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Preliminary communication

gem-DICHLOROALLYLLITHIUM: A SEEMINGLY AMBIDENT NUCLEOPHILE

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Summary

gem-Dichloroallyllithium may be prepared by the reaction of n-butyllithium with 3,3,3-trichloropropene or, better, by reaction of n-butyllithium with $Ph_3PbCH_2CH{=}CCl_2$ in THF at low temperatures. In reactions with trimethylchlorosilane, iodomethane and water the products are indicative of the presence of $LiCCl_2CH{=}CH_2$, but its reactions with trimethyltin bromide and mercuric chloride give products indicative of the presence of $LiCH_2CH{=}CCl_2$; its reaction with trimethylchlorogermane gives both types of products. An explanation for this duality of behavior is offered.

We report concerning the preparation of *gem*-dichloroallyllithium and its reactions as an alkylating agent. Two routes serve in its preparation. It may be generated by the lithium—halogen exchange reaction between n-butyllithium and 3,3,3-trichloropropene (eqn. 1) in diethyl ether—tetrahydrofuran (THF) medium at −105° or by the transmetalation reaction occurring between 3,3-dichloro-2-propenyltriphenyllead* and n-butyllithium in THF at −95° (eqn. 2). Of these, the latter is preferred since it is a very clean reaction that proceeds as written in virtually quantitative yield. On the other hand, when $CCl_3CH{=}CH_2$ is treated with n-butyllithium, secondary reactions involving this olefin and the dichloroallyllithium species appear to lead to destruction of the latter with formation of polymer. As a result, product yields are low,

$$CCl_3CH{=}CH_2 + n\text{-}C_4H_9Li \xrightarrow{-105^\circ} n\text{-}C_4H_9Cl + Li(CCl_2CHCH_2) \quad (1)$$

$$Ph_3PbCH_2CH{=}CCl_2 + n\text{-}C_4H_9Li \xrightarrow{-95^\circ} n\text{-}C_4H_9PbPh_3 + Li(CCl_2CHCH_2) \quad (2)$$

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*Prepared in 84% yield by reaction of $Ph_3PbMgBr$ with 1,1,3-trichloropropene in THF.

usually below 50%. The n-C_4H_9Li—$CCl_3CH{=}CH_2$ reaction mixtures are deep purple due to these side reactions; in contrast, the n-$C_4H_9Li/Ph_3PbCH_2CH{=}CCl_2$ reaction mixtures are light amber in color.

gem-Dichloroallyllithium is stable in THF solution only at low temperatures. At —95° it appears to be quite stable, but on warming to —65° color changes indicative of beginning decomposition are observed. Such decomposition appears to be rapid above —60°. The reagent solutions prepared by reactions (1) and (2) showed identical chemical behavior toward a number of different substrates and we will restrict our discussion to the reagent prepared by the n-$C_4H_9Li/Ph_3PbCH_2CH{=}CCl_2$ reaction.

In a typical reaction, 42 mmol of n-butyllithium in 17.5 ml of hexane was added dropwise (30 min) with stirring under nitrogen to 39.8 mmol of $Ph_3PbCH_2CH{=}CCl_2$ in 300 ml of THF at —95°. The resulting light amber solution was stirred at —95° for 1 h. Subsequently, the substrate was added slowly. Generally the resulting reaction mixture was allowed to warm slowly to room temperature and then was hydrolyzed with saturated aqueous NH_4Cl. Trap-to-trap distillation at reduced pressure in most cases served to remove the solvent and the volatile product from the nonvolatile n-butyltriphenyllead formed in the transmetalation step.

In such a reaction in which trimethylchlorosilane was added to the lithium reagent solution, the sole product was $(CH_3)_3SiCCl_2CH{=}CH_2$, m.p. 64—65° (99% yield by GLC, 73% isolated yield after sublimation). None of the isomeric $(CH_3)_3SiCH_2CH{=}CCl_2$ was present (by GLC and proton NMR). In contrast, the sole product obtained from a similar reaction in which trimethyltin bromide was added to the dichloroallyllithium solution was $(CH_3)_3SnCH_2CH{=}CCl_2$, b.p. 48—49° (0.5 mm), n_D^{25} 1.5205, in 95% distilled yield. This result was obtained after a hydrolytic work-up. In view of the known hydrolytic instability of $(CH_3)_3SnCCl_3$ and $(CH_3)_3SnCCl_2C_6H_5$ [1], it was conceivable that any $(CH_3)_3SnCCl_2CH{=}CH_2$ which might have been formed could have been destroyed by hydrolysis. However, when this reaction was repeated without hydrolytic work-up and with careful exclusion of moisture throughout all steps 3,3-dichloro-2-propenyltrimethyltin again was the exclusive product (93% yield). A similar result was obtained when the cold lithium reagent solution was added to a twofold excess of trimethyltin bromide in THF solution which had been precooled to —95°; the $(CH_3)_3SnCH_2CH{=}CCl_2$ yield was 97% and there was no evidence for the presence of the other isomer.

Similar regiospecific behavior was observed in other reactions of *gem*-dichloroallyllithium. In its reaction with mercuric chloride the only product (83% yield) was the known [2] $CCl_2{=}CHCH_2HgCl$, m.p. 99—100°. Its reaction with iodomethane gave only $CH_3CCl_2CH{=}CH_2$, n_D^{25} 1.4440, in 98% yield. Its hydrolysis produced $CHCl_2CH{=}CH_2$ (87%); the isomeric $CH_3CH{=}CCl_2$ was not detected (GLC, NMR).

In marked contrast to these examples, the reaction of *gem*-dichloroallyllithium with an equimolar quantity of trimethylchlorogermane under the same conditions gave a 5.66/1 mixture of $(CH_3)_3GeCCl_2CH{=}CH_2$, m.p. 70.5—71°, and $(CH_3)_3GeCH_2CH{=}CCl_2$, a liquid with n_D^{25} 1.4833, in quantitative yield. Proton NMR spectroscopy served well in distinguishing these isomers (and in assigning structures to all of the products reported above). $(CH_3)_3GeCCl_2CH{=}CH_2$ showed the three vinyl protons as an ABC multiplet at δ 5.03—6.31 ppm; $(CH_3)_3GeCH_2CH{=}CCl_2$ showed its one vinyl proton as a triplet (J 9.0 Hz) at δ 5.98 and the CH_2 protons as a doublet (J 9.0 Hz) at δ 2.80 ppm. It is significant that this isomer ratio could be changed by changing the stoichiometry. Use of an excess of $Li(CCl_2CHCH_2)$, i.e., addition of one-half molar equivalent of trimethylchlorogermane to one of the lithium reagent, gave a $(CH_3)_3GeCCl_2CH{=}CH_2/(CH_3)_3GeCH_2CH{=}CCl_2$ ratio of 0.65, with again a virtually quantitative product yield. Such a change in stoichiometry was without effect in the reaction of $Li(CCl_2CHCH_2)$ with trimethylchlorosilane.

In a tentative explanation of these results we assume that the products derivable from the lithium reagent reacting as $LiCCl_2CH{=}CH_2$ are those of kinetic control. In the case of the reactions with trimethylchlorosilane, iodomethane and water, such a product, once formed, is stable. With trimethylchlorogermane, however, transmetalation equilibria can lead to the formation of the other isomer, the product of apparently greater thermodynamic stability (eqn. 3). The use of an excess of the lithium reagent then would be

$$(CH_3)_3GeCCl_2CH{=}CH_2 + Li(CCl_2CHCH_2) \rightleftharpoons (CH_3)_3GeCH_2CH{=}CCl_2 + Li(CCl_2CHCH_2) \qquad (3)$$

expected to lead to a decrease of the $(CH_3)_3GeCCl_2CH{=}CH_2/(CH_3)_3GeCH_2CH{=}CCl_2$ ratio, as was observed. Furthermore, treatment of $(CH_3)_3GeCCl_2CH{=}CH_2$ with *gem*-dichloroallyllithium would be expected to result in partial isomerization to $(CH_3)_3GeCH_2CH{=}CCl_2$. Such was found to be the case. Treatment of isomerically pure $(CH_3)_3GeCCl_2CH{=}CH_2$ with a ca. 50% excess of $Li(CCl_2CHCH_2)$ for 2 h at —97° resulted in formation of a 0.51 ratio of $(CH_3)_3GeCCl_2CH{=}CH_2$ to $(CH_3)_3GeCH_2CH{=}CCl_2$. The silicon compound, $(CH_3)_3SiCCl_2CH{=}CH_2$, could be expected to be unreactive with respect to such transmetalation*. The organotin analog, $(CH_3)_3SnCCl_2CH{=}CH_2$, on the other hand, would be expected to be very reactive in such a transmetalation with *gem*-dichloroallyllithium, and this, at first sight, could explain why $(CH_3)_3SnCH_2CH{=}CCl_2$ was the only product obtained in the $Li(CCl_2CHCH_2)/(CH_3)_3SnBr$ reaction. However, if that were the only factor of importance in the organotin case, then one might have expected to find some of the other isomer when the $Li(CCl_2CHCH_2)$ solution was added to an excess of trimethyltin bromide. Since only $(CH_3)_3SnCH_2CH{=}CCl_2$ was obtained under these conditions, another explanation must hold or it may be that any $(CH_3)_3SnCCl_2CH{=}CH_2$ formed is isomerized by other means (action of $(CH_3)_3SnBr$, of THF, of mild heating up to 60° in the trap-to-trap distillation during the non-hydrolytic work-up, or two or all three of these in combination). In this connection, the known facile isomerization of allylic tin compounds by the action of Lewis bases and Lewis acids under mild conditions is to be noted [5]. The exclusive formation of $CCl_2{=}CHCH_2HgCl$ can also be explained in terms of such isomerization of any initially formed $CH_2{=}CHCCl_2HgCl$

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*For examples of the resistance of some other polyhaloalkylsilanes to attack by organolithium reagents at silicon, see ref. 3 and 4.

induced by mercuric chloride since this reagent is known to effect isomerization of allylic mercurials [6].

Our studies of the chemistry of *gem*-dichloroallyllithium are continuing. Of some interest is that preliminary studies have shown a similar duality of behavior in its additions to the C=O bonds of aldehydes and ketones. These results will be reported in the near future.

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