

THE REACTION OF *gem*-DICHLOROALLYLLITHIUM WITH HALIDES OF SILICON, GERMANIUM, TIN AND MERCURY, AND WITH TRIPHENYLBORANE. EQUILIBRIUM vs. KINETIC CONTROL OF REGIOSELECTIVITY *

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Summary

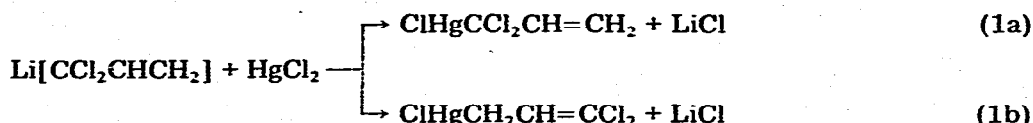
The reactions of *gem*-dichloroallyllithium, which was prepared by the low temperature reactions of *n*-butyllithium with 3,3,3-trichloropropene or with 3,3-dichloroallyltriphenyllead, with trimethylchlorosilane, trimethylchlorogermane, trimethyltin bromide, mercuric chloride and iodomethane were examined. With trimethylchlorosilane and iodomethane, 1,1-dichloroallyl products were obtained exclusively and with trimethyltin bromide and mercuric chloride, only 3,3-dichloroallyl products were obtained. The reaction with trimethylchlorogermane (equimolar amount) gave a 5.7/1 mixture of $\text{Me}_3\text{GeCCl}_2\text{CH}=\text{CH}_2$ and $\text{Me}_3\text{GeCH}_2\text{CH}=\text{CCl}_2$. This ratio was decreased to 0.65 when a deficiency of trimethylchlorogermane was used because, as a control experiment confirmed, *gem*-dichloroallyllithium equilibrates with $\text{Me}_3\text{GeCCl}_2\text{CH}=\text{CH}_2$ to form $\text{Me}_3\text{GeCH}_2\text{CH}=\text{CCl}_2$. *gem*-Dichloroallyllithium formed an adduct with triphenylborane with structure $\text{Li}[\text{Ph}_3\text{BCH}_2\text{CH}=\text{CCl}_2]$, and its hydrolysis (acid medium) gave $\text{HCCl}_2\text{CH}=\text{CH}_2$.

Introduction

During the course of our studies of functional halomethylmercury reagents of the type RHgCX_2Z ($\text{Z} = \text{CF}_3, \text{Ph}, \text{CO}_2\text{R}, \text{SO}_2\text{R}, \text{etc.}$) [2] we became interested in the possibility of generating vinylchlorocarbene, $\text{ClCCH}=\text{CH}_2$, via the organomercury route. For this purpose reagents such as $\text{PhHgCClXCH}=\text{CH}_2$, $\text{ClHgCClXCH}=\text{CH}_2$ or $\text{Hg}(\text{CClXCH}=\text{CH}_2)_2$ ($\text{X} = \text{Cl}$ or Br) were required. One possible route for their preparation which we considered involved the use of the at that time unknown organolithium reagent, *gem*-dichloroallyllithium. The hoped-for reaction with mercuric chloride was that shown in eq. 1a, although

* Preliminary communication: Ref. 1.

the reaction shown in eq. 1b also was possible since allylic lithium reagents of types $\text{Li}[\text{RCHCHCH}_2]$ and $\text{Li}[\text{R}_2\text{CCHCH}_2]$ are known to be ambident nucleophiles [3]. *gem*-Dichloroallyllithium itself was of some interest in other respects.



A halogenated allyllithium reagent had not yet been prepared and it was not even certain that it would be sufficiently stable to allow its use in synthesis even at low temperatures. In view of its potential ambident character, its reactions with substrates other than mercuric halides, both organic and inorganic, would be of considerable interest.

The present paper describes our studies devoted to the synthesis of *gem*-dichloroallyllithium and its reactions with inorganic and organometallic substrates. We have reported separately on its reactions with organic substrates such as aldehydes and ketones, esters and halides [4].

Results and discussion

The commercial availability of 1,1,1,3-tetrachloropropane (PCR Chemicals, Inc.) and its facile dehydrochlorination to 3,3,3-trichloropropene [5] provided the basis for two routes to *gem*-dichloroallyllithium. The first used the well-known and often used lithium/halogen exchange reaction (eq. 2). When this reaction was carried out at about -110° in THF or in a THF/ether solvent system using commercial *n*-butyllithium in hexane, a deep purple solution was formed. When the reaction mixture was allowed to warm slowly, the color changed to blue at about -105 to -100°C and then to red-brown at about -85 to -90°C .



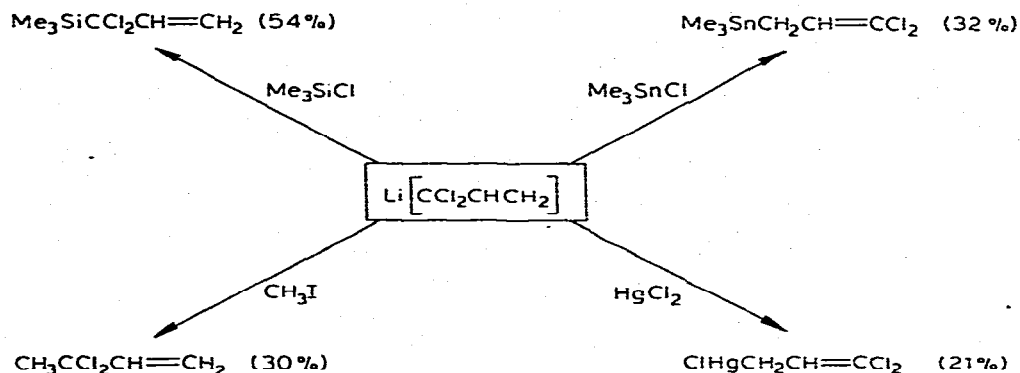
This color persisted to room temperature and was indicative of complete decomposition of the reagent which proceeded with formation of an insoluble, brown and foul-smelling residue. If a substrate capable of reaction with an organolithium reagent was added to the reaction mixture at the purple or the blue stage, then products derived from reactions of *gem*-dichloroallyllithium were obtained in moderate yield (Scheme 1).

The fact that trimethylchlorosilane and iodomethane, on the one hand, and trimethyltin chloride and mercuric chloride, on the other hand, reacted with *gem*-dichloroallyllithium to form the new element-carbon bonds at opposite termini of the ambident lithium reagent was of considerable interest, and this remarkable finding will receive further attention below. However, in order to develop the chemistry of *gem*-dichloroallyllithium in the desired breadth, a better synthesis of this reagent was desirable.

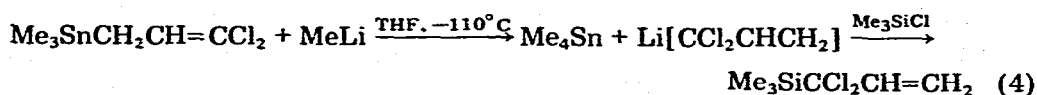
It was the observation that *gem*-dichloroallyllithium also could be prepared

* The temperatures cited in this paper are stem temperatures on pentane thermometers (bulb immersion) and are around $8-10^\circ\text{C}$ higher than the actual temperatures in the cooled reaction mixtures.

SCHEME 1

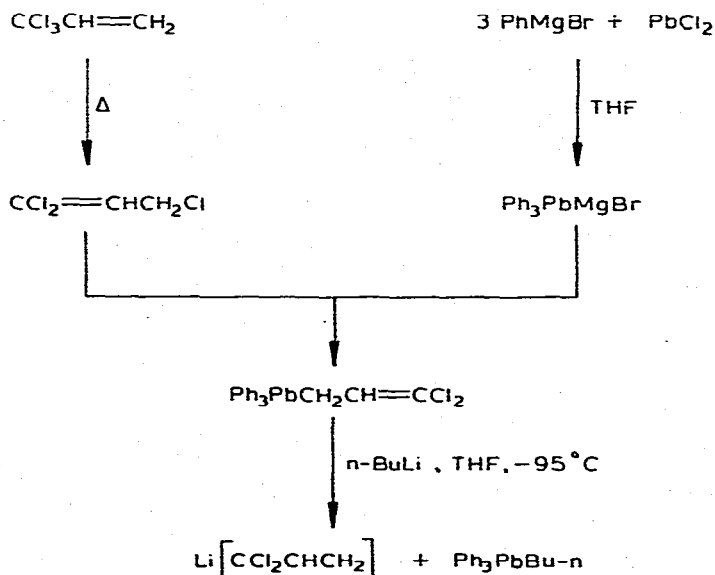


from 3,3-dichloroallyltrimethylmethyltin (eq. 4) which provided the basis for



an alternate and much-improved route to this reagent (Scheme 2). An initial

SCHEME 2

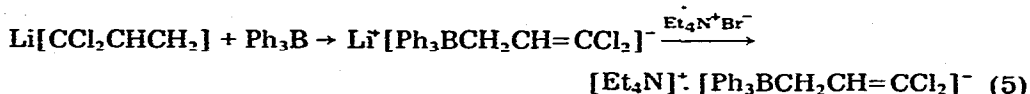


attempt to prepare either $\text{Ph}_3\text{PbCH}_2\text{CH}=\text{CCl}_2$ or $\text{Ph}_3\text{PbCCl}_2\text{CH}=\text{CH}_2$ by the reaction of triphenylleadlithium with 3,3,3-trichloropropene was only partially successful, giving 3,3-dichloroallyltriphenyllead, but only in low yield [6]. The reaction of triphenylleadmagnesium bromide with $\text{CCl}_2=\text{CHCH}_2\text{Cl}$, on the

other hand, was quite clean and gave $\text{Ph}_3\text{PbCH}_2\text{CH}=\text{CCl}_2$ in high yield.

The reaction of 3,3-dichloroallyltriphenyllead with *n*-BuLi in THF proceeded very cleanly at -95°C , giving *gem*-dichloroallyllithium in virtually quantitative yield. The resulting reagent solution is light amber in color, so the purple and blue color of the solutions formed in the reaction of *n*-butyllithium with $\text{CCl}_3\text{CH}=\text{CH}_2$ must have been a result of species formed in some secondary process. (Although we have no evidence on this point, it seems likely that a reaction of *gem*-dichloroallyllithium with $\text{CCl}_3\text{CH}=\text{CH}_2$ is involved). *gem*-Dichloroallyllithium, as prepared in THF by the $\text{Ph}_3\text{PbCCH}_2\text{CH}=\text{CCl}_2$ /*n*-BuLi reaction, appears to be quite stable at -95°C , but when it is allowed to warm to -65°C , color changes indicative of beginning decomposition are observed. Such deterioration appears to be rapid above -60°C .

The reactions of *gem*-dichloroallyllithium generated via $\text{Ph}_3\text{PbCH}_2\text{CH}=\text{CCl}_2$ with trimethylchlorosilane, trimethyltin chloride, mercuric chloride and iodo-methane proceeded as shown in Scheme 1. The product yields, however, were much better. Thus, $\text{Me}_3\text{SiCCl}_2\text{CH}=\text{CH}_2$ was formed in 99% yield (by GLC; 73% isolated yield), $\text{Me}_3\text{SnCH}_2\text{CH}=\text{CCl}_2$ in 95% yield (distilled), $\text{ClHgCH}_2\text{CH}=\text{CCl}_2$ in 98% yield. In none of these reactions was the other, isomeric dichloroallyl product detected. It is clear that the $\text{Ph}_3\text{PbCH}_2\text{CH}=\text{CCl}_2$ /*n*-BuLi route to *gem*-dichloroallyllithium is the procedure of choice. The hydrolysis of the reagent thus prepared gave exclusively $\text{CHCl}_2\text{CH}=\text{CH}_2$ (87% yield) [4] and its reaction with triphenylborane gave the $[\text{Ph}_3\text{BCH}_2\text{CH}=\text{CCl}_2]^-$ anion as the sole product (eq. 5).



The substrate dependent regiospecificity with respect to the ambident allyl reagent in these reactions was rather puzzling. For instance, the exclusive formation of $\text{Me}_3\text{SnCH}_2\text{CH}=\text{CCl}_2$ in the reaction of $\text{Li}[\text{CCl}_2\text{CHCH}_2]$ with trimethyltin bromide, in contrast to the exclusive production of $\text{Me}_3\text{SiCCl}_2\text{CH}=\text{CH}_2$ in its reaction with trimethylchlorosilane, was surprising.

It was the reaction of *gem*-dichloroallyllithium with trimethylchlorogermane which provided a plausible and experimentally verifiable explanation of the regiospecificity of these reactions of this lithium reagent. Reaction of $\text{Li}[\text{CCl}_2\text{CHCH}_2]$ with trimethylchlorogermane in a 1/1 molar ratio gave a 5.7/1 mixture of both possible isomers: $\text{Me}_3\text{GeCCl}_2\text{CH}=\text{CH}_2$ (a solid, m.p. $70.5-71^\circ\text{C}$) and $\text{Me}_3\text{GeCH}_2\text{CH}=\text{CCl}_2$, a liquid, in essentially quantitative yield. Proton NMR spectroscopy served well in distinguishing these isomers (and in assigning structures to all of the products reported in this paper). The 1,1-dichloroallyl product, $\text{Me}_3\text{GeCCl}_2\text{CH}=\text{CH}_2$, showed the three vinyl protons as an ABC multiplet at δ 5.08–6.34 ppm; $\text{Me}_3\text{GeCH}_2\text{CH}=\text{CCl}_2$ showed its one vinyl proton as a triplet (J 9.3 Hz) at δ 5.88 ppm and the CH_2 protons as a doublet at δ 1.74 ppm. (cf. Fig. 1). A finding of significance to the problem of regioselectivity of the ambident lithium reagent was that the product isomer ratio, $\text{Me}_3\text{GeCCl}_2\text{CH}=\text{CH}_2$ / $\text{Me}_3\text{GeCH}_2\text{CH}=\text{CCl}_2$, could be changed by changing the reactant stoichiometry. When only 0.63 molar equivalent of trimethylchlorogermane was added to the *gem*-dichloroallyllithium solution, i.e., when a reaction was carried out with an

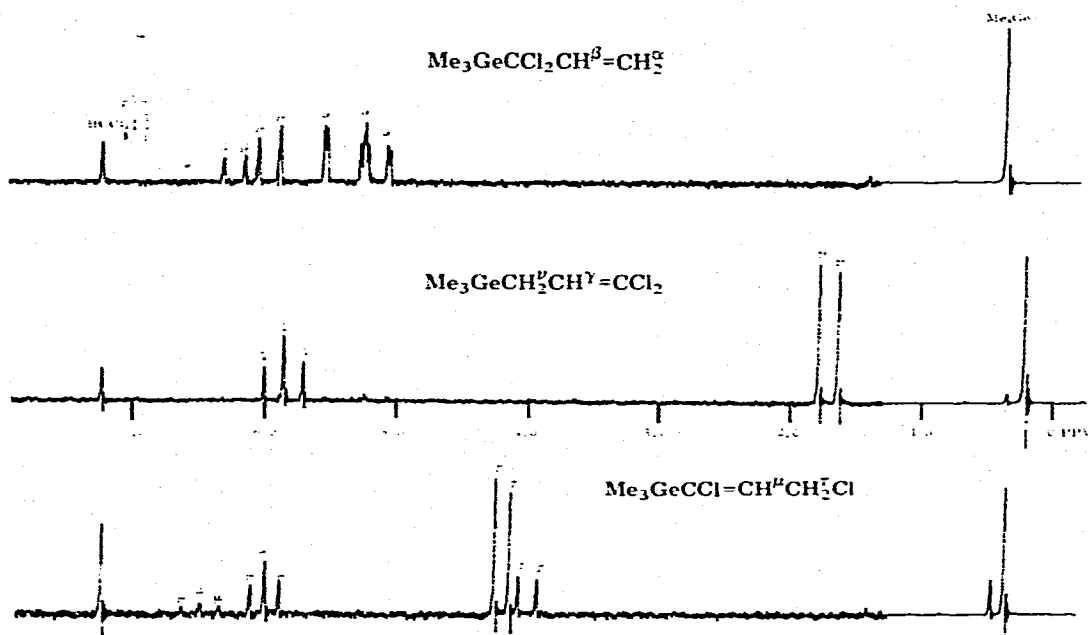
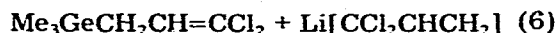


Fig. 1. Proton NMR spectra of isomeric dichloroallyltrimethylgermanes.

excess of the lithium reagent, the product ratio, as defined above, was 0.65 (vs. 5.7 for a 1/1 reaction). Such a change in stoichiometry was without effect in the reaction of $\text{Li}[\text{CCl}_2\text{CHCH}_2]$ with trimethylchlorosilane.

A reasonable explanation of these results is that $\text{Me}_3\text{GeCCl}_2\text{CH}=\text{CH}_2$ is the product of kinetic control and that $\text{Me}_3\text{GeCH}_2\text{CH}=\text{CCl}_2$ is the product of thermodynamic control. Formation of the latter at the expense of the former is achieved through repeated transmetalation reactions between $\text{Me}_3\text{GeCCl}_2\text{CH}=\text{CH}_2$ and *gem*-dichloroallyllithium (an equilibrium process) (eq. 6). In a 1/1 reaction, the lithium reagent is completely consumed and hence the product of

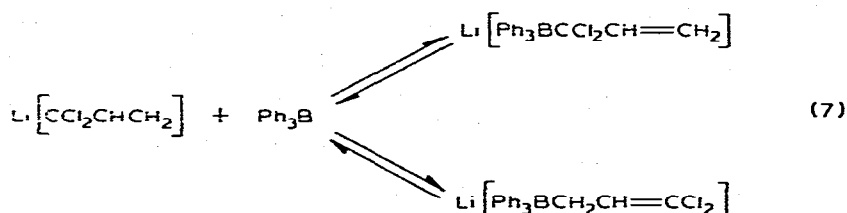


kinetic control predominates. Confirmation of these ideas was provided by the observation that treatment of isomerically pure $\text{Me}_3\text{GeCCl}_2\text{CH}=\text{CH}_2$ with a ca. 50% excess of *gem*-dichloroallyllithium for 2 h at -97°C resulted in formation of the other isomer, with a final $\text{Me}_3\text{GeCCl}_2\text{CH}=\text{CH}_2/\text{Me}_3\text{GeCH}_2\text{CH}=\text{CCl}_2$ ratio of 0.51.

The other results of this study may now be explained. The silicon compound, $\text{Me}_3\text{SiCCl}_2\text{CH}=\text{CH}_2$, is stable to such transmetalation, so it is the product of kinetic control which is isolated. The iodomethane product, $\text{CH}_3\text{CCl}_2\text{CH}=\text{CH}_2$, also is stable to further change by a transmetalation process. Allyltin compounds, on the other hand, are very reactive toward organolithium reagents [7], so $\text{Me}_3\text{SnCCl}_2\text{CH}=\text{CH}_2$, the assumed product of kinetic control of the $\text{Me}_3\text{SnBr}/$

$\text{Li}[\text{CCl}_2\text{CHCH}_2]$ reaction, would be expected to be very reactive in such transmetalation with *gem*-dichloroallyllithium. On that basis, the isolation of $\text{Me}_3\text{SnCH}_2\text{CH}=\text{CCl}_2$ as the exclusive product of this reaction when it is carried out in 1/1 stoichiometry is not surprising. However, the chemistry in this reaction must be more complicated. In an attempt to produce some of the other isomer, $\text{Me}_3\text{SnCCl}_2\text{CH}=\text{CH}_2$, a reaction was carried out in which the lithium reagent was added to a separate flask which contained an excess of trimethyltin bromide. In the presence of an excess of Me_3SnBr , the effect of an organotin equilibrium analogous to that shown in eq. 6 should be minimal, yet in this reaction $\text{Me}_3\text{SnCH}_2\text{CH}=\text{CCl}_2$ again was produced as the sole product. Allylic tin compounds are known to undergo facile isomerization induced by Lewis acids and Lewis bases under mild condition [8], and so it may be that $\text{Me}_3\text{SnCCl}_2\text{CH}=\text{CH}_2$ -to- $\text{Me}_3\text{SnCH}_2\text{CH}=\text{CCl}_2$ isomerization can be induced by other components of our reaction mixtures (Me_3SnBr , LiBr , THF), especially upon mild heating up to 60°C in the trap-to-trap distillation during non-hydrolytic work-up.

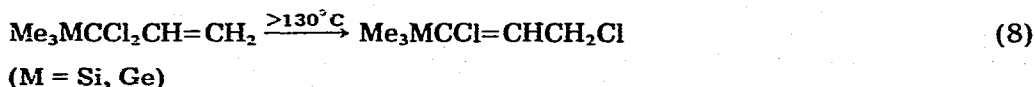
The exclusive formation of $\text{CCl}_2=\text{CHCH}_2\text{HgCl}$ also can be explained in terms of such isomerization of an initially formed $\text{CH}_2=\text{CHCCl}_2\text{HgCl}$ induced by mercuric chloride since this reagent is known to effect isomerization of allylic mercurials [9]. The formation of only the $[\text{Ph}_3\text{BCH}_2\text{CH}=\text{CCl}_2]^-$ ion in the reaction of *gem*-dichloroallyllithium with triphenylborane can be rationalized in terms of a reversible addition process which would lead to the formation of the thermodynamically more stable product (eq. 7).



In summary, *gem*-dichloroallyllithium is a useful reagent in organometallic synthesis, but one must accept that the new element-carbon bond ($\text{M}-\text{CCl}_2\text{CH}=\text{CH}_2$ or $\text{M}-\text{CH}_2\text{CH}=\text{CCl}_2$) is not always the one which is desired. Thus, for instance, our initial objective, the synthesis of a $\text{CH}_2=\text{CHCCl}_2$ -substituted mercurial, was not realized. In most cases, experimental manipulation cannot effect a change in the product formed because the isolated product either is kinetically stable (e.g., $\text{Me}_3\text{SiCCl}_2\text{CH}=\text{CH}_2$) or because it is the thermodynamically more stable product of facile isomerization processes (e.g., $\text{Me}_3\text{SnCH}_2\text{CH}=\text{CCl}_2$ and $\text{CCl}_2=\text{CHCH}_2\text{HgCl}$).

In conclusion, we take note of some further chemistry of the products of type $\text{Me}_3\text{MCCl}_2\text{CH}=\text{CH}_2$ ($\text{M} = \text{Si}, \text{Ge}$). In their preparation by the *gem*-dichloroallyllithium route, an excess of *n*-butyllithium must be avoided. During the course of this work it was found that $\text{Me}_3\text{SiCCl}_2\text{CH}=\text{CH}_2$ undergoes lithium/chlorine exchange on treatment with *n*-butyllithium, giving the new reagent $\text{Li}[\text{Me}_3\text{SiCClCHCH}_2]$, whose chemistry will be the subject of a subsequent report [10]. Also, it was found that the $\text{Me}_3\text{MCCl}_2\text{CH}=\text{CH}_2$ undergo facile allylic rear-

rangement via chloride migration when they are heated above 130°C (eq. 8). The



silane thus produced may itself find useful application in synthetic organosilicon chemistry.

Experimental

General comments. All reactions were carried out in flame-dried glassware under an atmosphere of prepurified nitrogen. Rigorously dried solvents were used in all organolithium reactions. The reaction temperatures which are reported are uncorrected. They were obtained using a pentane (total immersion) thermometer immersed to a depth of about 3 cm in the stirred solution. The actual solution temperatures thus were about 8–10°C lower than the thermometer reading. Gas-liquid chromatography was employed for collection of samples for analysis, spectroscopic measurements and refractive index determination and for yield determinations using internal standards and empirically determined response factors. Nuclear magnetic resonance spectra were recorded using a Varian Associates T60 or an Hitachi-Perkin-Elmer R20-B high resolution spectrometer. Proton chemical shifts are reported in δ units (ppm) using tetramethylsilane (TMS) as internal standard. Infrared spectra were obtained using a Perkin-Elmer 457A grating infrared spectrophotometer.

n-Butyllithium in hexane was purchased from Alfa/Ventron. 1,1,1,3-Tetrachloropropane was purchased from PCR Chemicals, Inc. Trimethylchlorosilane was donated by the Union Carbide Corp.

Preparation of starting materials

1,1,1,3-Tetrachloropropane was dehydrochlorinated to give 3,3,3-trichloropropene by the method of Haszeldine [5]. The thermal isomerization of $\text{CCl}_3\text{CH}=\text{CH}_2$ to $\text{CCl}_2=\text{CHCH}_2\text{Cl}$ by a variation of Haszeldine's procedure [5] is described in detail in our paper on the organic reactions of *gem*-dichloroallyllithium [1], as is the preparation of $\text{Ph}_3\text{PbCH}_2\text{CH}=\text{CCl}_2$.

Preparation of *gem*-dichloroallyllithium by the reaction of *n*-butyllithium with 3,3,3-trichloropropene

(a) *Reaction with trimethylchlorosilane.* A 500 ml Morton (creased) three-necked, round-bottomed flask, equipped with a high-speed stirring unit, a pentane (low temperature) thermometer and a pressure-equalizing addition funnel, was charged with 7.07 g (~5 ml, 48.5 mmol) of 3,3,3-trichloropropene, 100 ml of THF (distilled from sodium benzophenone ketyl) and 50 ml of dry diethyl ether. The solution was stirred and cooled to about -110°C. n-Butyllithium (35 ml of 1.6 M solution in hexane, ca. 55 mmol) then was added via the addition funnel, dropwise, with external cooling to maintain the temperature below -105°C. The first drops of n-butyllithium solution resulted in the formation of a deep purple color. Upon completion of the addition, the solution still was colored deep purple. The mixture was stirred at -105° to -110°C for 30 min

and then 7.3 g (67 mmol) of trimethylchlorosilane was added dropwise with stirring. The resulting reaction mixture was stirred below -90°C for 1 h and then was allowed to warm slowly to room temperature, giving a clear red-orange solution which contained a white, crystalline precipitate of lithium chloride. This mixture was poured into 500 ml of water. The separated organic layer was dried and distilled to give 90% pure $\text{Me}_3\text{SiCCl}_2\text{CH}=\text{CH}_2$, 3.75 g, b.p. 65°C at 15 torr, in 36% yield. Purification by GLC gave the pure material as a solid, m.p. $66-68^{\circ}\text{C}$.

A better product yield was obtained when the $\text{Li}[\text{CCl}_2\text{CHCH}_2]$ was prepared by addition of the trichloropropene to the *n*-butyllithium solution, i.e., by inverse addition. Thus, 23 mmol of $\text{CCl}_3\text{CH}=\text{CH}_2$ was added by syringe over a 5 min period to a solution of 20 ml of 1.6 *M* *n*-butyllithium (32 mmol) in hexane in 50 ml of THF and 15 ml of diethyl ether at -110°C . The resulting purple solution was stirred at -110°C for 15 min and then 35 mmol of Me_3SiCl was added. The reaction mixture was stirred at -110° to -100°C for 45 min and then was allowed to warm slowly. At -30°C , 3 ml of conc. HCl was added and the resulting mixture was poured into 200 ml of water. The dried organic layer was examined by GLC and found to contain 12.4 mmol (54%) of $\text{Me}_3\text{SiCCl}_2\text{CH}=\text{CH}_2$. The solvent was removed at reduced pressure and the residue was distilled to give a fraction boiling at $55-65^{\circ}\text{C}$ 5 torr. Preparative GLC served to separate a small amount of high-boiling component which was identified as 3-chloro-2,2,6,6-tetramethyl-2,6-disilahept-3-ene, $\text{Me}_3\text{SiCCl}=\text{CHCH}_2\text{SiMe}_3$ *, obtained in 17% yield.

(b) *Reaction with iodomethane.* A solution of *gem*-dichloroallyllithium was prepared as described above from 59 mmol of *n*-butyllithium and 48.8 mmol of $\text{CCl}_3\text{CH}=\text{CH}_2$. To this reagent solution was added slowly, with stirring, 4.05 ml (65 mmol) of iodomethane. After it had been stirred for 1 h below -90°C , the mixture was allowed to warm to room temperature and hydrolyzed. Trap-to-trap distillation (at 0.05 torr and room temperature) of the organic layer into a receiver at -196°C was followed by removal of solvents from the distillate. GLC analysis of the residue showed the presence (30%) of $\text{CH}_3\text{CCl}_2\text{CH}=\text{CH}_2$. Pure samples were isolated by preparative GLC (6 ft UCW 98 silicone column).

(c) *Reaction with trimethyltin bromide.* Using the procedure described in (a), a solution of $\text{Li}[\text{CCl}_2\text{CHCH}_2]$ was prepared by treatment of 53 mmol of *n*-butyllithium with 47.7 mmol of $\text{CCl}_3\text{CH}=\text{CH}_2$. To this solution was added slowly a solution of 6.1 g (25 mmol) of Me_3SnBr in 20 ml of THF. The mixture was allowed to warm slowly to -80°C and then was treated with 50 ml of 1 *M* HCl. The resulting red reaction mixture was poured into water and extracted with ether. The dried organic layer was concentrated at reduced pressure and the residue was distilled to give 1.90 g (29%) of $\text{Me}_3\text{SnCH}_2\text{CH}=\text{CCl}_2$, b.p. $73-78^{\circ}\text{C}$ at 7 torr.

Preparation of the lithium reagent by addition of 21.6 mmol of $\text{CCl}_3\text{C}=\text{CH}_2$ to 25.6 mmol of *n*-butyllithium at -110°C (inverse addition), followed by addition of 24 mmol of trimethyltin bromide, and with the same work-up with an

* This product was formed by Li/Cl exchange between the slight excess of *n*-butyllithium used and $\text{Me}_3\text{SiCCl}_2\text{CH}=\text{CH}_2$, giving the allylic lithium reagent $\text{Li}[\text{Me}_3\text{SiCClCHCH}_2]$, which reacted with trimethylchlorosilane to form the new Si-C bond at the CH_2 terminus. This lithium reagent will be the subject of a subsequent paper [10].

added wash of the organic layer with aqueous/methanolic KF to remove Me_3SnBr , gave $\text{Me}_3\text{SnCH}_2\text{CH}=\text{CCl}_2$, b.p. $41-45^\circ\text{C}$ at 1.1 torr, in 32% yield.

(d) *Reaction with mercuric chloride.* The *gem*-dichloroallyllithium was prepared by adding 59 mmol of 1.6 M *n*-butyllithium in hexane to 49 mmol of $\text{CCl}_3\text{CH}=\text{CH}_2$ in 100 ml of THF and 50 ml of diethyl ether at -105°C . To this solution was added, at -105°C , a solution of 5.43 g (20 mmol) of HgCl_2 in 20 ml of THF. The reaction mixture was stirred for 1 h at -105°C and then was allowed to warm slowly to room temperature. The mixture was filtered and the filtrate was concentrated at reduced pressure. Addition of hexane to the residual oil gave a white solid which was recrystallized from 1/1 CHCl_3 /hexane, giving white needles, m.p. $99-100^\circ\text{C}$ (1.5 g, 21% yield). The product was identified as the known (lit. [11] m.p. 100°C) $\text{CCl}_2=\text{CHCH}_2\text{HgCl}$. NMR (CDCl_3): δ (ppm) 2.60 (d, J 9 Hz, 2H, HgCH_2 , with mercury satellites, $J(\text{Hg}-\text{H})$ 293 Hz) and 6.15 ppm (t, J 9 Hz, $\text{CH}=\text{}$).

Preparation of gem-dichloroallyllithium by reaction of n-butyllithium with 3,3-dichloroallyltriphenyllead

(a) *Reaction with trimethylchlorosilane*

A 500 ml, three-necked Morton flask equipped with a mechanical stirrer, a pressure-equalizing addition funnel, a nitrogen inlet tube and a pentane thermometer was charged with 21.82 g (39.8 mmol) of $\text{Ph}_3\text{PbCH}_2\text{CH}=\text{CCl}_2$ and 300 ml of dry THF. The solution was cooled to -95°C and then a solution of 2.4 M (by Gilman titration) *n*-butyllithium in hexane (17.5 ml, 42 mmol) was added dropwise over a 30 min period. During the initial stages of the addition a light purple-pink coloration was observed, but this eventually was replaced by a light amber. The reaction mixture was stirred at -95°C for 1 h and subsequently 6.4 ml (~ 50 mmol) of freshly distilled trimethylchlorosilane was added dropwise. The reaction mixture was allowed to warm slowly to room temperature and was hydrolyzed with saturated, aqueous ammonium chloride to the dry end-point. The dried organic layer was trap-to-trap distilled at 0.1 torr into a receiver at -196°C , leaving a residue of *n*-butyltriphenyllead (19.3 g, 98%). Recrystallization from ethanol gave white needles, m.p. $47-48^\circ\text{C}$ (lit. [12] m.p. 47°C). GLC analysis of the distillate (4 ft. UCW-98 column) showed the presence of $\text{Me}_3\text{SiCCl}_2\text{CH}=\text{CH}_2$ in 99% yield. The solvents were removed at reduced pressure and the product was sublimed at 40°C and 0.5 torr to give 5.34 g (73%), of material with m.p. $64-65^\circ\text{C}$ whose IR and NMR spectra were identical with those of the product of the $\text{BuLi}/\text{CCl}_3\text{CH}=\text{CH}_2 + \text{Me}_3\text{SiCl}$ reaction.

(b) *Reaction with trimethyltin bromide*

The lithium reagent was prepared as described in (a) from 43.5 mmol of $\text{Ph}_3\text{PbCH}_2\text{CH}=\text{CCl}_2$ and 46.7 mmol of *n*-BuLi in hexane in 300 ml of THF at -95°C . To this solution was added, dropwise with stirring, 13.0 g (53.5 mmol) of Me_3SnBr . After it had warmed to room temperature, the reaction mixture was hydrolyzed with saturated, aqueous ammonium chloride. The organic layer was washed with 300 ml of 10% KF in 50% aqueous methanol (to remove Me_3SnBr), diluted with 300 ml of chloroform, washed with water, dried and trap-to-trap distilled (60°C at 0.1 torr) into a receiver at -196°C . The residue, a light yellow

oil, crystallized on cooling, giving *n*-butyltriphenyllead, 21.4 g (100%), as long white needles. The distillate was concentrated at reduced pressure and then was distilled to give 11.28 g (95%) of 3,3-dichloroallyltrimethyltin, b.p. 48–49°C at 0.5 torr, n_D^{25} 1.5205.

Since the hydrolytic work-up could have destroyed any $\text{Me}_3\text{SnCCl}_2\text{CH}=\text{CH}_2$ which might have been formed, this reaction was repeated using 32.2 mmol of $\text{Ph}_3\text{PbCH}_2\text{CH}=\text{CCl}_2$, 35 mmol of *n*-BuLi and 42 mmol of Me_3SnBr . The reaction mixture was trap-to-trap distilled directly, leaving a quantitative yield of Ph_3PbBu -*n* and LiBr. The volatiles were concentrated and distilled to give 0.59 g (25% recovery) of Me_3SnBr and 8.16 g (93%) of $\text{Me}_3\text{SnCH}_2\text{CH}=\text{CCl}_2$. The spectroscopic properties of the latter did not indicate any contamination by the 1,1-dichloroallyl isomer.

This reaction was repeated using an inverse addition procedure. *gem*-Dichloroallyllithium was prepared in one flask from 43.5 mmol of $\text{Ph}_3\text{PbCH}_2\text{CH}=\text{CCl}_2$ and 44.6 mmol of *n*-butyllithium. Another one-liter, three-necked Morton flask equipped with a mechanical stirrer, no-air stopper and Claisen adapter holding a pentane thermometer and nitrogen inlet was charged with 68 mmol of trimethyltin bromide in 200 ml of THF and cooled to –95°C. The two flasks were connected by a stainless steel cannula which was insulated by wrapping it in aircraft insulation soaked with acetone and frozen solid with liquid nitrogen. The lithium reagent solution then was transferred, under nitrogen pressure, into the Me_3SnBr solution over a period of 20 min. The temperature of both flasks was maintained at –95°C. When the transfer was complete, the reaction mixture was allowed to warm to room temperature. Trap-to-trap distillation (60°C at 0.05 torr), without hydrolysis, was followed by GLC analysis of the distillate. It was established that $\text{Me}_3\text{SnCH}_2\text{CH}=\text{CCl}_2$ had been formed in 97% yield. The only other product present (by GLC and NMR) was Me_3SnBr .

(c) Reaction with mercuric chloride

The lithium reagent was prepared by the usual procedure from 41.3 mmol of $\text{Ph}_3\text{PbCH}_2\text{CH}=\text{CCl}_2$ and 43.2 mmol of *n*-BuLi. To this solution was added, at –90°C, a solution of 12.48 g (46.0 mmol) of mercuric chloride in 35 ml of THF, dropwise with stirring. Upon completion of the addition, the reaction mixture was allowed to warm slowly to room temperature and hydrolyzed with saturated aqueous NH_4Cl to the dry end point. The dried organic layer was evaporated at reduced pressure to give a residue of 27.3 g. This material was dissolved in 200 ml of THF and treated with 50 g of mercuric chloride dissolved in THF in order to insure conversion to $\text{CCl}_2=\text{CHCH}_2\text{HgCl}$. (Addition of such an excess of mercuric chloride also would convert all of the phenyl groups attached to lead to phenylmercuric chloride, but this compound is very insoluble in organic solvents). Filtration of the reaction mixture after it had been stirred for an hour at room temperature was followed by evaporation of the filtrate at reduced pressure. The resulting residue was recrystallized from *n*-heptane to give, in two crops, 11.88 g (83%) of 3,3-dichloroallylmercuric chloride, m.p. 99–100°C (lit. [11] m.p. 100°C).

(d) Reaction with triphenylborane

To the lithium reagent, which had been prepared from 40.7 mmol of

$\text{Ph}_3\text{PbCH}_2\text{CH}=\text{CCl}_2$ and 39.8 mmol of $n\text{-BuLi}$, was added at -90°C dropwise with stirring a warm solution of 9.31 g (38.5 mmol) of triphenylborane (Orgmet, Inc.) in 50 ml of THF. The reaction mixture was allowed to warm slowly to room temperature and then was evaporated at reduced pressure. The residue was dissolved in 400 ml of anhydrous methanol, filtered and added to a solution of 10.0 g (48 mmol) of tetraethylammonium bromide in 300 ml of methanol. A white solid precipitated within 1 min. The mixture was cooled in a refrigerator and then filtered to yield 6.57 g (35%) of $[\text{Et}_4\text{N}]^+[\text{Ph}_3\text{BCH}_2\text{CH}=\text{CCl}_2]^-$. A portion of this sample which was not stored under nitrogen, as well as that additional product in the mother liquor, decomposed on standing overnight. An analytically pure sample, m.p. $207.5\text{--}209^\circ\text{C}$, was obtained by a second recrystallization from methanol.

(e) Reaction with trimethylchlorogermane

(i) With an equimolar amount of trimethylchlorogermane. The lithium reagent was prepared from 41.1 mmol of $\text{Ph}_3\text{PbCH}_2\text{CH}=\text{CCl}_2$ and 40.9 mmol of $n\text{-BuLi}$ at -90°C as described in (a). To this solution was added dropwise with stirring 6.62 g (43.3 mmol) of trimethylchlorogermane during a period of 3 min. The reaction mixture was allowed to warm slowly to room temperature, and was hydrolyzed with saturated aqueous NH_4Cl . The organic layer, after treatment with 200 ml of diethyl ether and 300 ml of water, was dried and trap-to-trap distilled (60°C at 0.05 torr) into a receiver at -196°C , leaving a quantitative yield of $n\text{-butyltriphenyllead}$ as residue. GLC analysis of the distillate showed the presence of two products (4 ft. UCW-98 silicone oil column at 95°C): $\text{Me}_3\text{GeCCl}_2\text{CH}=\text{CH}_2$ (85% yield) and $\text{Me}_3\text{GeCH}_2\text{CH}=\text{CCl}_2$ (15% yield). The former was isolated by low temperature recrystallization from pentane, followed by sublimation (25°C at 0.1 torr), as colorless crystals, m.p. $70.5\text{--}71^\circ\text{C}$. The minor product was isolated as the pure liquid by preparative GLC.

(ii) With 0.63 molar equivalents of trimethylchlorogermane. The same procedure was used in the reaction of the lithium reagent prepared from 42.4 mmol of $\text{Ph}_3\text{PbCH}_2\text{CH}=\text{CCl}_2$ and 42.2 mmol of $n\text{-BuLi}$ with 26.7 mmol of Me_3GeCl . The reaction mixture was stirred at -90°C for 1.5 h after the addition was completed and worked up as described in (i) above. GLC analysis of the final trap-to-trap distillate (conditions as in (i)) showed the presence of $\text{Me}_3\text{GeCCl}_2\text{CH}=\text{CH}_2$ (39% yield) and $\text{Me}_3\text{GeCH}_2\text{CH}=\text{CCl}_2$ (60% yield).

(iii) The action of gem-dichloroallyllithium on 1,1-dichloroallyltrimethylgermane. The lithium reagent was prepared from 19.6 mmol of $\text{Ph}_3\text{PbCH}_2\text{CH}=\text{CCl}_2$ and 17.7 mmol of $n\text{-BuLi}$ at -97°C by the procedure outlined in (a) and then a solution of 2.76 g (12.1 mmol) of pure $\text{Me}_3\text{GeCCl}_2\text{CH}=\text{CH}_2$ (m.p. $70\text{--}71^\circ\text{C}$) in 25 ml of THF was added dropwise over a period of 5 min. After a period of 2 h at -97°C , the reaction mixture was allowed to warm to room temperature, hydrolyzed with 25 ml of 1 M HCl , and worked up as in (i). GLC analysis of the final trap-to-trap distillate showed the presence of $\text{Me}_3\text{GeCCl}_2\text{CH}=\text{CH}_2$ (32%) and $\text{Me}_3\text{GeCH}_2\text{CH}=\text{CCl}_2$ (64%), confirming that the lithium reagent induces isomerization of $\text{Me}_3\text{GeCCl}_2\text{CH}=\text{CH}_2$.

A similar reaction carried out with $\text{Me}_3\text{SiCCl}_2\text{CH}=\text{CH}_2$ gave no evidence of any isomerization to $\text{Me}_3\text{SiCH}_2\text{CH}=\text{CCl}_2$. An authentic sample of the latter was available for comparison [10]. The recovery of $\text{Me}_3\text{SiCCl}_2\text{CH}=\text{CH}_2$ was only 61%, however.

TABLE I
NEW DICHLOROALLYL COMPOUNDS

Compound	B.P. (°C/ torr) or m.p. (°C)	n_D^{25}	Analysis (found/calcd)(%)			NMR spectrum, (δ (ppm) in CCl_4)	IR Spectrum, (cm^{-1})
			C	H	Cl		
$(\text{CH}_3)_3\text{SiCCl}_2\text{CH}=\text{CH}_2$	m.p. 66–68		39.11 (39.34)	6.85 (6.61)	39.13 (38.71)	0.23(s, 9H); 5.15–6.13(ABC m, 3H, $\text{CH}=\text{CH}_2$)	1655w, 1613m, 1405m, 1254s, 1101w, 975m, 930s, 883s, 851s, 636w (in CCl_4)
$(\text{CH}_3)_3\text{SiCCl}=\text{CHCH}_2\text{Cl}$		1.4710	39.67 (39.34)	6.64 (6.61)	39.44 (38.71)	0.15(s, 9H); 4.13(d, J 7 Hz, 2H, CH_2); 6.05(t, J 7 Hz, 1H, $=\text{CH}$) (major isomer)	1610w, 1440w, 1413w, 1290w, 1255s, 1173w, 955s, 875s, 849s, 761s, 693w (major isomer) (film)
$(\text{CH}_3)_3\text{GeCCl}_2\text{CH}=\text{CH}_2$	m.p. 70.5–71.0		31.63 (31.65)	5.29 (5.31)	31.42 (31.15)	0.38(s, 9H); 5.08–6.34(ABC m, 3H, $\text{CH}=\text{CH}_2$)	1630m, 1405s, 1245s, 1110m, 982m, 971(sh), 929s, 835s, 750s, 613s, 572w (in CCl_4)
$(\text{CH}_3)_3\text{GeCH}_2\text{CH}=\text{CH}_2$		1.4833	32.05 (31.65)	5.71 (5.31)	31.07 (31.15)	0.25(s, 9H); 1.74(d, J 9.3 Hz, 2H, CH_2); 5.88(t, J 9.3 Hz, $=\text{CH}$)	1627m, 1413m, 1405(sh), 1297w, 1280w, 1239s, 1160m, 1133m, 1032s, 978w, 922(sh), 900s, 854(sh), 826s, 801s, 759w, 734w, 603s, (in CCl_4)
$(\text{CH}_3)_3\text{GeCCl}=\text{CHCH}_2\text{Cl}$		1.4898 (mixed isomers)	31.65 (31.65)	5.31 (5.31)	31.16 (31.15)	major isomer: 0.39(s, 9H); 4.21(d, J 7.2 Hz, 2H, CH_2); 6.01(t, J 7.2 Hz, 1H, $=\text{CH}$) minor isomer: 0.48(s, 9H); 4.01(d, J 8.4 Hz, 2H, CH_2); 6.52(t, J 8.4 Hz, 1H, $=\text{CH}$)	1609w, 1440m, 1415m, 1290m, 1254(sh), 1244s, 1173w, 1079(sh), 1058w, 940w, 834s, 765m, 689w, 612m, 578w (film)
$(\text{CH}_3)_3\text{SnCH}_2\text{CH}=\text{CCl}_2$	b.p. 48–49/0.5	1.5205	26.49 (26.32)	4.48 (4.42)	26.04 (25.90)	0.21(s, J($^{119}\text{Sn}-^1\text{H}$) 54 Hz, J($^{117}\text{Sn}-^1\text{H}$) 52 Hz, 9H); 1.81(d, J 9 Hz, J($^{119}\text{Sn}-^1\text{H}$) 65 Hz, J($^{117}\text{Sn}-^1\text{H}$) 63 Hz, 2H, CH_2); 6.0(t, J 9 Hz, 1H, $=\text{CH}$)	1611w, 1555w, 1293w, 1255w, 1194w, 1166m, 1089m, 1034s, 899s, 860m, 770s (film)

Thermal isomerization of 1,1-dichloroallyltrimethylsilane

A 524 P/P medium-thickness-walled NMR tube (Wilmad, Inc.) was charged with a solution of 0.2 g of $\text{Me}_3\text{SiCCl}_2\text{CH}=\text{CH}_2$ (m.p. $64-65^\circ\text{C}$) in 1 ml of 99.5% benzene- d_6 . The tube was topped with a no-air stopper and syringe needle to vacuum. The solution was degassed by a freeze-thaw cycle and sealed in vacuo at liquid nitrogen temperature. Initially, only the NMR spectrum of pure starting material was observed. After the tube had been heated for 4 h at 135°C , 58% isomerization had occurred. After another 16 h of heating at 135°C , the expected *cis/trans* isomers of $\text{Me}_3\text{SiCCl}=\text{CHCH}_2\text{Cl}$ (1/3 ratio) were the only products present. Further heating failed to change this ratio.

Thermal isomerization of 1,1-dichloroallyltrimethylgermane

Heating pure $\text{Me}_3\text{GeCCl}_2\text{CH}=\text{CH}_2$ (m.p. $68-70^\circ\text{C}$) at 155°C using the procedure described above for the silicon analog gave a 2.9/1 mixture of the isomers of $\text{Me}_3\text{GeCCl}=\text{CHCH}_2\text{Cl}$. After 90 min at 155°C , the isomerization had progressed to the extent of 60%, and the reaction was complete after 4 h at 155°C .

New compounds

The new dichloroallyl compounds which have been characterized during the course of this study, together with their characterizing data, are listed in Table 1.

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References

- 1 D. Seyferth, G.J. Murphy and R.A. Woodruff, *J. Organometal. Chem.*, **66** (1974) C29.
- 2 D. Seyferth and R.A. Woodruff, *J. Organometal. Chem.*, **71** (1974) 335, and preceding papers of this series.
- 3 (a) G. Courtois and L. Miginiac, *J. Organometal. Chem.*, **69** (1974) 1; (b) D. Seebach and K.-H. Geiss, *J. Organometal. Chem. Library*, **1** (1976) 1.
- 4 D. Seyferth, G.J. Murphy, and B. Mauzé, *J. Amer. Chem. Soc.*, in press.
- 5 R.N. Haszeldine, *J. Chem. Soc.* (1953) 3372.
- 6 D. Seyferth, G.J. Murphy, R.L. Lambert, Jr., and R. E. Mammarella, *J. Organometal. Chem.*, **90** (1975) 173.
- 7 (a) D. Seyferth and M.A. Weiner, *J. Org. Chem.*, **26** (1961) 4797; (b) D. Seyferth and T.F. Julia, *J. Organometal. Chem.*, **66** (1974) 195.
- 8 E. Matarasso-Tchiroukhine and P. Cadiot, *C.R. Acad. Sci. Paris*, **276** (1973) 1637.
- 9 W. Kitching, M.L. Bullpitt, P.D. Sleezer, S. Winstein and W.G. Young, *J. Organometal. Chem.*, **34** (1972) 233.
- 10 D. Seyferth and R.E. Mammarella, report in preparation.
- 11 A.N. Nesmeyanov, R. Kh. Freidlina and F.K. Velichko, *Dokl. Akad. Nauk SSSR*, **114** (1957) 557.
- 12 R.W. Leeper, L. Summers and H. Gilman, *Chem. Rev.*, **54** (1954) 101.
- 13 R. Kh. Freidlina, V.N. Kost, M.Ya. Khorlina and A.N. Nesmeyanov, *Dokl. Akad. Nauk SSSR*, **137** (1961) 341.