suitable starting material for the preparation of the required lead compound. Allylic bromination of $Me_3SiCH_2CH{=}CCl_2$ might provide a route to $Me_3SiCHBrCH{=}CCl_2$, whose reaction with $Ph_3PbMgBr$ then would be expected to give the desired VI. However, such allylic bromination of $Me_3SiCH_2CH{=}CCl_2$ could well proceed with allylic rearrangement, giving $Me_3SiCH{=}CHCCl_2Br$ rather than the desired bromide. Indeed, Corriu et al. [4] had reported that allylic bromination of allyltriphenylsilane with *N*-bromosuccinimide gave the rearranged bromide, $Ph_3SiCH{=}CHCH_2Br$. Nevertheless, we examined the allylic bromination of $Me_3SiCH_2CH{=}CCl_2$ with *N*-bromosuccinimide in carbon tetrachloride in the presence of a catalytic amount of benzoyl peroxide. This reaction gave a 91% yield of a monobromination product. The NMR and IR spectra of this product, however, showed it to be $Me_3SiCH{=}CHCCl_2Br$, rather than the desired $Me_3SiCHBrCH{=}CCl_2$. Presumably, rapid rearrangement of the initially formed radical, VII, to the more stable VIII took place before bromine atom abstraction occurred.

$$Me_3Si\dot{C}HCH{=}CCl_2 \qquad\qquad Me_3SiCH{=}CH\dot{C}Cl_2$$

(VII) (VIII)

Such allyl radical rearrangements have been discussed in a review by Walling [11].

It would appear that there is no easy route to $Li(Me_3SiCHCHCCl_2)$.

Experimental

General comments. The "general comments" in the preceding paper [1] are applicable.

Preparation of 3,3-dichloroallyltrichlorosilane and 3,3-dichloroallyltrimethylsilane

(a) $Cl_3SiCH_2CH{=}CCl_2$. A two-liter, three-necked round-bottomed flask, equipped with a 500 ml pressure-equalizing addition funnel, a mechanical stirrer and a Claisen adapter fitted with a no-air stopper and a nitrogen inlet, was charged with 4.95 g (50 mmol) of CuCl, 139 ml (1.0 mol) of triethylamine (distilled from NaOH pellets) and 500 ml of diethyl ether. The addition funnel was topped with a no-air stopper and charged by syringe with 100.0 ml (1.0 mol) of 1,1,3-trichloropropene and 99.7 ml (1.0 mol) of trichlorosilane. The Claisen adapter was replaced with a reflux condenser topped with a nitrogen inlet tube and then the contents of the addition funnel were added dropwise during 80 min while the reaction mixture was stirred and maintained at reflux. During the course of the addition the following color changes were observed: initially, olive green, to colorless (after the first drops had been added) to yellow, then orange and, finally, brown. Subsequently, the addition funnel and the reflux condenser were replaced by a glass stopper and a still head. About 400 ml of a trichlorosilane/diethyl ether mixture was distilled at 37°C. The residue was transfered, under nitrogen, to a distillation flask and was trap-to-trap distilled at 0.03 mmHg, temperature to ~150°C, into a receiver cooled with liquid nitrogen. The distillate was fractionally distilled at reduced pressure

to give 85.0 g (35%) of $Cl_3SiCH_2CH{=}CCl_2$, b.p. 87—88.5°C/26 mmHg. (Found: C, 14.99; H, 1.32. $C_3H_3Cl_5Si$ calcd.: C, 14.74; H, 1.24%.) NMR (CCl_4): δ 2.49 (d, J 8 Hz, 2H, CH_2) and 5.87 ppm (t, J 8 Hz, 1H, =CH).

(b) $Me_3SiCH_2CH{=}CCl_2$. The reaction of 85.0 g (0.35 mol) of $Cl_3SiCH_2CH{=}CCl_2$ with methylmagnesium bromide in diethyl ether from 1.40 mol of magnesium, using standard Grignard alkylation procedure (non-hydrolytic work-up), gave 54.35 g (85%) of $Me_3SiCH_2CH{=}CCl_2$, b.p. 73—74°C/31 mmHg, n_D^{25} 1.4604. (Found: C, 39.47; H, 6.63; Cl, 38.77. $C_6H_{12}Cl_2Si$ calcd.: C, 39.35; H, 6.60; Cl, 38.71%.) NMR (CCl_4): δ 0.12 (s, 9H, Me_3Si), 1.65 (d, J 9 Hz, 2H, CH_2) and 5.85 ppm (t, J 9 Hz, 1H, =CH). IR (film): ν(C=C) 1615 cm^{-1}.

Reaction of 3,3-dichloroallyltrimethylsilane with n-butyllithium

A 500 ml, three-necked Morton flask, equipped with a mechanical stirrer, no-air stopper and a Claisen adapter fitted with a low-temperature thermometer and a nitrogen inlet tube, was charged with 2.874 g (15.7 mmol) of $Me_3SiCH_2CH{=}CCl_2$ dissolved in 250 ml of THF. The solution was cooled to —91 ± 2°C * and then a 2.57 N solution of n-butyllithium (17.2 mmol) in hexane was added by syringe over a 15 min period. The resulting clear, lavendar solution was stirred at —90°C for 30 min and then 2.60 ml (~20 mmol) of trimethylchlorosilane was added during a 2 min period. The reaction mixture was stirred at —90°C for 30 min. The clear, colorless solution which resulted was allowed to warm slowly to room temperature and then was hydrolyzed to a dry end-point with saturated aqueous ammonium chloride. Filtration was followed by concentration of the filtrate at reduced pressure. GLC analysis of the residue (4 ft., 20% SE-30 at 110°C and 6 ft. Carbowax at 110°C) showed the presence of three components. These were isolated by GLC and were identified as starting material, $Me_3SiCH_2CH{=}CCl_2$, 10.7 mmol, 68% recovery (by IR and NMR); $Me_3SiC{\equiv}CCH_2SiMe_3$, 4.08 mmol (26%), whose NMR spectrum (in CCl_4: δ 0.17 (s, 18H, Me_3Si), and 1.52 ppm (s, 2H; CH_2)) matched that reported for this compound by West and Jones [6]; $Me_3SiC(Cl){=}CHCH_2SiMe_3$, 0.94 mmol (6%), n_D^{25} 1.4530 (lit. [1] n_D^{25} 1.4529), whose NMR and IR spectra matched those of an authentic sample (cf. preceding paper [1]).

The results of other 1/1 $Me_3SiCH_2CH{=}CCl_2$/n-BuLi/Me_3SiCl reactions are given in Table 1.

A similar reaction was carried out in which 3.63 mmol of $Me_3SiCH_2CH{=}CCl_2$ in 200 ml of THF at 1°C was treated with 7.97 mmol of n-butyllithium in hexane. The caramel-colored reaction mixture was treated with 10 mmol of trimethylchlorosilane. Work-up as above, followed by GLC analysis and product isolation by GLC, showed the following compounds to be present: $Me_3SiC{\equiv}CCH_2SiMe_3$, 1.34 mmol (37%) and $Me_3SiC{\equiv}CCH(SiMe_3)_2$, 0.69 mmol (19%), whose IR and NMR spectra matched the published spectra of this compound [6,12] (NMR (CCl_4): δ 0.15 (s, 27H, Me_3Si) and 1.05 ppm (s, 1H, CH)).

Reaction of 3,3-dichloroallyltrimethylsilane with N-bromosuccinimide

A 200 ml, three-necked Morton flask, equipped with a reflux condenser and

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* Reaction temperatures are uncorrected. They were obtained using a pentane (total immersion type) thermometer which was immersed into the reaction mixture to a depth of ~3 cm. A stem correction of 8—10°C (to lower temperature) is appropriate.

a nitrogen inlet tube was charged with 8.898 g (48.6 mmol) of $Me_3SiCH_2CH{=}CCl_2$, 9.225 g (46.2 mmol) of *N*-bromosuccinimide, a spatula tip-ful of benzoyl peroxide and 100 ml of carbon tetrachloride. The mixture was stirred and heated at reflux for 5 h, at which time iodide-starch paper was negative. The succinimide was filtered and the filtrate was trap-to-trap distilled (room temperature at 0.03 mmHg). The distillate was concentrated (to 75°C/33 mmHg) and the residue was trap-to-trap distilled at 0.07 mmHg (heat gun), to give 11.6 g (91%) of $Me_3SiCH{=}CHCCl_2Br$, n_D^{25} 1.5082 (Found: C, 27.95; H, 4.36; total halogen, 56.83%. $C_6H_{11}Cl_2BrSi$ calcd.: C, 27.50; H, 4.23; total halogen, 57.56%.) NMR (CCl_4): δ 0.23 (s, 9H, Me_3Si), 4.03 (d, J 12 Hz, 1H, Si—CH=), 6.00 ppm (d, J 12 Hz, 1H, $=CHCCl_2Br$). The NMR spectrum was almost superimposable with that of $Me_3SiCH{=}CHCBr_3$ [13]. IR (film): ν(C=C) 1605(sh), 1595 cm^{-1}.

Acknowledgments

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