(10) F. W. Walker and E. C. Ashby, *J. Chem. Educ.*, **45**, 654 (1968).
(11) Methyllithium has been found to be a tetramer in both diethyl ether and THF.[12] Lithium dimethylcuprate has been found to be dimeric in diethyl ether.[13] The results of this work show that $LiCu(CH_3)_2$ is dimeric in THF; and, in addition, that $Li_2Cu(CH_3)_3$ is monomeric in THF. Since dimethyl ether is similar in many respects to THF, one would expect CH_3Li, $LiCu(CH_3)_2$, and $Li_2Cu(CH_3)_3$ to have the same association in dimethyl ether as in THF.
(12) P. West and R. Waack, *J. Am. Chem. Soc.*, **89**, 4395 (1967).
(13) R. G. Pearson and G. D. Gregory, *J. Am. Chem. Soc.*, **98**, 4098 (1976).

Reaction of *gem*-Dichloroallyllithium with Aldehydes, Ketones, and Other Organic Substrates. An Example of Electronic Control of Regioselectivity in the Reactions of an Ambident Nucleophile[1]

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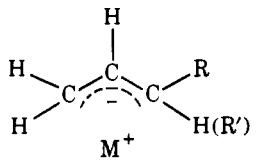
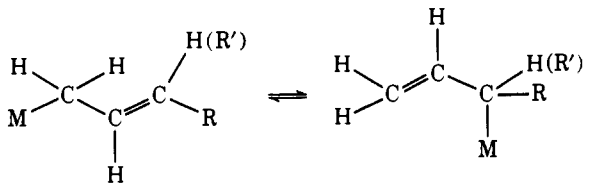
Abstract: The reactions of *gem*-dichloroallyllithium, obtained by the action of *n*-butyllithium on 3,3-dichloroallyltriphenyllead in THF at −95 °C, with a variety of organic substrates have been investigated. Hydrolysis gives $HCCl_2CH{=}CH_2$ and alkylation of the reagent with organic halides and acylation using esters occurred with formation of the new C–C bond at the CCl_2 terminus of the reagent. The addition of this reagent to the C=O bond of aldehydes and ketones proceeded with C–C bond formation at either terminus. Dialkyl ketones gave alcohols (after hydrolysis) of type $RR'C(OH)CCl_2CH{=}CH_2$, while PhCHO, Ph_2CO, $(CF_3)_2CO$, and $RC(O)CF_3$ (R = Me, Ph) reacted to give products of type $RR'C(OH)CH_2CH{=}CCl_2$. Aliphatic aldehydes, acetophenone, and substituted acetophenones gave both types of products. In the case of substituted acetophenones, the ratio of the $CH_2{=}CHCCl_2$- and $CCl_2{=}CHCH_2$-substituted products appeared to depend on electronic factors; the regioselectivity observed in $Li(CCl_2CHCH_2)$ additions to other carbonyl systems also can be rationalized in terms of electronic factors in the substrate.

Unsymmetrically substituted allylic metal reagents react readily with aldehydes and ketones to form products which are characteristic of reaction at either or both termini of the propenylic system. In the cases studied to date[4] the major emphasis has been on alkyl-substituted reagents of type I and II,



I (M = Li, Na)



II (M = MgX, Mg/2, ZnX, Zn/2)

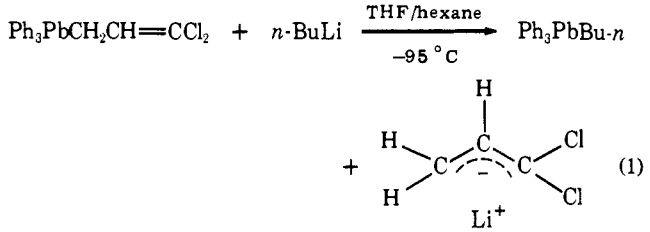
although such reactions of a few organofunctional allylic lithium reagents (e.g., R = alkoxy or thioalkoxy) have been reported.[5]

For purposes not related to the present study, we required such an unsymmetrical allylic lithium reagent, *gem*-dichloroallyllithium. Initially it was prepared by the reaction of 3,3,3-trichloropropene with *n*-butyllithium in tetrahydrofuran/diethyl ether medium at −115 to −100 °C.[6,7] Among the reactions of this reagent which we studied was that with benzaldehyde which gave the alcohol $C_6H_5CH(OH)CH_2CH{=}CCl_2$ in 52% yield after hydrolysis.[7] In subsequent work,[6,8] a much better synthesis of *gem*-dichloroallyllithium was developed, as shown in eq 1. Although our interests were directed more toward the organometallic applications of this novel reagent, we felt that it would be of interest to examine more thoroughly its reactions with aldehydes and ketones. It was by no means certain that the result obtained with benzaldehyde, C–C bond formation exclusively at the CH_2 terminus, would be observed with every other carbonyl compound.

The results of this study are of considerable interest since they provide the first example of exclusive electronic control of regioselectivity in the reactions of unsymmetrically substituted allyl anions.

Results and Discussion

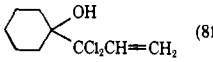
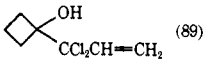
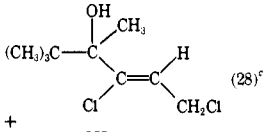
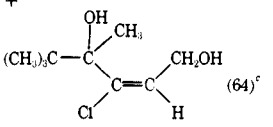
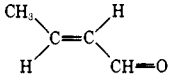
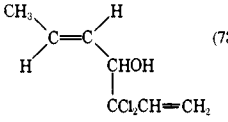
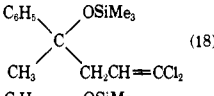
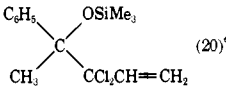
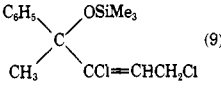
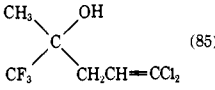
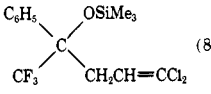
The first carbonyl substrate examined using the new route (eq 1) to *gem*-dichloroallyllithium was acetone, and we were



(1)

surprised to find that in this reaction C–C bond formation occurred exclusively at the CCl_2 end of the *gem*-dichloroallyl anion, giving the alcohol $Me_2C(OH)CCl_2CH{=}CH_2$ after hydrolysis of the reaction mixture. Since the two carbonyl compounds examined had given completely opposite results in their reactions with *gem*-dichloroallyllithium, we carried out *gem*-dichloroallyllithium addition reactions to a fairly large number of other carbonyl substrates in order to identify the factors which are important in determining the regioselectivity of addition. In all of these reactions the *gem*-dichloroallyllithium was prepared at −90 °C in THF by the transmetalation

Table I. Reactions of *gem*-Dichloroallyllithium with Aldehydes and Ketones[a]

Carbonyl substrate	Products (% yield)	C–C bond formation, %, at[b] CCl_2 terminus	C–C bond formation, %, at[b] CH_2 terminus
$(CH_3)_2C{=}O$	$(CH_3)_2C(OH)CCl_2CH{=}CH_2$ (90)	100	
	 (81)	100	
	 (89)	100	
$(CH_3)_3CCCH_3$ ‖ O	 (28)[c] +  (64)[c]	100	
	 (73)	100	
$CH_2{=}CHCH{=}O$	$CH_2{=}CHCH(OH)CH_2CH{=}CCl_2$ (82)		100
$CH_3CH{=}O$	$CH_3CH(OH)CCl_2CH{=}CH_2$ (62) + $CH_3CH(OH)CH_2CH{=}CCl_2$ (26)	70	30
$CH_3CH_2CH{=}O$	$CH_3CH_2CH(OH)CCl_2CH{=}CH_2$ (69) + $CH_3CH_2CH(OH)CH_2CH{=}CCl_2$ (28)	71	29
$C_6H_5CH{=}O$	$C_6H_5CH(OH)CH_2CH{=}CCl_2$ (97)		100
$CCl_3CH{=}O$	$CCl_3CH(OH)CH_2CH{=}CCl_2$ (23)[d]		100
$C_6H_5CCH_3$ ‖ O	 (18)[e,f]		
	 (20)[e,f]	62	38
	 (9)[c,e,f] (cis and trans isomers)		
CH_3CCF_3 ‖ O	 (85)		100
$C_6H_5CCF_3$ ‖ O	 (88)[e]		100
$(CF_3)_2C{=}O$[g]	$(CF_3)_2C(OH)CH_2CH{=}CCl_2$ (90)		100
$(C_6H_5)_2C{=}O$	$(C_6H_5)_2C(OH)CH_2CH{=}CCl_2$ (91)		100
CO_2[g,h]	$CH_2{=}CHCCl_2CO_2H$[h] (91)	100	

[a] All reactions were carried out and all reaction mixtures were worked up under essentially identical conditions as described in detail for the reaction of benzaldehyde with $Li(CCl_2CHCH_2)$ in the Experimental Section, except as noted. [b] Percentages given are the normalized distributions. [c] Product derived from allylic rearrangement of initial $CH_2{=}CHCCl_2$-substituted product; see Discussion. [d] The low product yield was due to competing polymerization, giving nonvolatile products. [e] The reaction mixture was worked up by addition of trimethylchlorosilane rather than by hydrolysis since the alcohol product(s) were unstable. This procedure is described in detail for the reaction of acetophenone with $Li(CCl_2CHCH_2)$. [f] In addition to these products, 1-phenyl-1-trimethylsiloxyethylene was formed in 43% yield, implicating enolization as a competitive side reaction to carbonyl addition. [g] Reactant added as a gas. [h] Isolated as the methyl ester after reaction with diazomethane.

reaction (eq 1) and the aldehyde or ketone was added at that temperature. The results of these reactions are shown in Table I. It may be noted that in these reactions the product yields were high, usually 80–95%, a result which emphasizes the superiority of the transmetalation route in the preparation of this reagent.

Of the 17 reactants listed in Table I, the majority reacted with *gem*-dichloroallyllithium to form alcohols derived from addition of only one terminus of the anion. Seven of the carbonyl substrates, including benzaldehyde, benzophenone, acrolein, chloral, trifluoroacetone, hexafluoroacetone, and trifluoroacetophenone, reacted to form the new C–C bond at the CH_2 terminus of $Li(CCl_2CHCH_2)$. These were the exclusive products; none of the other possible isomer in which bond formation had occurred at the CCl_2 terminus could be detected. All of the 1,1-dichlorobutenols obtained were ther-

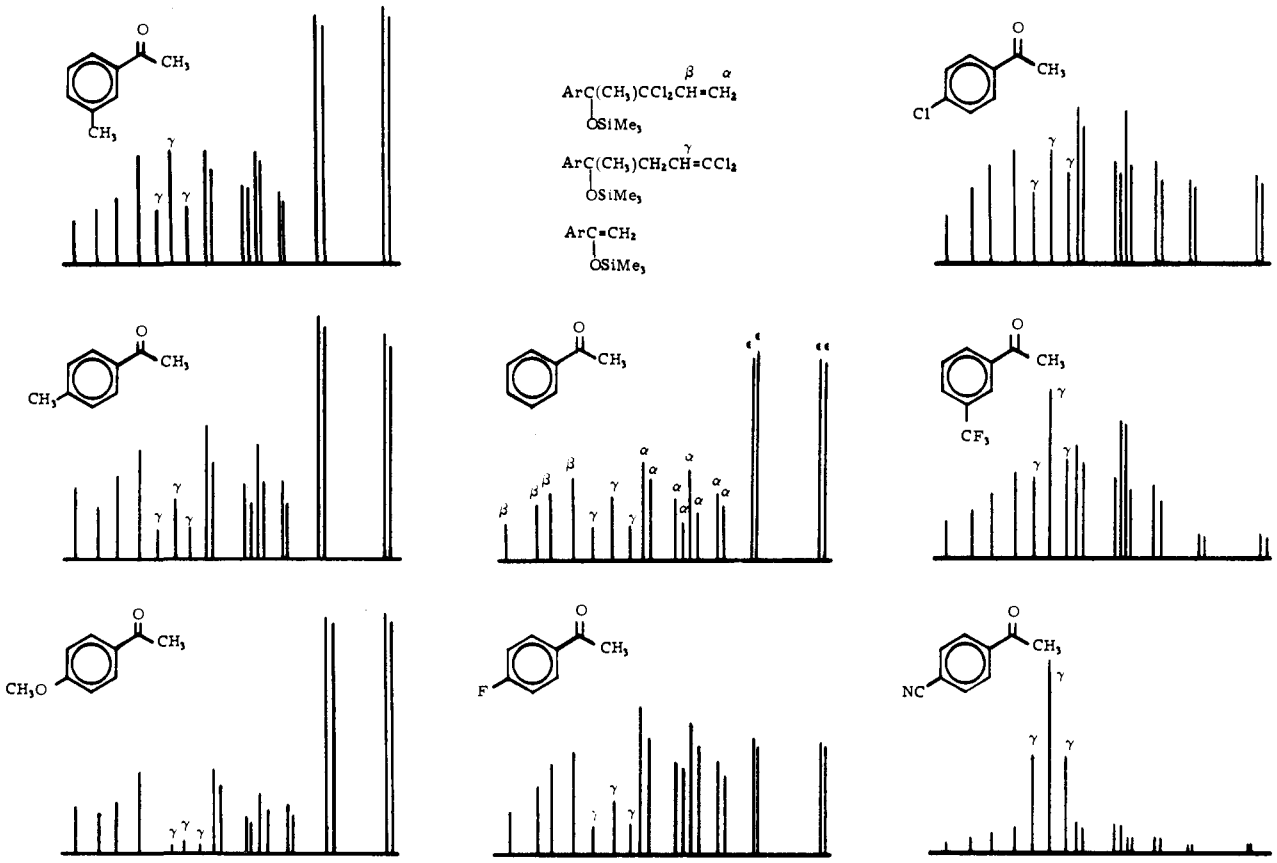


Figure 1. NMR spectra of the reactions of *gem*-dichloroallyllithium with substituted acetophenones.

mally stable toward isomerization and were fully characterized by combustion analysis and NMR and IR spectroscopy. Their NMR spectra, which clearly showed one vinyl proton and two methylene protons, were decisive in establishing their structure.

In contrast, the products formed in the reactions of *gem*-dichloroallyllithium with acetone, cyclohexanone, cyclobutanone, pinacolone, and crotonaldehyde were those derived from exclusive C–C bond formation at the CCl_2 terminus of the reagent. Except for pinacolone, these carbonyl compounds gave 3,3-dichlorobutenols (eq 2) of sufficient thermal stability to permit their isolation by vacuum distillation. However, when heated above 120 °C, they all isomerized via allylic chloride migration (eq 3). Again, NMR spectroscopy served well in

$$CH_3C(O)CH_3 + Li(CCl_2CHCH_2) \longrightarrow \xrightarrow{H_3O^+} Me_2C(OH)CCl_2CH{=}CH_2 \quad (2)$$

$$Me_2C(OH)CCl_2CH{=}CH_2 \xrightarrow{120\ °C} Me_2C(OH)CCl{=}CHCH_2Cl \quad (3)$$

establishing the structure of the primary products with their characteristic $CH{=}CH_2$ groups. In the reaction with pinacolone the initial adduct which had resulted from formation of the C–C bond at the CCl_2 terminus underwent isomerization at room temperature, and one of the allylic chlorides formed was hydrolyzed during the dilute acid workup (eq 4). Although we have no experimental evidence concerning the stereochemistry of the two products which were isolated, we suggest that the diol has the two hydroxyalkyl substituents cis with respect to one another. We make this assignment on the basis of a possible anchimeric assistance by the hydroxyl function in the hydrolysis of the allylic chloride when it is cis to the chloromethyl group.

Other carbonyl substrates, aliphatic aldehydes and acetophenone, gave both possible products, a mixture of isomers in

$$(CH_3)_3CC(CH_3)(OH)CCl_2CH{=}CH_2 \xrightarrow{25\ °C} \textit{trans}\text{-}(CH_3)_3CC(CH_3)(OH)CCl{=}CHCH_2Cl + \textit{cis}\text{-}(CH_3)_3CC(CH_3)(OH)CCl{=}CHCH_2Cl \xrightarrow{H_3O^+} \textit{cis}\text{-}(CH_3)_3CC(CH_3)(OH)CCl{=}CHCH_2OH \quad (4)$$

which the new C–C bond had been formed at the CH_2 as well as at the CCl_2 terminus of *gem*-dichloroallyllithium, with a preference for the latter isomer. In our initial reactions of $Li(CCl_2CHCH_2)$ with acetophenone, hydrolysis of the reaction mixture invariably gave the product alcohol in less than 50% yield and large amounts of unconverted acetophenone were recovered, even when the lithium reagent was used in excess. When such a reaction mixture was treated with trimethylchlorosilane instead of with aqueous HCl, the expected silyl ethers were formed in 47% yield, in the same ratio as that observed for the alcohols in reaction mixtures which had been hydrolyzed. In addition, 1-phenyl-1-trimethylsiloxyethylene was formed in 43% yield (eq 5), which indicates that 43% of

$$PhC(O)CH_3 + Li(CCl_2CHCH_2) \xrightarrow{\text{enolization}} HCCl_2CH{=}CH_2 + PhC(OLi){=}CH_2$$

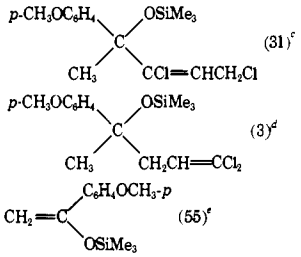
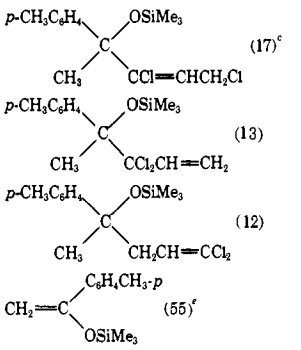
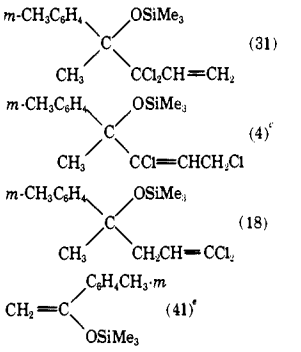
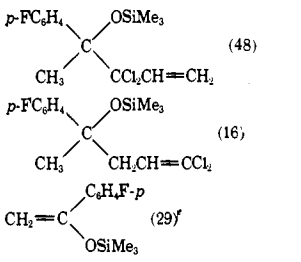
$$\downarrow \text{addition} \qquad\qquad \downarrow Me_3SiCl$$

$$PhC(CH_3)(OLi)(CCl_2CHCH_2) \qquad\qquad PhC(OSiMe_3){=}CH_2 \quad (5)$$

$$\downarrow Me_3SiCl$$

$$PhC(CH_3)(OSiMe_3)CCl_2CH{=}CH_2 + PhC(CH_3)(OSiMe_3)CH_2CH{=}CCl_2$$

Table II. Reactions of *gem*-Dichloroallyllithium with Substituted Acetophenones[a]

Ketone substrate	Products (% yield)	C–C bond formation, %, at[b] CCl_2 terminus	C–C bond formation, %, at[b] CH_2 terminus
p-$CH_3OC_6H_4C(O)CH_3$	 (31)[c] (3)[d] (55)[e]	91	9
p-$CH_3C_6H_4C(O)CH_3$	 (17)[c] (13) (12) (55)[e]	72	28
m-$CH_3C_6H_4C(O)CH_3$	 (31) (4)[c] (18) (41)[e]	64	36
p-$FC_6H_4C(O)CH_3$	 (48) (16) (29)[e]	76	24

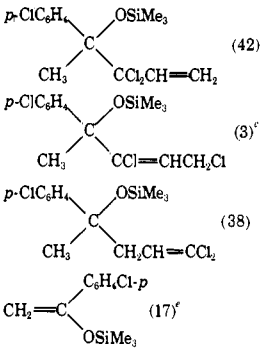
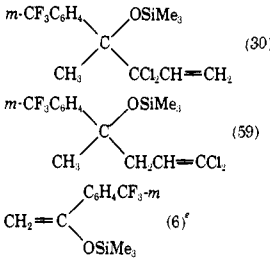
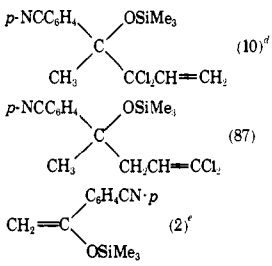
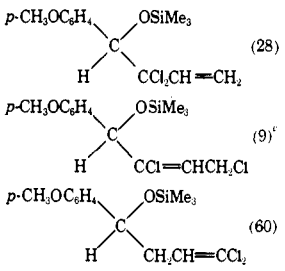
[a] Reaction conditions and workup procedure as described for the reaction of acetophenone with $Li(CCl_2CHCH_2)$ in the Experimental Section. [b] Percentages given are the normalized distributions. [c] Product derived from allylic rearrangement of the initial $CH_2{=}CHCCl_2$-substituted

the lithium reagent reacted with the ketone to form the ketone enolate.

Both acrolein and crotonaldehyde showed exclusive 1,2-addition with the exclusion of 1,4-addition, which is typical for allylic organometallic reagents,[9,10] except when highly hindered ketones are involved,[11] even in the presence of CuCl.[10] However, these unsaturated aldehydes show opposite regioselectivity in their reactions with *gem*-dichloroallyllithium.

Examination of Table I suggests that electronic, not steric, factors determine whether the new C–C bond is formed at the CCl_2 or the CH_2 terminus of the allylic lithium reagent. Comparison of the regioselectivity observed with acetophenone vs. benzaldehyde, acetone vs. acetaldehyde, and pinacolone vs. trifluoroacetone shows that the greater steric requirement of the CCl_2 terminus does not deter its preferential reaction with the sterically more hindered compound in each of these pairs. The trends in Table I strongly suggest that increased electron withdrawal by the substituents on the C=O function increases the amount of CH_2-ended addition. The majority of cases, however, are ones in which replacement of hydrogen by chlorine or fluorine or of methyl by phenyl involves both an increase in the steric factors and an increase in electron withdrawal from the C=O group.

A study of the reactions of *gem*-dichloroallyllithium with a number of substituted acetophenones allowed us to probe more effectively the question of the effect of electronic factors which obtain in the carbonyl substrate on the regioselectivity of the addition reaction. Since a mixture of both isomers was obtained when *gem*-dichloroallyllithium reacted with aceto-

Ketone substrate	Products (% yield)	C–C bond formation, %, at[b]	
		CCl_2 terminus	CH_2 terminus
p-$ClC_6H_4C(O)CH_3$	 (42) (3)[c] (38) (17)[e]	54	46
m-$CF_3C_6H_4C(O)CH_3$	 (30) (59) (6)[e]	33	67
p-$NCC_6H_4C(O)CH_3$	 (10)[d] (87) (2)[e]	10	90
p-$CH_3OC_6H_4CH{=}O$	 (28) (9)[c] (60)	38	62

product; see Discussion. [d] The low yield of this product precluded its separation for complete characterization; its presence was determined by NMR. [e] Product derived from enolization of the substituted acetophenone.

phenone, it seemed reasonable to expect that the ratio of products formed at the CCl_2 and the CH_2 termini should change as electron-attracting and electron-releasing substituents are introduced into the phenyl group of the ketone. Such changes in the electronic properties of the substituents on the C=O function should be accompanied by at the most minimal changes in steric factors if the substituents on the phenyl ring are introduced at the para and meta positions. These reactions were carried out with three substituted acetophenones with electron-releasing substituents (p-CH_3, m-CH_3, p-OCH_3) and with four with electron-attracting substituents (p-F, p-Cl, m-CF_3, and p-CN). In each case the lithium alkoxides formed in the addition reaction were converted to the trimethylsilyl ethers rather than to the much less stable alcohols. The reaction mixture then was concentrated and the residue was examined by NMR spectroscopy before the application of any heat. In all cases, varying ratios of the two possible products were present. The NMR spectra of these product mixtures between 4.5 and 6.5 ppm are shown in schematic fashion in Figure 1. Subsequently, the product mixtures were distilled at reduced pressure and the composition of the distillate was determined by NMR. With those products of type $Ar(CH_3)C(OSiMe_3)$-$CCl_2CH{=}CH_2$ formed in the reactions of *gem*-dichloroallyllithium with acetophenone and substituted acetophenones the problem of allylic rearrangement during their isolation by distillation was particularly acute, and in all cases either partial or complete rearrangement occurred. All attempts to isolate these 1,1-dichloroallyl-substituted products by GLC failed and only their rearrangement products, $Ar(CH_3)C(OSiMe_3)$-$CCl{=}CHCH_2Cl$, could be characterized as pure compounds.

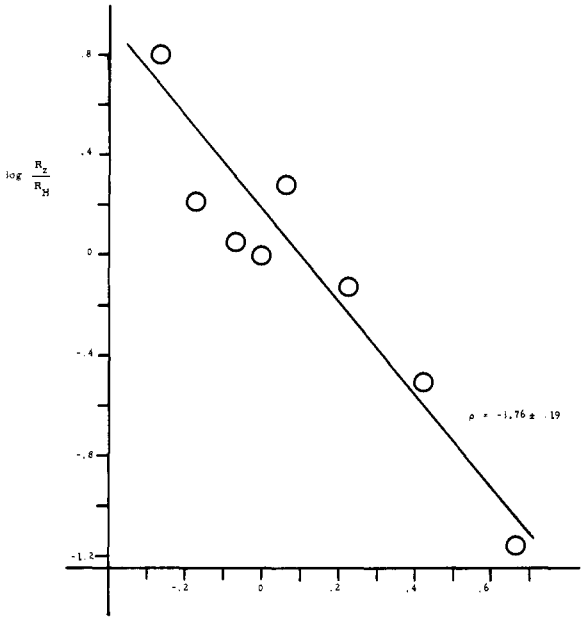


Figure 2. Plot of log R_z/R_H vs. Hammett σ values.[31] R_z = relative weight ratios CCl_2/CH_2 for substituted acetophenones; R_H = relative weight ratios CCl_2/CH_2 for acetophenone.

The isomeric $Ar(CH_3)C(OSiMe_3)CH_2CH{=}CCl_2$, on the other hand, were thermally stable and could be isolated by GLC.

The results of these experiments are presented in Table II. The *total* yield obtained with any substrate represents the weight of distilled product mixture; the individual product composition was obtained by NMR analysis of the distillate. The sum of the $CH_2{=}CHCCl_2$- and $ClCH_2CH{=}CCl$-substituted products reflects the proportion of C-C bond formation at the CCl_2 terminus of the lithium reagent.

Inspection of the results in Table II shows that a marked electronic effect is evident: electron-releasing substituents resulted in an enhancement of the relative yield of the product in which the C-C bond was formed at the CCl_2 terminus of the reagent; electron-attracting substituents favored bond formation at the CH_2 end, relative to acetophenone itself. *p*-Fluoroacetophenone is the only substrate which is not in line with this trend. A fairly good (considering the experimental method) linear correlation of the CCl_2/CH_2 derived product ratios with Hammett σ constants was found to obtain, with a computed (least-squares analysis) ρ value of -1.76 ± 0.19 (Figure 2).

Since substituents on the phenyl group of substituted acetophenones had such a marked effect on the ratio of CCl_2- and CH_2-terminus-derived products formed in the addition of *gem*-dichloroallyllithium, and since aliphatic aldehydes reacted to give a mixture of CCl_2- and CH_2-terminus derived alcohols, the reaction of *gem*-dichloroallyllithium with *p*-anisaldehyde was examined. In contrast to the result obtained with benzaldehyde, a mixture of isomers was produced (eq 6). The second product in eq 6 is the rearrangement product of the first. When

$$p\text{-}MeOC_6H_4CH{=}O + Li(CCl_2CHCH_2) \xrightarrow{-95\,^\circ C} \xrightarrow{Me_3SiCl} \xrightarrow{\text{distill}} p\text{-}MeOC_6H_4\underset{\underset{OSiMe_3}{|}}{C}HCCl_2CH{=}CH_2 \quad (28\%)$$

$$+\ p\text{-}MeOC_6H_4\underset{\underset{OSiMe_3}{|}}{C}HCCl{=}CHCH_2Cl \quad (9\%)$$

$$+\ p\text{-}MeOC_6H_4\underset{\underset{OSiMe_3}{|}}{C}HCH_2CH{=}CCl_2 \quad (60\%) \qquad (6)$$

this is taken into consideration, the ratio of CCl_2- to CH_2-terminus-derived product is 38/62.

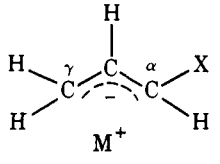
Reactions of some other organic substrates with *gem*-dichloroallyllithium were studied as well: carbon dioxide, ethylene oxide, esters, and organic halides.

The carboxylation of *gem*-dichloroallyllithium with gaseous carbon dioxide gave $CH_2{=}CHCCl_2CO_2H$ as the sole product in 91% yield. Gaseous ethylene oxide reacted with the lithium reagent to give, after hydrolysis, the alcohol $CH_2{=}CHCCl_2CH_2CH_2OH$ in low yield, which on attempted isolation underwent allylic rearrangement to $ClCH_2CH{=}CCClCH_2CH_2OH$. In reactions with esters, the new C-C bond always was formed at the CCl_2 terminus of the reagent (eq 7).

$$RCO_2CH_3 + Li(CCl_2CHCH_2) \xrightarrow{-95\,^\circ C} \xrightarrow{1\ N\ HCl} R\underset{\underset{O}{\|}}{C}CCl_2CH{=}CH_2 \quad (7)$$

Thus treatment of $Li(CCl_2CHCH_2)$ with methyl formate gave the aldehyde, $CH_2{=}CHCCl_2CH{=}O$, in 63% yield, while reactions with methyl acetate, methyl α-methylpropionate, methyl chloroacetate, and methyl benzoate resulted in formation of the ketones $CH_3C(O)CCl_2CH{=}CH_2$ (64%), $Me_2CHC(O)CCl_2CH{=}CH_2$ (84%), $ClCH_2C(O)CCl_2CH{=}CH_2$ (64%), and $PhC(O)CCl_2CH{=}CH_2$ (58%), respectively. Alkylations of *gem*-dichloroallyllithium with methyl iodide, allyl bromide, and benzyl bromide proceeded well with formation of the new C-C bond at the CCl_2 terminus, giving $CH_3CCl_2CH{=}CH_2$ (98%), $CH_2{=}CHCH_2CCl_2CH{=}CH_2$ (50%), and $PhCH_2CCl_2CH{=}CH_2$ (75%), respectively. The hydrolysis of *gem*-dichloroallyllithium gave $HCCl_2CH{=}CH_2$ as the sole product.

A discussion of these varied reactions of *gem*-dichloroallylithium is in order, although a satisfactory explanation of its behavior toward the various substrates used cannot be given. The alkylation and acylation reactions gave the product expected on the basis of the "allopolarization principle" of Gompper and Wagner,[12] i.e., the new C-C bond was formed at the CCl_2 terminus, chlorine being an "acceptor" substituent. This is the case also with ethylene oxide and carbon dioxide. With addition reactions to the C=O bonds of aldehydes and ketones the situation is more complicated: the regioselectivity of the addition reaction appears to depend solely on electronic factors in the substrate. This is a situation which has not been encountered before in allyl anion chemistry.[13] However, a number of other factors have been found to influence α/γ selectivity in unsymmetrical allyl anion (II)/carbonyl reactions:



III

the nature of X, the substituents on X (i.e., "R" when X = OR and SR), the counterion M, the solvent system, the presence of additives (e.g., tetramethylethylenediamine, hexamethylphosphoramide, etc.), temperature, and time of reaction.[5] Seebach and Geiss,[5] in their review which covers this subject, conclude that "the regiochemistry of II depends on so many factors that it appears to be a fair statement to say: α/γ control is an art (or alchemy?)". Gompper and Wagner,[12] commenting in their review on the same question, state that "the exceptional situation in the case of carbonyl compounds probably arises from their tendency to undergo multicenter processes on the one hand and thermodynamically controlled reactions on the other".

In considering possible explanations for the dual reactivity of *gem*-dichloroallyllithium toward carbonyl compounds, one possibility is that the product of C–C bond formation at the CH_2 terminus arises through an equilibrium favoring the thermodynamically more stable product. Such was the case for the formation of $MCH_2CH{=}CCl_2$-type products in reactions of $Li(CCl_2CHCH_2)$ with Me_3GeCl, Me_3SnCl, and $HgCl_2$.[6] It has been established that allylic zinc and magnesium reagents can add reversibly to carbonyls,[4] and there is some indication that such may be the case with at least one allylic lithium reagent, $Li(CH_2CHCHN(NO)CMe_3)$.[5] In the present instance, reversible addition of the dichloroallyl anion to the C=O bond followed by formation of the thermodynamically more stable alcoholate anion might merit serious consideration. However, results of experiments in which reaction mixtures were allowed to warm slowly to room temperature and stirred for more than 1 h before hydrolytic workup showed that acetone and benzaldehyde still exhibit the same exclusive and opposite preference for the CCl_2 and CH_2 termini, respectively, of the anion. Further experiments with acetophenone established that the nearly 60/40 CCl_2/CH_2 product ratio observed at −95 °C was unchanged when the reaction mixture was allowed to warm slowly and stirred for 1 h at room temperature prior to hydrolysis. As a final check for reversible addition to the C=O bond, a solution of $Li(CCl_2CHCH_2)$ was treated with 1 equiv of acetone at −90 °C in THF. After 5 min 6 equiv of hexafluoroacetone was added and the reaction mixture was allowed to warm slowly to room temperature and was stirred for another 1 h before workup. Only the alcohol derived from the reaction with acetone, 3,3-dichloro-4-methylpenten-4-ol, was detected in the reaction mixture, with no trace of the hexafluoroacetone-derived alcohol. When the reaction was repeated with the exception of inverting the ratios of the ketones and their order of addition, only the hexafluoroacetone-derived alcohol was obtained and none of that derived from acetone. Therefore, at least under the reaction conditions used in this study, reversible addition of *gem*-dichloroallyllithium does not occur and cannot be considered responsible for the observed alcohol product ratios.

A second alternative, which cannot be lightly excluded, would consider that the two different products are formed by two different, competing mechanisms. Thus the product in which the CCl_2 terminus of the reagent becomes bonded to the carbonyl carbon atom could be formed by a nucleophilic addition process (eq 8), while the other type of product could be formed in a two-step electron-transfer process (eq 9). Mech-

$$\underset{\underset{O}{\|}}{PhCCH_3} + Li(CCl_2CHCH_2) \longrightarrow \underset{\underset{O^-Li^+}{|}}{PhC(CH_3)CCl_2CH{=}CH_2} \quad (8)$$

$$\underset{\underset{O}{\|}}{PhCCH_3} + Li(CCl_2CHCH_2) \longrightarrow \underset{\underset{O^-Li^+}{|}}{Ph\dot{C}CH_3} + (CCl_2CHCH_2)^{\cdot}$$

$$\longrightarrow \underset{\underset{O^-Li^+}{|}}{PhC(CH_3)CH_2CH{=}CCl_2} \quad (9)$$

anistic pathways of the latter type have been demonstrated for reactions of Grignard reagents with ketones, usually in the presence of traces of transition metal catalysts, and lead to formation of varying amounts of pinacols instead of the expected C=O addition product.[14]

This possibility also is consistent with the observed Hammett σ correlation. The half-wave potentials for the substituted acetophenones used in this study decrease in a linear fashion[15] when compared with the Hammett σ constants for increased electron-withdrawing ability for the group. If an electron transfer process were operative, the decreased reduction potential of the carbonyl group would facilitate its reaction, thus leading to increased yields of the alcohol derived from bond formation at the CH_2 terminus of *gem*-dichloroallyllithium. Of course, there is no available information at the present time concerning the ability of this reagent to act as an electron donor, but the dichloroallyl radical has been postulated as an intermediate in the reductive coupling of 3,3,3-trichloropropene with copper in pyridine (eq 10).[16]

$$CCl_3CH{=}CH_2 \xrightarrow{Cu/pyridine} CCl_2{=}CHCH_2CH_2CH{=}CCl_2\ (71\%)$$
$$+\ CCl_2{=}CHCH_2CCl_2CH{=}CH_2\ (25\%)$$
$$+\ CH_2{=}CHCCl_2CCl_2CH{=}CH_2\ (4\%) \quad (10)$$

However, there are factors which speak against an electron transfer mechanism. The high isolated yields of the tertiary alcohol and the absence of pinacol-type products mean that if such a process is operating, it does so with a high degree of selectivity and probably is a rapid process within a solvent cage. There also is some chemical evidence which speaks against an electron transfer mechanism, and the case of *p*-cyanoacetophenone is pertinent. Although acetophenone has a much lower reduction potential than benzonitrile, in *p*-cyanoacetophenone the cyano group is readily reduced via an imine to an aminomethyl group before electrochemical reduction of the carbonyl group.[17] If, in our reactions, an electron transfer process were responsible for the product formed via the CH_2 terminus of $Li(CCl_2CHCH_2)$, one might have expected to find attack of this reagent at the C≡N function via the CH_2 terminus. Preference for attack at the ketone function rather than at the C=N group would be expected in the case of a nucleophilic substitution process.[18] As noted in Table II, the attack of *gem*-dichloroallyllithium occurs exclusively at the C=O function of *p*-cyanoacetophenone, and we feel, therefore, that both types of products obtained in these $Li(CCl_2CHCH_2)$/carbonyl compound reactions arise in a polar, nucleophilic substitution process.

As mentioned briefly in our preliminary communication,[1] one may rationalize the results obtained in this study of *gem*-dichloroallyllithium in terms of Pearson's hard/soft acid/base (HSAB) approach. (The alkylation of ambident anions with competing carbon and oxygen reaction centers had already been explained using this model.[19]) The CCl_2 terminus of the *gem*-dichloroallyl anion, with its inductively electron-withdrawing chlorine substituents, will be much more efficient at delocalizing its share of the negative charge and as such is the "softer" end of the nucleophile. If hard/soft interactions are operative, the CCl_2 terminus should show a preference for reaction with "soft" electrophiles, such as dialkyl ketones with their two electron-releasing alkyl groups which help to "soften" the electrophilic C=O function. The converse also is true. The CH_2 terminus of the *gem*-dichloroallyl anion is the "harder" nucleophilic site and as such prefers to combine with "hard" electrophilic centers. Carbonyl compounds with inductively electron-withdrawing substituents such as phenyl-substituted aldehydes and ketones and hexafluoroacetone comply with this requirement and thus react to form the new C–C bond with the CH_2 terminus. Aliphatic aldehydes and acetophenone clearly are borderline cases, and the latter is susceptible to C=O "hardening" or "softening" via substituents on the phenyl group. This approach in the present case is only a rationalization, but in the absence of further mechanistic information it is a useful one because it does have predictive value. Since our initial communication, Barbot, Chan, and Miginiac[20] have used the HSAB approach to rationalize the regioselectivity observed in the addition reactions of the allylic lithium reagent

Table III

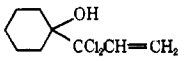
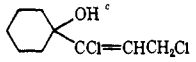
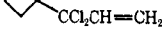
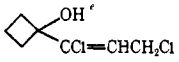
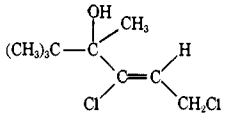
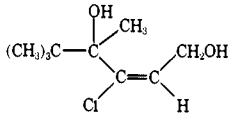
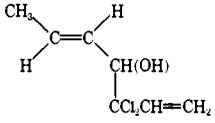
Compd	n^{25}D	Anal. found (calcd), % Carbon	Hydrogen	Chlorine	^{1}H NMR, δ (CCl_4 solution)
(1) $(CH_3)_2C(OH)CCl_2CH{=}CH_2$	1.4818	42.88 (42.63)	6.08 (5.96)	41.70 (41.95)	1.47 (s, 6 H, CH_3) 2.20 (s, 1 H, OH) 5.27–6.62 (ABC m, $CH{=}CH_2$)
(2) $(CH_3)_2C(OH)CCl{=}CHCH_2Cl$[a]	1.4926	42.72 (42.63)	6.22 (5.96)	41.81 (41.95)	1.47 (s, 6 H, CH_3) 2.68 (s, 1 H, OH) 4.19 (d, J = 7 Hz, 2 H, CH_2) 6.17 (t, J = 7 Hz, 1 H, =CH)
(3) 	1.5150	51.86[b] (51.69)	6.75 (6.75)	33.65 (33.91)	1.13–1.98 (m, 10 H, C_6H_{10}) 1.85 (s, 1 H, OH) 5.23–6.55 (ABC m, $CH{=}CH_2$)
(4) 	1.5298	*b*			1.33–1.87 (m, 10 H, C_6H_{10}) 1.95 (s, 1 H, OH) 4.17 (d, J = 7 Hz, 2 H, CH_2) 6.10 (t, J = 7 Hz, 1 H, =CH)
(5) 	1.5078	46.49[d] (46.43)	5.50 (5.57)	39.72 (39.16)	1.43–2.83 (m, 6 H, C_4H_6) 2.73 (s, 1 H, OH) 5.28–6.48 (ABC m, 3 H, $CH{=}CH_2$)
(6) 	1.5192	*d*			1.58–2.72 (m, 6 H, C_4H_6) 2.57 (s, 1 H, OH) 4.19 (d, J = 7 Hz, 2 H, CH_2) 5.87 (t, J = 7 Hz, 1 H, =CH)
(7) 	1.4936	51.29 (51.20)	7.90 (7.64)	33.85 (33.58)	1.00 (s, 9 H, Me_3C) 1.47 (s, 3 H, CH_3) 1.50 (s, 1 H, OH) 4.20 (d, J = 8 Hz, 2 H, CH_2) 6.20 (t, J = 8 Hz, 1 H, =CH)
(8) 	Solid, mp 89.5–91.0 °C	56.05 (56.10)	8.88 (8.89)	18.33 (18.40)	(in $CDCl_3$) 1.00 (s, 9 H, Me_3C) 1.43 (s, 3 H, CH_3) 2.35 (s, 1 H, tertiary OH) 2.55 (t, J = 6 Hz, 1 H, CH_2OH) 4.35 (t, J = 6 Hz, 2 H, CH_2) 6.12 (t, J = 6 Hz, 1 H, =CH)
(9) 	1.5030	46.49 (46.43)	5.60 (5.57)	39.16 (39.16)	1.76 (d, J = 5 Hz, 3 H, CH_3) 3.43 (s, 1 H, OH) 4.23 (d, J = 6 Hz, 1 H, C*H*(OH)) 5.22–6.37 (m, 5 H, vinyl)
(10) $CH_2{=}CHCH(OH)CH_2CH{=}CCl_2$	1.4966	43.07 (43.14)	5.06 (4.83)	42.91 (42.45)	2.40 (d of d, 2 H, C*H*CH_2C*H*) 2.83 (s, 1 H, OH) 4.15 (q, J = 6 Hz, 1 H, C*H*(OH) 5.02–6.13 (ABC m, $CH{=}CH_2$) 5.90 (t, J = 7 Hz, =C*H*CH_2)
(11) $CH_3CH(OH)CCl_2CH{=}CH_2$	1.4852	38.76[f] (38.74)	5.31 (5.20)	45.45 (45.39)	1.48 (d, J = 6 Hz, 3 H, CH_3) 2.90 (s, 1 H, OH) 4.02 (q, J = 6 Hz, 1 H, CH_3C*H*)
(12) $CH_3CH(OH)CCl{=}CHCH_2Cl$[g]	1.4967	*f*			1.38 (d, J = 6 Hz, 3 H, CH_3) 2.54 (d, J = 5 Hz, 1 H, OH) 4.17 (d, J = 8 Hz, 2 H, CH_2) 4.30 (quintet, 1 H, CH_3C*H*) 6.00 (t, 1 H, J = 8 Hz, C*H*CH_2)
(13) $CH_3CH(OH)CH_2CH{=}CCl_2$	1.4858	*f*			1.22 (d, J = 6 Hz, 3 H, CH_3) 2.28 (d of d, 2 H, CH_2) 2.80 (s, 1 H, OH) 3.86 (sextuplet, 1 H, CH_3C*H*) 5.95 (t, J = 7 Hz, 1 H, =CH)
(14) $CH_3CH_2CH(OH)CCl_2CH{=}CH_2$	1.4810	42.83 (42.63)	6.02 (5.96)	41.47 (41.95)	0.90–2.43 (m, 5 H, C_2H_5) 3.03 (s, 1 H, OH) 3.68 (d of d, 1 H, C*H*OH) 5.25–6.41 (ABC m, 3 H, $CH{=}CH_2$)

Table III (*Continued*)

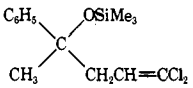
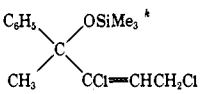
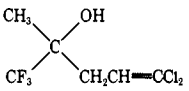
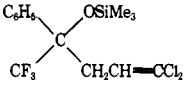
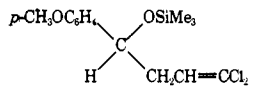
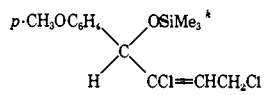
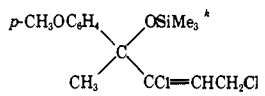
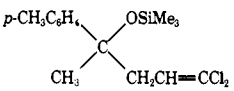
Compd	n^{25}D	Anal. found (calcd), % Carbon	Hydrogen	Chlorine	^{1}H NMR, δ (CCl_4 solution)
(15) $CH_3CH_2CH(OH)CH_2CH{=}CCl_2$	1.4826[h]	Known compound			0.95 (t, J = 6 Hz, 3 H, CH_3) 1.52 (q, J = 6 Hz, 2 H, CH_2) 2.28 (d of d, $CH_2CH{=}$) 2.41 (s, 1 H, OH) 3.58 (quintet, 1 H, $CHOH$) 5.95 (t, J = 7.5 Hz, 1 H, =CH)
(16) $C_6H_5CH(OH)CH_2CH{=}CCl_2$[i]	1.5610	55.39 (55.32)	4.66 (4.64)	32.39 (32.66)	2.10 (s, 1 H, OH) 2.5 (d of d, 2 H, CH_2) 4.63 (t, J = 6.5 Hz, 1 H, $CHOH$) 5.88 (t, J = 7 Hz, 1 H, =CH) 7.33 (m, 5 H, C_6H_5)
(17) $CCl_3CH(OH)CH_2CH{=}CCl_2$	1.5261	23.48 (23.24)	2.15 (1.95)	68.09 (68.62)	2.22–3.23 (m, 3 H, CH_2CHOH) 3.96–4.30 (m, 1 H, $CHOH$) 6.05 (t, J = 7 Hz, 1 H, =CH)
(18) 	1.5069	55.61[j] (55.44)	6.65 (6.65)	23.64 (23.37)	0.08 (s, 9 H, Me_3Si) 1.60 (s, 3 H, CH_3) 2.54 (d, J = 7 Hz, 2 H, CH_2) 5.68 (t, J = 7 Hz, 1 H, =CH) 7.00–7.43 (m, 5 H, C_6H_5)
(19) 	1.5143	*j*			0.03 (s, 9 H, Me_3Si) 1.80 (s, 3 H, CH_3) 4.49 (d, J = 7 Hz, 2 H, CH_2) 6.23 (t, J = 7 Hz, 1 H, =CH) 7.00–7.43 (m, 5 H, C_6H_5)
(20) 	1.4304	32.27 (32.31)	3.24 (3.17)	31.77 (31.79)	1.40 (s, 3 H, CH_3) 2.58 (d, J = 8 Hz, 2 H, CH_2) 3.13 (s, 1 H, OH) 6.00 (t, J = 8 Hz, =CH)
(21) 	1.4775	47.21 (47.06)	4.88 (4.80)	19.96 (19.85)	0.25 (s, 9 H, Me_3Si) 3.03 (d, J = 6 Hz, 2 H, CH_2) 5.57 (t, J = 6 Hz, 1 H, =CH) 7.18–7.58 (m, 5 H, C_6H_5)
(22) $(CF_3)_2C(OH)CH_2CH{=}CCl_2$	1.3883	26.03 (26.01)	1.55 (1.45)	25.49 (25.60)	2.83 (s, 1 H, OH) 2.90 (d, J = 8 Hz, 2 H, CH_2) 5.97 (t, J = 8 Hz, 1 H, =CH)
(23) $(C_6H_5)_2C(OH)CH_2CH{=}CCl_2$[l]	1.5969	65.14 (65.54)	4.81 (4.91)		2.33 (s, 1 H, OH) 3.07 (d, J = 8 Hz, 2 H, CH_2) 5.80 (t, J = 8 Hz, 1 H, =CH) 7.25 (m, 10 H, C_6H_5)
(24) 	1.5438	52.90[m] (52.66)	6.49 (6.31)	22.68 (22.21)	−0.03 (s, 9 H, Me_3Si) 2.43 (t, J = 7 Hz, 2 H, CH_2) 3.75 (s, 3 H, OCH_3) 4.57 (t, J = 6 Hz, 1 H, CHOSi) 5.75 (t, J = 7 Hz, 1 H, =CH) 6.62–7.17 (m, 4 H, C_6H_4)
(25) 	1.5223	*m*			0.07 (s, 9 H, Me_3Si) 3.77 (s, 3 H, OCH_3) 4.13 (d, J = 8 Hz, 2 H, CH_2) 5.00 (s, 1 H, CHOSi) 6.12 (t, J = 8 Hz, 1 H, =CH) 6.65–7.23 (m, 4 H, C_6H_4)
(26) 	1.5251	54.36 (54.04)	6.76 (6.66)	21.46 (21.27)	0.00 (s, 9 H, Me_3Si) 1.80 (s, 3 H, CH_3) 3.72 (s, 3 H, OCH_3) 4.14 (d, J = 7 Hz, 2 H, CH_2) 6.27 (t, J = 7 Hz, 1 H, =CH) 6.67–7.30 (m, 4 H, C_6H_4)
(27) 	1.5171	56.95[n] (56.77)	7.10 (6.99)	22.49 (22.34)	0.08 (s, 9 H, Me_3Si) 1.63 (s, 3 H, CH_3) 2.38 (s, 3 H, aryl CH_3) 2.56 (d, J = 7 Hz, 2 H, CH_2) 5.72 (t, J = 7 Hz, 1 H, =CH) 6.95–7.32 (m, 4 H, C_6H_4)

Table III (*Continued*)

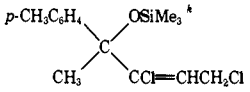
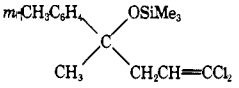
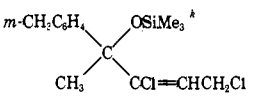
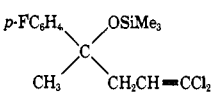
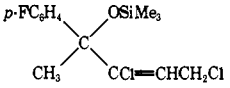
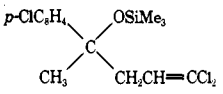
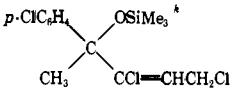
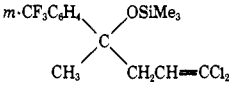
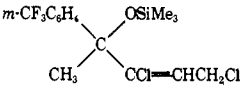
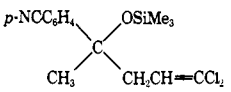
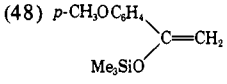
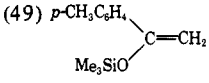
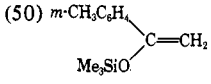
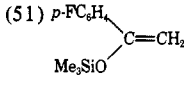
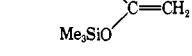
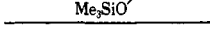
Compd	n^{25}D	Anal. found (calcd), % Carbon	Hydrogen	Chlorine	^{1}H NMR, δ (CCl_4 solution)
(28) 	1.5139	*n*			0.05 (s, 9 H, Me_3Si) 1.85 (s, 3 H, CH_3) 2.38 (s, 3 H, aryl CH_3) 4.16 (d, J = 8 Hz, 2 H, CH_2) 6.27 (t, J = 8 Hz, 1 H, =CH) 6.95–7.32 (m, 4 H, C_6H_4)
(29) 	1.5099	56.95[o] (56.77)	7.12 (6.99)	22.38 (22.34)	0.08 (s, 9 H, Me_3Si) 1.62 (s, 3 H, CH_3) 2.35 (s, 3 H, aryl CH_3) 2.55 (d, J = 7 Hz, 2 H, CH_2) 5.68 (t, J = 7 Hz, 1 H, =CH) 6.90–7.28 (m, 4 H, C_6H_4)
(30) 	1.5128	*o*			0.05 (s, 9 H, Me_3Si) 1.82 (s, 3 H, CH_3) 2.35 (s, 3 H, aryl CH_3) 4.18 (d, J = 8 Hz, 2 H, CH_2) 6.22 (t, J = 8 Hz, 1 H, =CH) 6.90–7.28 (m, 4 H, C_6H_4)
(31) 	1.5005	52.41[p] (52.33)	6.15 (5.96)	22.41 (22.07)	0.08 (s, 9 H, Me_3Si) 1.62 (s, 3 H, CH_3) 2.56 (d, J = 7 Hz, 2 H, CH_2) 5.67 (t, J = 7 Hz, 1 H, =CH) 6.77–7.41 (m, 4 H, C_6H_4)
(32) 	1.5057	*p*			0.07 (s, 9 H, Me_3Si) 1.82 (s, 3 H, CH_3) 4.17 (d, J = 7 Hz, 2 H, CH_2) 6.27 (t, J = 7 Hz, 1 H, =CH) 6.77–7.41 (m, 4 H, C_6H_4)
(33) 	1.5192	50.39[q] (49.78)	5.81 (5.67)	31.36 (31.49)	0.12 (s, 9 H, $SiMe_3$) 1.62 (s, 3 H, CH_3) 2.54 (d, J = 7 Hz, 2 H, CH_2) 5.67 (t, J = 7 Hz, 1 H, =CH) 7.27 (s, 4 H, C_6H_4)
(34) 	1.5243	*q*			0.08 (s, 9 H, Me_3Si) 1.82 (s, 3 H, CH_3) 4.15 (d, J = 8 Hz, 2 H, CH_2) 6.25 (t, J = 8 Hz, 1 H, =CH) 7.27 (s, 4 H, C_6H_4)
(35) 	1.4722	48.87[r] (48.52)	5.25 (5.16)	18.72 (19.09)	0.17 (s, 9 H, Me_3Si) 1.68 (s, 3 H, CH_3) 2.60 (d, J = 8 Hz, 2 H, CH_2) 5.73 (t, J = 8 Hz, 1 H, =CH) 7.37–7.70 (m, 4 H, C_6H_4)
(36) 	1.4800	*r*			0.10 (s, 9 H, Me_3Si) 1.87 (s, 3 H, CH_3) 4.20 (d, J = 8 Hz, 2 H, CH_2) 6.33 (t, J = 8 Hz, 1 H, =CH) 7.37–7.70 (m, 4 H, C_6H_4)
(37) 	1.5225	55.17[s] (54.87)	6.04 (5.83)	21.53 (21.60)	0.13 (s, 9 H, Me_3Si) 1.63 (s, 3 H, CH_3) 2.57 (d, J = 8 Hz, 2 H, CH_2) 5.63 (t, J = 8 Hz, 1 H, =CH) 7.27–7.70 (m, 4 H, C_6H_4)
(38) $CH_2{=}CHCCl_2CO_2CH_3$	1.4621	35.72 (35.53)	3.63 (3.58)	42.05 (41.95)	3.90 (s, 3 H, CH_3) 5.33–6.53 (ABC m, 3 H, $CH{=}CH_2$)
(39) $CH_2{=}CHCCl_2CH{=}O$	1.4636	34.31 (34.57)	3.02 (2.90)	50.37 (51.02)	5.43–6.40 (ABC m, 3 H, $CH{=}CH_2$) 9.17 (s, 1 H, CH=O)
(40) $CH_3\underset{\underset{O}{\|}}{C}CCl_2CH{=}CH_2$	1.4638	39.21 (39.25)	4.00 (3.95)	46.14 (46.34)	2.50 (s, 3 H, CH_3) 5.33–6.47 (ABC m, 3 H, $CH{=}CH_2$)
(41) $ClCH_2\underset{\underset{O}{\|}}{C}CCl_2CH{=}CH_2$		32.43 (32.03)	2.84 (2.69)	56.94 (56.74)	4.73 (s, 2 H, CH_2Cl) 5.45–6.48 (ABC m, 3 H, $CH{=}CH_2$)
(42) $(CH_3)_2CH\underset{\underset{O}{\|}}{C}CCl_2CH{=}CH_2$	1.4585	46.55 (46.43)	5.61 (5.57)	38.92 (39.16)	1.09 (d, J = 3.5 Hz, 6 H, Me_2C) 3.47 (m, 1 H, CHC=O) 5.33–6.53 (ABC m, 3 H, $CH{=}CH_2$)

Table III. (Continued)

Compd	n^{25}D	Anal. found (calcd), % Carbon	Hydrogen	Chlorine	^{1}H NMR, δ (CCl_4 solution)
(43) $C_6H_5\underset{\underset{O}{\|}}{C}CCl_2CH{=}CH_2$	1.5642	57.23[t] (55.84)	3.75 (4.00)	31.43 (32.97)	5.27–6.75 (ABC m, 3 H, CH=CH_2) 7.15–8.20 (m, 5 H, C_6H_5)
(44) $CH_3CCl_2CH{=}CH_2$[i]	1.4473	38.73 (38.43)	5.03 (4.84)	55.68 (56.73)	2.25 (s, 3 H, CH_3) 4.0–6.5 (ABC m, 3 H, CH=CH_2)
(45) $CH_2{=}CHCH_2CCl_2CH{=}CH_2$	1.4736	47.95 (47.71)	5.43 (5.34)	46.65 (46.95)	2.90–3.10 (m, 2 H, CH_2CCl_2) 5.00–6.37 (m, 6 H, CH=CH_2)
(46) $CH_2{=}CHCH_2CCl{=}CHCH_2Cl$[u]	1.4906	48.26 (47.71)	5.43 (5.34)	46.10 (46.95)	3.00–3.27 (m, 2 H, CH_2) 4.06–4.23 (m, 2 H, CH_2) 4.87–6.20 (m, 4 H, CH_2=CH and =CH)
(47) $C_6H_5CH_2CCl_2CH{=}CH_2$	1.5455	60.79[t] (59.72)	5.18 (5.01)		3.43 (s, 2 H, CH_2CCl_2) 4.93–6.23 (ABC m, 3 H, CH=CH_2) 7.20 (s, 5 H, C_6H_5)
(48) 	1.5147	64.81 (64.81)	8.15 (8.16)		0.30 (s, 9 H, Me_3Si) 3.73 (s, 3 H, OCH_3) 4.22 and 4.68 (2 d, 2 H, CH_2)[v] 6.63–7.48 (m, 4 H, C_6H_4)
(49) 	1.5016	69.78 (69.84)	8.88 (8.79)		0.27 (s, 9 H, Me_3Si) 2.33 (s, 3 H, CH_3) 4.27 and 4.75 (2 d, 2 H, CH_2)[v] 6.93–7.45 (m, 4 H, C_6H_4)
(50) 	1.4989	69.47 (69.84)	8.95 (8.79)		0.27 (s, 9 H, Me_3Si) 2.32 (s, 3 H, CH_3) 4.30 and 4.80 (2 d, 2 H, CH_2)[v] 6.88–7.35 (m, 4 H, C_6H_4)
(51) 	1.4841	62.75 (62.81)	7.37 (7.19)		0.27 (s, 9 H, Me_3Si) 4.28 and 4.73 (2 d, 2 H, CH_2)[v] 6.73–7.57 (m, 4 H, C_6H_4)
(52) 	1.5145	57.76 (58.25)	6.65 (6.67)		0.25 (s, 9 H, Me_3Si) 4.28 and 4.75 (2 d, 2 H, CH_2)[v] 7.07–7.47 (m, 4 H, C_6H_4)
(53) 	1.4541	55.09 (55.36)	5.88 (5.81)		0.28 (s, 9 H, Me_3Si) 4.45 and 4.92 (2 d, 2 H, CH_2)[v] 7.27–7.83 (m, 4 H, C_6H_4)

[a] Obtained by thermal allylic rearrangement of compound (1). [b] Analyzed as a mixture of compounds (3) and (4). [c] Obtained by thermal allylic rearrangement of compound (3). [d] Analyzed as a mixture of compounds (5) and (6). [e] Obtained by thermal allylic rearrangement of compound (5). [f] Analyzed as a mixture of compounds (11), (12), and (13). [g] Obtained by thermal allylic rearrangement of compound (11). [h] Lit. $n^{24.2}$D 1.4827: A. LeCoq and E. Levas, *C. R. Acad. Sci., Ser. C*, **264**, 1200 (1967). [i] First prepared by R. A. Woodruff using $Li(CCl_2CHCH_2)$ obtained by the $CCl_3CH{=}CH_2$ + n-C_4H_9Li reaction: R. A. Woodruff, Ph.D. Thesis, Massachusetts Institute of Technology, 1973. [j] Analyzed as a mixture of compounds (18) and (19). [k] The $CH_2{=}CHCCl_2$-substituted product could not be isolated by GLC, although its formation was evident from the NMR spectrum of the crude product mixture. Its allylic rearrangement product was obtained by GLC of the product mixture instead and was characterized. [l] This product was dehydrated by treatment with sulfuric acid to give $(C_6H_5)_2C{=}CHCH{=}CCl_2$: n^{25}D 1.6640; NMR δ 6.37 (d, J = 11 Hz, 1 H, $Ph_2C{=}CH$), 6.74 (d, J = 11 Hz, 1 H, $CCl_2{=}CH$), and 7.20 ppm (m, 10 H, C_6H_5). Anal. Calcd for $C_{16}H_{12}Cl_2$: C, 69.83; H, 4.40, Cl, 25.77. Found: C, 69.92; H, 4.68; Cl, 25.60. [m] Analyzed as a mixture of compounds (24) and (25). [n] Analyzed as a mixture of compounds (27) and (28). [o] Analyzed as a mixture of compounds (29) and (30). [p] Analyzed as a mixture of compounds (31) and (32). [q] Analyzed as a mixture of compounds (33) and (34). [r] Analyzed as a mixture of compounds (35) and (36). [s] N: found, 4.34; calcd, 4.27. [t] Analysis of crude distilled sample; decomposition on GLC. [u] Obtained by thermal allylic rearrangement of compound (45). [v] J_{gem} = 2 Hz.

$Li(MeEtCCHCH_2)$ with aldehydes and ketones. The HSAB model also has been used to explain the ambident reactivity of dilithiopropargylides.[21]

Whatever the explanation for the regioselectivity of the *gem*-dichloroallyllithium reagent with aldehydes and ketones, such a strong dependence on substrate electronic factors and not on substrate steric factors is unprecedented in allyl anion chemistry. The utility of *gem*-dichloroallyllithium in organic synthesis has been demonstrated with many examples. The chlorine substituents introduced into the product in its reactions with carbonyl compounds should be capable of further conversions, but this point is beyond the scope of our present interests.

Experimental Section

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 empiricially 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 using tetramethylsilane as internal standard. Infrared spectra were obtained using a Perkin-Elmer 457A grating infrared spectrophotometer.

n-Butyllithium in hexane was purchased from Alfa/Ventron. The carbonyl compounds were commercial products (Aldrich or Eastman) and were used as received or purified if necessary. 1,1,1,3-Tetrachloropropane was purchased from PCR Chemicals, Inc. Trimethylchlorosilane was donated by Union Carbide Corp.

Characterizing data for new compounds prepared in this study are collected in Table III.

Preparation of 3,3-Dichloroallyltriphenyllead ($Ph_3PbCH_2CH{=}CCl_2$). (a) Preparation of 3,3-Dichloroallyl Chloride ($CCl_2{=}CH{-}CH_2Cl$). A modification of Haszeldine's procedure[22] was used.

A flame-dried and nitrogen-flushed 75-mL Carius tube equipped with a no-air stopper and a syringe needle for evacuation was charged with 61.5 g (0.424 mol) of 3,3,3-trichloropropene (prepared by dehydrochlorination of 1,1,1,3-tetrachloropropane[22]) and degassed with one freeze-thaw cycle. The tube was sealed at liquid nitrogen temperature at 0.1 mmHg and then was placed in a bomb tube furnace for 20 h at 155 °C. Upon removal of the tube from the furnace the only apparent change in the liquid contents was a slight yellowing. The tube was cooled and opened. GLC analysis of the liquid showed it to contain a single component whose structure was confirmed as $CCl_2{=}CHCH_2Cl$ by its ^1H NMR spectrum. Distillation afforded 57.9 g (94%) of product: bp 132-134 °C (lit.[22] bp 130.0-131.5 °C); n^{25}_D 1.4943 (lit.[23] n^{18}_D 1.4960); NMR (CCl_4) δ 4.15 (d, J = 8.0 Hz, CH_2) and 6.12 ppm (t, J = 8.0 Hz, =CH); IR (film) 3062 m, 2968 m, 1619 vs, 1442 m, 1288 m, 1249 s, 1178 m, 950 s, 869 vs, 838 s, 693 m, 601 cm^{-1} m.

(b) Preparation of the Lead Reagent. A 3-L, three-necked Morton (creased) flask, which was equipped with a pressure-equalizing dropping funnel, a mechanical stirrer, and a reflux condenser topped with a nitrogen inlet tube, was flame dried, flushed with dry nitrogen, and charged with 48.6 g (2.0 mol) of magnesium turnings and 4 pints of THF (Mallinckrodt, freshly opened bottles). The dropping funnel was charged with 330 g (2.1 mol) of bromobenzene which then was added dropwise (after initiation) at such a rate as to maintain a gentle reflux. The Grignard solution was stirred overnight in order to ensure complete consumption of magnesium.[24] The reaction vessel containing the magnesium-free PhMgBr solution was cooled thoroughly with a wet ice bath and then 167 g (0.60 mol) of lead(II) chloride (Baker reagent, ground to a fine powder in a mortar and pestle before use) was added in one portion as rapidly as possible. It was necessary to continue vigorous stirring for 4 h to accomplish complete solution of the $PbCl_2$. The $Ph_3PbMgBr$ prepared in this manner was used in the subsequent step of the reaction.

A second 3-L, three-necked flask, which was equipped with a pressure-equalizing dropping funnel, a mechanical stirrer, and a nitrogen inlet, was charged with 102.0 g (0.70 mol) of 3,3-dichloroallyl chloride and 200 mL of dry tetrahydrofuran (THF) and was cooled with a wet ice bath. The triphenylleadmagnesium bromide solution was transferred under nitrogen to the dropping funnel and then was added dropwise to the cold $CCl_2{=}CHCH_2Cl$ solution over a period of 3 h. After the addition was complete, the reaction mixture was allowed to warm to room temperature, hydrolyzed with cold, saturated ammonium chloride solution to a "dry end point", and filtered. The magnesium salts were washed with two 200-mL portions of THF. The combined light yellow THF solutions were evaporated at reduced pressure and the residue was extracted with 1 L of chlorofrom. The chlorofrom solution was dried over magnesium sulfate and evaporated at reduced pressure, leaving yellow, crystalline solid. The latter was recrystallized from 1.4 L of hexane to give, in two crops, 275.7 g (0.506 mol, 84% yield) of $Ph_3PbCH_2CH{=}CCl_2$, mp 83-84 °C (lit.[25] mp 83-84.5 °C). Anal. Calcd for $C_{21}H_{18}Cl_2Pb$: C, 45.98; H, 3.31; Cl, 12.93. Found: C, 45.83; H, 3.24; Cl, 12.90. The IR and NMR spectra of the product were identical with those of authentic material obtained from the reaction of triphenylleadlithium with 3,3,3-trichloropropene.[25]

Reactions of *gem*-Dichloroallyllithium with Carbonyl Compounds. (a) Hydrolytic Workup. The reaction of *gem*-dichloroallyllithium with benzaldehyde is described in detail to illustrate the procedure used.

A 500-mL, three-necked Morton flask equipped with a pressure-equalizing dropping funnel, a mechanical stirrer, and a Claisen adapter fitted with a pentane thermometer and a nitrogen inlet ("standard apparatus") was flame dried, flushed with nitrogen, and charged with 20.89 g (38.1 mmol) of 3,3-dichloroallyltriphenyllead and 300 mL of THF (distilled from potassium benzophenone ketyl). The solution was cooled to −90 ± 2 °C while a solution of 38.3 mmol of *n*-butyllithium in 15 mL of hexane was added dropwise over a 10-min period. The reaction mixture was stirred at −90 °C for another 20 min and then 4.5 mL of freshly distilled benzaldehyde (ca. 45 mmol) was added dropwise, maintaining the temperature at −90 °C. The light amber color of the *gem*-dichloroallyllithium reagent was discharged immediately upon addition of the aldehyde. The mixture was stirred for 5 min at −90 °C and then was hydrolyzed by rapidly adding 50 mL of 1 N HCl. Subsequently the reaction mixture was allowed to warm to room temperature and extracted with 300 mL of diethyl ether and 200 mL of water. The organic layer was washed with two 500-mL portions of water and dried over magnesium sulfate and the solvents were removed at reduced pressure. Examination of the liquid residue before any application of heat by NMR spectroscopy showed that only $PhCH(OH)CH_2CH{=}CCl_2$ was present. Vacuum distillation of the residue gave 8.11 g (97%) of this alcohol, bp 88-92 °C (0.02 mmHg), n^{25}_D 1.5578. The pot residue solidified on cooling to afford 18.7 g (99%) of *n*-butyltriphenyllead. Recrystallization from ethanol gave pure material, mp 47-48 °C (lit.[26] mp 47 °C).

(b) Trimethylchlorosilane Workup. The reaction of *gem*-dichloroallyllithium with acetophenone is described as an example of the procedure used.

gem-Dichloroallyllithium was prepared as described in (a) by reaction of 45.3 mmol of $Ph_3PbCH_2CH{=}CCl_2$ in 300 mL of THF and 43.4 mmol of *n*-butyllithium in 18 mL of hexane at −90 ± 2 °C. The lithium reagent then was treated, at −90 °C, with 5.00 g (41.6 mmol) of freshly distilled acetophenone (dropwise addition). The light amber color of the lithium reagent solution was discharged immediately and the reaction mixture was stirred at −85 ± 5 °C for 30 min. Subsequently, 8.0 mL of freshly distilled trimethylchlorosilane (Union Carbide Corp.) was added. The resulting mixture was allowed to warm slowly to room temperature. It then was transferred, under nitrogen, to a 1-L, single-necked flask which was connected to a stillhead and a condenser, and the solvents were distilled at atmospheric pressure. After about 200 mL of THF had been removed, a large amount of lithium chloride was evident in the distilling flask. The flask was allowed to cool and the remainder of the solvents was removed at reduced pressure. The lithium chloride in the residue was removed by filtration under nitrogen and the salt cake was washed with 50 mL of carbon tetrachloride. NMR examination of the combined filtrate-CCl_4 washings showed the presence of both $CH_2{=}CHCCl_2$- and $CCl_2{=}CHCH_2$-type products, as well as of $Ph(Me_3SiO){=}CH_2$. Vacuum distillation afforded two fractions: 3.43 g (43%) of 1-phenyl-1-trimethylsiloxyethylene, bp 32-34 °C (0.02 mmHg), n^{25}_D 1.5001 (lit.[27] n^{20}_D 1.5008), whose IR and NMR spectra matched those reported,[28] and 6.01 g (47%) of the mixed dichloroallylation products. This fraction (by NMR) consisted of three components: $Ph(CH_3)C(OSiMe_3)CCl_2CH{=}CH_2$ (20%), $Ph(CH_3)C(OSiMe_3)$-$CH_2CH{=}CCl_2$ (18%), and the allylic chloride isomerization product of the first, $Ph(CH_3)C(OSiMe_3)CCl{=}CHCH_2Cl$ (9%). The first of these underwent complete rearrangement to the third on attempted isolation by GLC, and therefore only the second and third were characterized as pure compounds.

Reaction of *gem*-Dichloroallyllithium with Acetone Followed by Hexafluoroacetone. A Check for Reversible Addition to the Ketone. *gem*-Dichloroallyllithium was prepared as above by the reaction of 18.8 mmol of $Ph_3PbCH_2CH{=}CCl_2$ in 200 mL of THF and 19.3 mmol of *n*-butyllithium in 8 mL of hexane at −90 ± 2 °C. Subsequently 2.0 mL (ca. 27 mmol) of anhydrous acetone was added dropwise at this temperature. The reaction mixture was stirred for 5 min at −90 °C and then 29.2 g (ca. 176 mmol) of hexafluoroacetone (PCR, Inc., dried by passage through a column of P_2O_5) was condensed into the mixture. The resulting solution was allowed to warm slowly to room temperature and stirred for 1 h before hydrolytic workup as in (a) above. The organic layer was trap-to-trap distilled and the distillate was examined by GLC and NMR. Only $Me_2C(OH)CCl_2CH{=}CH_2$ was present; $(CF_3)_2C(OH)$-$CH_2CH{=}CCl_2$ could not be detected. A sample of the product was isolated by GLC and its identity was confirmed by means of its IR spectrum and its refractive index.

When the reaction was carried out in the reverse manner, i.e., when 1 molar equiv of hexafluoroacetone was added to the *gem*-dichloroallyllithium solution initially, followed by 9 molar equiv of acetone, only the hexafluoroacetone-derived alcohol was formed.

Carboxylation of *gem*-Dichloroallyllithium. The lithium reagent

was prepared from 40.9 mmol of $Ph_3PbCH_2CH{=}CCl_2$ in 300 mL of THF and 42.0 mmol of *n*-butyllithium in 16.5 mL of hexane at −90 ± 2 °C. Subsequently gaseous carbon dioxide was added by means of a gas inlet tube on top of the addition funnel at such a rate that the amber color of the lithium reagent was discharged in 3 min. The reaction mixture was stirred for 5 min more and then was hydrolyzed by addition of 50 mL of 1 N HCl. The contents of the flask were allowed to warm to room temperature and extracted with 300 mL of diethyl ether and 200 mL of water. The organic layer was extracted with two 500-mL portions of water and two portions of saturated sodium bicarbonate solution. The combined aqueous washings were acidified and extracted with two 200-mL portions of diethyl ether. The ether extracts were dried over magnesium sulfate and filtered, and the filtrate was concentrated under reduced pressure. The NMR spectrum of the crude product before any application of heat showed the distinctive ABC multiplet characteristic of the $CH_2{=}CHCCl_2$ substituent, with no evidence for the other isomer. The crude material was trap-to-trap distilled (100 °C at 0.05 mmHg) into a receiver at −78 °C. NMR analysis of the distillate showed the presence of 5.80 g (91%) of $CH_2{=}CHCCl_2CO_2H$ as the exclusive product: NMR (CCl_4) δ 5.0–6.2 (ABC multiplet, 3 H, $CH{=}CH_2$) and 9.0 ppm (s, 1 H, CO_2H). The acid darkened on storage under nitrogen in the refrigerator and therefore was converted to the methyl ester by treatment with ethereal diazomethane to facilitate its characterization.

Reaction of *gem*-Dichloroallyllithium with Ethylene Oxide. The lithium reagent was prepared from 40.3 mmol of $Ph_3PbCH_2CH{=}CCl_2$ and 40.9 mmol of *n*-butyllithium in the usual manner. To this solution, at −90 °C, was added 10 g (ca. 220 mmol) of ethylene oxide in 20 mL of THF, dropwise during a period of 10 min. Unlike the carbonyl reactions, the color of the reagent solution was not discharged. The reaction mixture was warmed cautiously to −72 °C and stirred at this temperature for 1 h without change in color. Subsequently, the mixture was hydrolyzed (50 mL of 1 N HCl), warmed to room temperature, extracted with 300 mL of ether and 200 mL of water, and washed with two 500-mL portions of water. The organic layer was dried, filtered, and concentrated at reduced pressure, and the residue was trap-to-trap distilled (to 100 °C at 0.02 mm). Concentration of the trap-to-trap distillate at room temperature under vacuum gave 0.99 g (16%) of $CH_2{=}CHCCl_2CH_2CH_2OH$: NMR (CCl_4) δ 2.58 (t, J = 7 Hz, 2 H, CCl_2CH_2), 3.08 (s, 1 H, OH), 3.92 (t, J = 7 Hz, 2 H, CH_2OH), and 5.18–6.42 ppm (ABC multiplet, 3 H, $CH{=}CH_2$). Attempts to isolate this compound by GLC failed, allylic rearrangement occurring to give $ClCH_2CH{=}CClCH_2CH_2OH$ (mixed isomers), a known compound[29] which was characterized spectroscopically: NMR (CCl_4) δ 2.63 and 2.68 (2 t, 2 H, $={}CClCH_2$), 2.70 (s, 1 H, OH), 3.78 (t, 2 H, CH_2OH), 4.06 and 4.16 (2 d, 2 H, CH_2Cl), and 5.81 and 5.97 ppm (2 t, 1 H, =CH). The mixture of isomers had n^{20}_D 1.5065.

Reaction of *gem*-Dichloroallyllithium with Esters. The lithium reagent was prepared from 39.6 mmol of $Ph_3PbCH_2CH{=}CCl_2$ in 300 mL of THF and 40.7 mmol of *n*-butyllithium in hexane at −95 °C by the usual procedure. To this solution was added dropwise with stirring 3.1 mL (ca. 50 mmol) of methyl formate. The amber color of the reagent was discharged. The reaction mixture was stirred at −95 °C for 30 min and then was hydrolyzed with 50 mL of 1 N HCl and warmed to room temperature. Subsequently it was extracted with three 100-mL portions of diethyl ether. The organic layer was washed with two 100-mL portions of water, dried, filtered, and concentrated at reduced pressure. The residue was trap-to-trap distilled under vacuum into a receiver at −78 °C to give 3.5 g (63%) of product, $CH_2{=}CHCCl_2CHO$. Samples for analysis and spectroscopic measurements were collected by GLC.

Alkylation of *gem*-Dichloroallyllithium. The reaction with methyl iodide is illustrative.

gem-Dichloroallyllithium was prepared from 37.1 mmol of $Ph_3PbCH_2CH{=}CCl_2$ in 300 mL of THF and 40.7 mmol of *n*-butyllithium in 17 mL of hexane at −90 °C. After the reagent solution had been stirred at −90 °C for 45 min, 7.1 g (50 mmol) of methyl iodide was added dropwise with stirring. The reaction mixture was allowed to warm to room temperature and hydrolyzed to the "dry end point" with saturated ammonium chloride solution and the organic layer was extracted with 200 mL of diethyl ether and 300 mL of water. The organic layer was dried, filtered, and trap-to-trap distilled (60 °C at 0.05 mmHg), leaving a residue of 18.2 g of *n*-butyltriphenyllead. The distillate was concentrated using a Widmer column to give a residue which NMR analysis showed to contain 4.55 g (98%) of $CH_3CCl_2CH{=}CH_2$. Samples for analysis and spectroscopy were isolated by GLC.

Similar procedures were used in the reactions of *gem*-dichloroallyllithium with allyl bromide and benzyl bromide. *gem*-Dichloroallyllithium did not react under these conditions with allyl chloride and $CCl_2{=}CHCH_2Cl$.

Hydrolysis of *gem*-Dichloroallyllithium. The lithium reagent was prepared in the usual manner from 36.5 mmol of $Ph_3PbCH_2CH{=}CCl_2$ in 300 mL of THF and 40.7 mmol of *n*-butyllithium in 17 mL of hexane at −90 °C. After the mixture had been stirred for 45 min at −90 °C, a saturated aqueous solution of ammonium chloride was added dropwise. As the addition progressed, a color change to dark purple began to take place and therefore the remainder of the ammonium chloride solution (50 mL) was added as rapidly as possible. Subsequently 50 mL of 1 N HCl was added. A light yellow organic layer resulted. Extraction with 200 mL of diethyl ether and 300 mL of water followed. The organic layer was washed with 500 mL of water, dried over magnesium sulfate, filtered, and trap-to-trap distilled (60 °C at 0.05 mm) into a receiver at −78 °C. Concentration of the distillate using a Widmer column left a residue, NMR analysis of which showed the presence of $HCCl_2CH{=}CH_2$, the sole product, in 87% yield. A GLC sample had n^{20}_D 1.4521 (lit.[30] n^{20}_D 1.4510), NMR (CCl_4) δ 5.00–6.30 ppm (ABCD multiplet).

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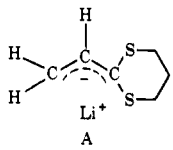

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Stereochemistry of Addition of 2-Cyano-1,3-diphenylallyllithium to *trans*-Stilbene, an Anionic [3 + 2] Cycloaddition

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Abstract: Cycloaddition of 2-cyano-1,3-diphenylallyllithium to *trans*-stilbene produces detectable amounts (by NMR) of only two of the ten possible diastereomeric 2,3,4,5-tetraphenylcyclopentane-1-carbonitriles. The structure of the *r*-1,*c*-2,*c*-3,*t*-4,*c*-5 isomer (**1**) was established by x-ray analysis. Treatment of **1** with NaOH in aqueous dioxane inverts its configuration at C(1) to form the *r*-1,*t*-2,*c*-3,*t*-4,*t*-5 isomer (**2**), which is also the other compound formed by cycloaddition. Under identical conditions *cis*-stilbene does not react with 2-cyano-1,3-diphenylallyllithium. This is the first determination of the stereochemical course of cycloaddition of an allyl anion to a carbon–carbon double bond to form a five-membered carbocycle. The observed stereospecific cycloaddition with retention of the configuration of the *trans*-stilbene is predicted for a concerted reaction by conservation of orbital symmetry, but a stepwise cycloaddition mechanism cannot be ruled out.

The number of known examples of cycloadditions of allyl anions to carbon–carbon multiple bonds is small but growing. The oldest examples are the dimerizations of α-methylstyrene in the presence of an alkylbenzene and sodium or potassium metal,[2] which likely proceed by addition of 2-phenylallylsodium and 2-phenylallylpotassium to α-methylstyrene. 2-Phenylallyllithium in THF (tetrahydrofuran) and 2-phenylallylmagnesium phenoxide in THF/HMPA (hexamethylphosphoramide) add to *trans*-stilbene to give *r*-1,*t*-2,*c*-4-triphenylcyclopentane.[3] 2-Phenylallylmagnesium phenoxide in THF/HMPA also cycloadds to a variety of other electron-deficient olefins.[4] Treatment of 1,3-diphenylpropyne with lithium diisopropylamide (LDIA) in hexane gives a cyclic dimer.[5] 2-Cyano-1,3-diphenylallyllithium cycloadds to styrene, *trans*-stilbene, 1,1-diphenylethylene, and acenaphthylene.[6] Reaction of a 2-thiomethylenecyclohexanone derivative with LDIA forms a thioallyl anion which adds to ethyl acrylate and to diethyl fumarate to form hydrindanones.[7]

Conservation of orbital symmetry predicts that if these cycloadditions are concerted, they will proceed by a $_{\pi}4_s + {}_{\pi}2_s$ mechanism in which the configurations of both the allyl anion and the olefin are retained in the cyclopentyl anion.[8] All previous attempts to determine the stereochemical courses of these reactions have failed because of rapid isomerization of the reactants (and perhaps also isomerization of the products). For example, *cis*-stilbene isomerizes to *trans*-stilbene in 2-phenylallyllithium and 2-phenylallylmagnesium solutions more rapidly than either 2-phenylallylmetal compound adds to *trans*-stilbene,[4] and diethyl maleate apparently isomerizes to diethyl fumarate faster than diethyl fumarate adds to the lithium derivative of a 2-thiomethylenecyclohexanone.[7]

The stereochemical courses of cycloadditions of some heteroatom analogues of allyl anions to electron-deficient double bonds are known. (*E*,*E*)-1,3-Diphenyl-2-azaallyllithium cycloadds to both *cis*-stilbene and *trans*-stilbene to give different 2,3,4,5-tetraphenylpyrrolidines with "no detectable mutual contamination".[9] The ^{1}H NMR spectra of the pyrrolidines are consistent with the isomers expected from concerted $_{\pi}4_s + {}_{\pi}2_s$ reactions. Several examples of 1,3-dipolar cycloadditions with complete retention of configuration of both the 1,3-dipole and the dipolarophile are known, and "*no exceptions* have been observed" to the stereospecificity.[10] Among the 1,3-dipoles known to undergo stereospecific cycloadditions are the azomethine ylides obtained from ring openings of aziridines and the carbonyl ylides obtained from ring openings of oxiranes, both of which are isoelectronic with allyl anions.

Boche and Martens[6] reported previously that 2-cyano-1,3-diphenylallyllithium and *trans*-stilbene form a cycloadduct, but they did not determine which of the ten diastereomeric 2,3,4,5-tetraphenylcyclopentane-1-carbonitriles they isolated. This paper describes the isolation and determinations of structure of the only two of these diastereomers formed in large amounts.

Results

2-Cyano-1,3-diphenylallyllithium was prepared by treatment of *cis*,*trans*-2,3-diphenylcyclopropane-1-carbonitrile with 1 equiv of LDIA in THF at −78 °C followed by warming to room temperature for 1 h to complete electrocyclic opening of the cyclopropyllithium intermediate.[6,11] *trans*-Stilbene (1 equiv) was added, and the disappearance of stilbene was followed by GLC. Only two GLC peaks due to 1:1 adducts were detected after reaction times ranging from 5 to 150 min. Their yields reached constant values of 23 and 25% after 1 h. When the same procedure was employed with *cis*-stilbene, no 1:1 adducts could be detected at any time over a period of 96 h. Cycloaddition clearly occurred only with *trans*-stilbene.

The mixture of 1:1 adducts was purified by liquid chromatography. From the resulting oil one isomer crystallized. Its structure was established as *r*-1,*c*-2,*c*-3,*t*-4,*c*-5-tetraphenylcyclopentane-1-carbonitrile (**1**) by x-ray analysis (provided us by Drs. Chian C. Chiang and Iain C. Paul). A stereoscopic view of **1** is shown in Figure 1.

Treatment of **1** with NaOH in refluxing aqueous dioxane converted it to an oily mixture containing 97.7% of another isomer **2** and 2.3% of **1** by GLC analysis. (Isomer **1** appeared as the peak of shorter retention time. Isomer **2** appeared as the peak of longer retention time.) When the isomerization of **1**