

aminolysis of alkyl thiolacetates and thiolactones involving symmetrical partitioning of intermediates. Symmetrical partitioning of T in eq. 18 would destroy the dependence on acidity of the neutral water rate, k_{H_2O} . Thus, k_{obsd} would be equal to $k_1k_3/(k_3 + k_2)$, an expression which does not predict inhibition of ester solvolysis at high acidity. Catalysis of the collapse of T to products by carboxylic acid (eq. 21) would yield a rate expression containing square carboxylate terms in the numerator of the rate expression. The mechanism suggested by Jencks and Gilchrist⁹ for the hydroxylaminolysis of formamide and acetamide also involves unsymmetrical partitioning of intermediates (see eq. 1). Our failure to observe thiol ester formation from ethyl mercaptan and trifluoroacetic acid in 1 M HCl solution demonstrates that inhibition

of spontaneous solvolysis in acid solution is not due to an equilibrium situation between ester and products.

A kinetic analysis of experimental data cannot be said to prove a mechanism but can be employed to disprove mechanisms. An attempt has been made to consider kinetically all reasonable mechanisms for the hydrolytic behavior of ethyl trifluorothiolacetate. The favored interpretations are consonant with the experimental data in H₂O and D₂O.

Acknowledgment. We thank Mr. David Auld for doing the Fortran programming used in the evaluation of some of the constants and Professor S. J. Benkovic for helpful discussion. We also thank the National Science Foundation and the National Institutes of Health for financial support during the course of this investigation.

Preparation and Chemistry of α -Chloroalkyllithium Compounds. Their Role as Carbenoid Intermediates¹

Donald F. Hoeg, Donald I. Lusk, and Alvin L. Crumbliss

*Contribution from the Borg-Warner Research Center, Des Plaines, Illinois.
Received April 2, 1965*

*The reaction of polychloromethanes with *n*-butyllithium in tetrahydrofuran at low temperatures (-100°) via α -metalation or halogen-metal interconversion has been used to prepare a new class of organolithium reagents, the α -chloroalkyllithium compounds I-IV. The procedure was based on our observation of the remarkable stabilizing influence of tetrahydrofuran on α -chloroalkyllithium structures. At low temperatures, these compounds behave as typical organolithium structures and have been characterized by hydrolysis, deuterolysis, and direct carbonation to the corresponding acids (or derivatives). They react (couple) readily with the more reactive alkyl halides, presumably via nucleophilic displacements of the chloro carbanion on carbon. While these compounds were indefinitely stable at -100° , they decomposed spectacularly above -65° , suggestive of carbene formation via elimination of LiCl. If olefins were present during this decomposition (they were added without evidence of reaction at -100°), good yields of the corresponding cyclopropanes were obtained from α,α -dichlorobenzylithium and trichloromethylithium. In contraindication of a free carbene mechanism in the formation of the cyclopropanes, however, the stability of α -chloroalkyllithium compounds appears influenced by the more nucleophilic olefins, suggestive of a direct reaction of the olefin with the organolithium compound (or its structural equivalent), the reactivity (nucleophilic olefin sequence) and specificity in qualitative accord with results previously thought indicative of a free carbene intermediate. Several mechanisms are considered in the light of these results.*

(1) Paper II in the series Chemistry of α -Halocarbanion Intermediates; presented before the 149th National Meeting of the American Chemical Society, Detroit, Mich., April 1965.

α -Haloalkyllithium compounds have been suggested to have transient existence in the proposed carbene-forming reactions of alkyl halides (via α -dehydrohalogenation) and polyhalomethanes (via α -dehalogenation) with organolithium compounds, leading, in the presence of olefins, to cyclopropane ring systems.² The apparent high instability of these compounds, however, had, for the most part, prevented their isolation to date, and even their detection via diverting reactions as carbonation, hydrolysis, and deuterolysis had had but limited success.^{3,4} Distinguishing between the α -haloalkyllithium compounds existing as high energy intermediates in their own right or simply transition states in concerted α -eliminations leading to the free carbene had, therefore, been difficult.

More recently, Miller and Whalen reported the detection of trichloromethylithium as a distinct structural entity, possessing limited stability, in the reaction of bromotrichloromethane with *n*-butyllithium in ethyl ether at -115° .⁵ Moreover, of great significance with respect to the evidence of free carbenes in reactions of this type, they reported its direct rapid reaction at -100° with cyclohexene to yield dichloronorcaradiene.

Several years ago, an extraordinary and apparently unique stabilizing influence of tetrahydrofuran on α -chloroalkyllithium structures was discovered in this laboratory which led to a broad study of their behavior

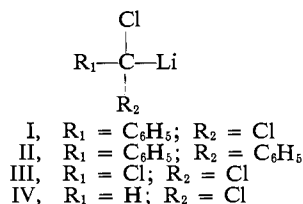
(2) For a recent review of the subject of carbene chemistry, see J. Hine, "Divalent Carbon," The Ronald Press Co., New York, N. Y., 1964, and W. Kirmse, "Carbene Chemistry," Academic Press Inc., New York, N. Y., 1964.

(3) G. L. Closs and L. E. Closs, *J. Am. Chem. Soc.*, **81**, 4996 (1959).

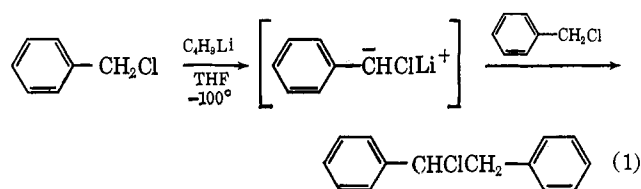
(4) W. T. Miller and C. S. Y. Kim, *ibid.*, **81**, 5008 (1959).

(5) W. T. Miller and D. M. Whalen, *ibid.*, **86**, 2089 (1964).

as intermediates in organic reactions. One aspect of this study resulted in the discovery of the preparation of stable α -chloroalkyllithium compounds I-IV. This present paper now reports on the preparation and chemistry of these mono-, di-, and trichloroalkyllithium structures prepared *via* the metalation route of the corresponding halomethane, independently also discovered by Köbrich and co-workers,⁶ and the halogen-metal interconversion route, and, in particular, to their reactions in which carbenoid character is evidenced.



The α -metalation procedure used is based on our observation, recently reported, that tetrahydrofuran exerted an extraordinary and apparently unique influence on the reaction of benzyl chloride with *n*-butyllithium. The data indicated that at low temperatures (-100°) in this solvent the reaction proceeded exclusively *via* α -hydrogen-metal interconversion (α -metalation), leading to the formation of α -chlorobenzyllithium, C₆H₅-CHClLi, as the active intermediate. The α -chlorobenzyllithium was rapidly consumed in subsequent reaction with excess benzyl chloride, presumably *via* nucleophilic displacement of the chlorocarbion formed on the benzyl chloride, leading to the formation of α -chlorobibenzyl in good yield.⁷



This procedure has since proven of general value for the synthesis of α -chlorobibenzyls from a variety of substituted benzyl chlorides, and, from these, their readily derived dehydrochlorinated products, the stilbenes.⁸ Moreover, the formation of α -chloroalkyllithium structures (or α -chlorocarbions) as transient intermediates appeared to be a general reaction of a variety of substituted chloromethanes with *n*-butyllithium.⁹

Synthesis of α -Chloroalkyllithium Compounds. In applying this reaction (-100° , THF solvent) to polychloromethanes, coupling of the chloromethylithium compound formed with excess of the polychloromethanes does not appear to occur to any significant degree at these low temperatures, and the intermediate mono-, di-, and trichloroalkyllithium compounds can be isolated in good yield.¹⁰ These compounds, possibly

(6) G. Köbrich, K. Flory, and W. Drischel, *Angew. Chem.*, **76**, 536 (1964), and references cited therein. See also G. Köbrich, H. R. Merkle, and H. Trapp, *Tetrahedron Letters*, **15**, 969 (1965), and G. Köbrich, K. Flory, and H. R. Merkle, *ibid.*, **15**, 973 (1965), which appeared during preparation of this manuscript.

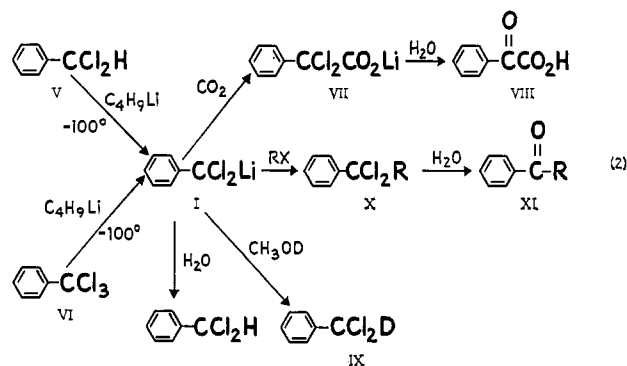
(7) D. F. Hoeg and D. I. Lusk, *J. Am. Chem. Soc.*, **86**, 928 (1964).

(8) D. F. Hoeg and D. I. Lusk, *J. Organometal. Chem.*, in press.

(9) D. F. Hoeg, J. E. Forrette, and D. I. Lusk, *Tetrahedron Letters*, **30**, 2059 (1964).

(10) The reduced coupling appears to be due to a combination of several factors: (a) the reduction in the nucleophilicity of the carbion

solvated, appear to precipitate out of the tetrahydrofuran solution at -100° . Moreover, *these compounds were indefinitely stable in tetrahydrofuran at -100°* and could be stored for hours without decomposition. We stress the point that these compounds under these reaction conditions were not detected as transient intermediates, but rather as stable "reagents" promising a wealth of opportunities for synthetic applications. This unique stability in tetrahydrofuran offered an opportunity for study of these structures not previously possible. These compounds (as typical organolithium reagents) have been characterized by hydrolysis, deuterolysis, and direct carbonation to the corresponding acids. Thus, the reaction of *n*-butyllithium in tetrahydrofuran at -100° with benzal chloride (V) (*via* hydrogen-metal interconversion) or benzotrichloride (VI) (*via* halogen-metal interconversion) gives the same product: α, α -dichlorobenzyllithium (I).



Carbonation of I yielded the lithium salt of α, α -dichlorophenylacetic acid (VII), which on dissolving in water rapidly liberated HCl; the acid finally isolated and characterized was phenylglyoxylic acid (VIII). Hydrolysis of I yielded benzal chloride, and methanolysis with CH_3OD gave benzal chloride- α - d_1 (IX). Reaction of I with methyl iodide produced the α, α -dichloroalkylbenzene (X), and hydrolysis led to the ketone XI identified as the 2,4-dinitrophenylhydrazone (dehydrochlorination of X yielded the α -chloroolefin). In view of the extremely low temperatures of these reactions and the rapidity of the displacement reactions with methyl iodide (93% of the theoretical amount of iodide ion was found to have been displaced within a 2-hr. period) and benzyl chloride, the α, α -dichlorobenzyl carbion would appear to be a moderately strong nucleophile. All of these compounds were isolated in pure form in good yields (50–80%). While the α, α -dichlorobenzyllithium reacted rapidly with methyl iodide and benzyl chloride, it was completely unreactive toward less reactive alkyl halides, like butyl chloride, at -80° .

In similar fashion, the other α -chloroalkyllithium compounds were prepared and identified. The acids and yields derived on carbonation of the organolithium structures are shown in Table I. The halogen-metal interconversion route, where applicable, gave somewhat better yields of the α -chloroalkyllithium structures, as deduced from their carbonation to the derivative acids,

with substitution of α -chloro groups, (b) the steric strain in forming the transition state for displacement of halogen from the polychloromethane by a di- or trichloro carbion, and finally (c) the decreased susceptibility of the polychloromethanes to nucleophilic attack.¹¹

(11) J. Hine, *ref. 2*, p. 37.

than did the hydrogen-metal interconversion (metallation) route. In particular, it was interesting to us that diphenylchloromethylithium was obtained from dichlorodiphenylmethane in modest yields, but not from benzhydriyl chloride. This latter compound apparently reacted *via* halogen-metal interconversion to give diphenylmethylithium, and the coupling product, tetraphenylethane.

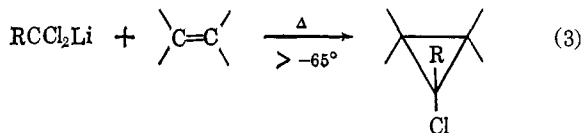
Table I. Carbonation of α -Chloroalkyllithium Compounds

Starting polychloromethane	α -Chloroalkyllithium formed	Acid from carbonation	% yield
PhCCl ₃	PhCCl ₂ Li	PhCOCO ₂ H	70
PhCHCl ₂	PhCHClLi	PhCHCO ₂ H	50
Ph ₂ CCl ₂	Ph ₂ CClLi	Ph ₂ COHCO ₂ H	40
CCl ₄	CCl ₃ Li	CCl ₃ CO ₂ H	80
CHCl ₃	CHCl ₂ Li	CHCl ₂ CO ₂ H	50
Cl ₂ CH ₂	Cl ₂ CHLi	Cl ₂ CHCO ₂ H	60

An attempt was also made to prepare tribromomethylithium from carbon tetrabromide and *n*-butyllithium, but no acid was isolated after carbonation of the reaction mixture.

Cyclopropane Synthesis. While these compounds were indefinitely stable at -100° , they (α,α -dichlorobenzylithium and trichloromethylithium) decomposed spectacularly and exothermally above -65° . Dichloromethylithium was apparently more stable in THF and did not decompose until above about -30 to -40° . As the cooling bath was lowered away from the reaction flask and the temperature allowed to rise slowly, several changes occurred almost simultaneously at about -65° . The precipitate dissolved, the temperature jumped *ca.* 20° , and the color of the solution darkened dramatically. This change was irreversible; recooling did not reform the original condition, and carbonation of the mixture after the decomposition did not produce any acid fragments. Apparently no stable carbon-lithium bonds were present after the decomposition.

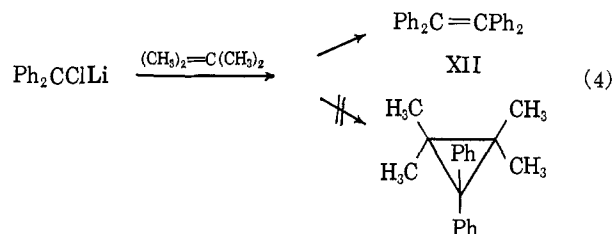
If olefins were present during this decomposition (they were added without evidence of reaction at -100°), good yields of the corresponding cyclopropanes were obtained with α,α -dichlorobenzylithium



R	Olefin	% yield cyclopropane (pure)
C ₆ H ₅	Tetramethylethylene	70
Cl	Tetramethylethylene	60
	1,1-Diphenylethylene	70
	Cyclohexene	60
	Butadiene	50

and trichloromethylithium (eq. 3). In contrast, this same procedure with diphenylchloromethylithium and dichloromethylithium did not produce cyclopropanes in very good yields from tetramethylethylene. With the former, a major product was tetraphenylethylene (XII), as if the α -chloroalkyllithium compound ignored the presence of the olefin as it decomposed (eq. 4).

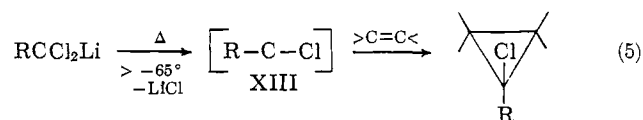
With the latter compound, a black resinous uncharacterized structure¹² and predominantly products of low boiling points were obtained. These results were



strongly suggestive that the α -chloroalkyllithium compounds decomposed above -65° by elimination of lithium chloride to yield the corresponding carbene as the active intermediate.

On the basis of the formation of cyclopropanes by the decomposition of the chloroalkyllithium compounds by heating over -65° in the presence of olefin, the reactivity of these α -chloroalkyllithium compounds in tetrahydrofuran would appear to decrease in the order PhCCl₂Li \sim CCl₃Li \gg Ph₂CClLi \sim Cl₂CHLi, suggestive of a general increase in electrophilicity with α -chloro substitution (within a family of structures).

The Role of α -Chloroalkyllithium Compounds as Carbenoid¹³ Reagents. On the one hand, the apparent lack of reaction of olefins with the α -chloroalkyllithium compounds at -100° in THF, contrasted with the apparent rapid formation of cyclopropanes by decomposing the compounds in the presence of olefins above -65° , was very suggestive of the involvement of a chlorocarbene intermediate (XIII).



On the other hand, the work of Simmons and Smith¹⁵ and Hoberg¹⁶ with analogous systems suggested that the cyclopropane was formed by the direct reaction of the haloalkylmetal compound, that is, the free carbene precursor, with the olefin. More recently, the studies of Miller and Whalen⁵ and Closs and Moss¹⁴ have given substantial support to the latter theory. The work of Hodgkins and co-workers had also served to question the general validity of free carbene intermediates in reactions of this type.^{17,18} Apart from the obvious potential synthetic utility of these α -chloroalkyllithium reagents described here, their stability in tetrahydrofuran offered a unique opportunity to explore this question of a *free* carbene *vs.* α -haloalkyllithium intermediate and, in particular, to what extent are the characteristics of reaction of α -haloalkyllithium compounds with olefins in accord

(12) It was particularly interesting to note that, using ethyl ether as solvent, the reaction of methylene chloride with *n*-butyllithium in the presence of tetramethylethylene at -30° gave tetramethylchlorocyclopropane (*ca.* 17% yield), as reported by Closs and Closs.³ In contrast, using tetrahydrofuran as the solvent in a similar experiment, we did not obtain a significant amount of the cyclopropane.

(13) After the usage given by Closs and Moss.¹⁴

(14) G. L. Closs and R. A. Moss, *J. Am. Chem. Soc.*, **86**, 4042 (1964).

(15) H. E. Simmons and R. D. Smith, *ibid.*, **81**, 4256 (1959).

(16) H. Hoberg, *Ann.*, **656**, 1 (1962).

(17) J. E. Hodgkins and M. P. Hughes, *J. Org. Chem.*, **27**, 4187 (1962).

(18) J. E. Hodgkins, J. D. Woodyard, and D. L. Stephenson, *J. Am. Chem. Soc.*, **86**, 4080 (1964).

with results thought previously indicative of a free carbene intermediate.

One requirement of the *free* carbene mechanism would be that the decomposition rate of the α -chloroalkyllithium structure would be independent of the presence of the olefin. Direct measurements of the relative stabilities of α,α -dichlorobenzyl lithium and trichloromethyl lithium in the presence of olefins at various temperatures below the decomposition temperature of the α -chloroalkyllithium compound suggest, however, that the stability of the α -chloroalkyllithium structure is influenced by the presence of a nucleophilic olefin, as shown in Table II. The reaction between the olefin and the organolithium reagent appears negligibly slow at -100° , but becomes significant at -78° . Clearly, α,α -dichlorobenzyl lithium is too weak an electrophile to add to the electron-rich olefin at -100° . At -78° , however, a slow, but discernible, reaction becomes evident. In comparison with the facile displacement of halide from methyl iodide by α,α -dichlorobenzyl lithium at -100° , its rate of reaction with tetramethylethylene is very slow indeed.

Table II. Cyclopropane Formation from α,α -Dichlorobenzyl lithium and Tetramethylethylene^a

Olefin	Temp., °C.	PhCCl ₂ H from methan- olysis of Ph- CCl ₂ Li, %	1-Chloro- 1-phenyl- tetra- methyl- cyclo- propane
None	-100	69	0
Fourfold Molar excess	-100	62	Trace
None	-78	52	0
Fourfold Molar excess	-78	28	26%




^a All reaction times, 3 hr.

The data shown in Table II were obtained in a variety of experiments—all showing about the same result. Since no significant reaction occurred at -100° , the olefin was added to the α,α -dichlorobenzyl lithium slurry at below -100° and the reaction then was warmed to -78° and maintained there for a 3-hr. period. Alternatively, the olefin was present during the preparation of the α,α -dichlorobenzyl lithium at -100° , and then the reaction temperature was raised to -78° for 3 hr. In either case, about the same results were obtained. The amount of α,α -dichlorobenzyl lithium left after 3 hr., as measured by the yield of benzal chloride isolated after quenching with methanol, was significantly less when olefin was present than in the control reaction. Moreover, 1-chloro-1-phenyltetramethylcyclopropane was isolated in about the yields corresponding to the decrease in the amount of α,α -dichlorobenzyl lithium observed. Inasmuch as the stability of these α -chloroalkyllithium compounds appeared highly sensitive to solvent, it occurred to us that perhaps the olefin was inducing decomposition of the α -haloalkyllithium compound in a related manner; that is, simply a poorer solvating media for the α -chloroalkyllithium compounds. To check this possi-

bility, a nonreactive hydrocarbon, cyclohexane, expected to be an even poorer solvent for the α -chloroalkyllithium reagent than the olefin, was added to a slurry of α,α -dichlorobenzyl lithium at -78° in quantities equivalent to those of the olefin used in earlier experiments. The yield of benzal chloride obtained upon quenching after 3 hr. was essentially unaffected (53%). Moreover, when butadiene was added to α,α -dichlorobenzyl lithium at -78° (ca. 9–10-fold molar excess), the yield of benzal chloride isolated after 2 hr. was 61%. A small amount of product of reaction (less than 5%) by infrared and g.l.c. analyses was a mixture of products, containing what appeared to be the mixed isomers of 1-chloro-1-phenyl-2-vinylcyclopropane. *The internal olefin, tetramethylethylene, appeared much more reactive than butadiene.*

In a similar manner, the stability of trichloromethyl lithium was measured in the presence and absence of olefins. In this case, it was more convenient to quench the reaction by pouring the reaction mixture into powdered Dry Ice after a given period of time. The unreacted trichloromethyl lithium was isolated as trichloroacetic acid (Table III). Again, the rate of reaction of trichloromethyl lithium with olefins at -78° in THF is very slow. Nevertheless, the same conclusion is indicated; that in some manner the stability of the α -chloroalkyllithium compound is influenced by the presence of the more nucleophilic olefin indicating that the cyclopropane arises by the direct reaction of the olefin and trichloromethyl lithium or its structural equivalent. It would also appear that α,α -dichlorobenzyl lithium is somewhat more reactive (based on tetramethylethylene) than trichloromethyl lithium.

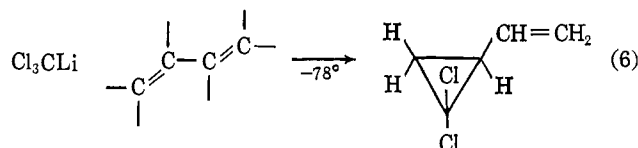
Table III. Reactions of Trichloromethyl lithium with Olefins^a

Olefin ^b	Temp., °C.	Cl ₃ CO ₂ H from carbo- nation, ^c %	Cyclo- propane, %
None	-100	75	...
	-100	67	Trace
None	-78	77	...
	-78	27	Ca. 30
(CH ₃) ₂ C=C(CH ₃) ₂	-78	48	Ca. 10
Ph ₂ C=CH ₂	-78	59	Trace
	-78	58	<5

^a All reaction times, 3 hr. ^b 3–4-fold molar excess over CCl₃Li
^c These are yields of pure acid obtained *via* distillation.

Competitive experiments will have to be run in which mixtures of olefins compete for reaction with these α -chloroalkyllithium compounds to establish a quantitative order of reactivity. The data at hand do demonstrate, however, at least qualitatively, that internal olefins (tetramethylethylene and cyclohexene) react more rapidly than vinylolefins (conjugated), as observed with α,α -dichlorobenzyl lithium, indicating a nucleophilic order of reactivity for the olefins. Again, this is consistent with results thought indicative of a *free* carbene mechanism.

Finally, the product of this very slow, but seemingly direct, reaction of trichloromethylithium with butadiene at -78° yields the compound described by Woodworth and Skell¹⁹ as 1,1-dichloro-2-vinylcyclopropane (as we also obtained earlier in 50% yield by decomposing trichloromethylithium in the presence of butadiene), indicating exclusive 1,2 addition (eq. 6) in accord with the stereochemistry previously attributed to *free* carbene intermediates.



In summary, then, the data would suggest that the reactions of α -chloroalkyllithium compounds with olefins at low temperature show essentially the same characteristics as earlier ascribed to a *free* carbene agent, *viz.*, cyclopropane ring formation, nucleophilic olefin reactivity sequence (for halocarbenes at least), and stereospecific addition. To this extent, the data would support the suggestions of Hoberg, Miller, and Whalen, and Closs and Moss, that the formation of cyclopropanes can occur *via* a direct reaction of the α -chloroalkyllithium compound with the olefin, bypassing the *free* carbene.

On the other hand, it is interesting to note that several inconsistencies develop in attempting to formulate the formation of the cyclopropane *via* a simple addition-cyclization reaction, either stepwise as suggested by Hoberg, or concerted as presented by the other proposals, in particular by the suggestion of Miller and Whalen of a nucleophilic attack of the olefin on the chlorocarbanion. As judged by the mode of reaction of α -chloroalkyllithium structures with carbonyl compounds⁶ and alkyl halides,^{7,8} the chloro carbanions derived from the α -chloroalkyllithium structures are nucleophilic in character. Moreover, trihalo carbanions in general appear to be nucleophilic.²⁰ One might have expected, therefore, contrary to observation, that attack of a nucleophilic chloro carbanion on the olefin to yield a cyclopropane by a stepwise or concerted process would follow an electrophilic reactivity sequence with respect to the olefins; *i.e.*, tetramethylethylene would be much slower than butadiene.

It is also interesting to note the marked sluggishness of the reactions of trichloromethylithium with olefins in tetrahydrofuran, compared to its rapid reaction with cyclohexene in ethyl ether at -100° , recently reported by Miller and Whalen.⁵ This is in rather sharp contrast to the usual marked accelerating influence high solvating media like tetrahydrofuran have on the reactions of organolithium reagents, particularly with respect to their addition to olefins (*e.g.*, to conjugated dienes, styrene, etc.), in which case it is generally held that in THF the alkyl carbanion adds to the electron-deficient center, to a greater degree independently of its counterion (Li^+). Again, one might have expected that, had the formation of the cyclopropane involved simply the interaction of the olefin and the chlorocar-

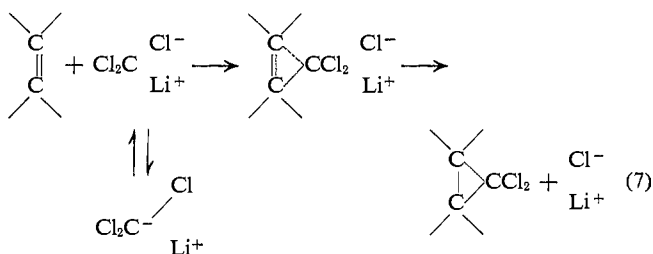
(19) R. C. Woodworth and P. S. Skell, *J. Am. Chem. Soc.*, **79**, 2542 (1957).

(20) D. Seyferth and J. B. Burlitch, *ibid.*, **84**, 1757 (1962); *J. Organometal. Chem.*, in press.

banion, it would have been facilitated in the more highly dissociating solvent, *viz.*, THF. Rather, it would appear that the lithium ion plays an important role in the transition leading to formation of the cyclopropane.

Moreover, the reaction leading to the formation of cyclopropanes appears characterized by a very large experimental activation energy in THF. For all intents and purposes, the reaction does not occur at -100° in THF. At -78° , it is still very slow even for the more nucleophilic olefins. Above -65° , it appears to be over in an instant, results not easily accommodated by a simple anion addition reaction, be it concerted or stepwise. In particular, this is apparent with 1,1-diphenylethylene, one of the more highly electrophilic olefins of the series, which for all practical purposes does not react with trichloromethylithium at -78° , yet reacts rapidly as the trichloromethylithium is decomposed above -65° to give an excellent yield of the cyclopropane. In this case, the requirement of the *free* carbene mechanism that the olefin not influence the decomposition rate of the α -chloroalkyllithium structure would appear satisfied, within experimental error.

In our view, an alternate possibility exists which appears to accommodate these seemingly contradictory properties, involving an equilibrium between the α -chloroalkyllithium structure and the "carbene-salt complex," the latter being the actual carbenoid intermediate as suggested by Wittig and Schwarzenbach,²¹ Closs and Closs,²² and Simmons and Smith,²³ their mechanism being slightly modified to accommodate this equilibrium²⁴ (eq. 7). At about -70° and below,



the equilibrium lies far to the side of the carbanion, constrained, in part, because of the insolubility of the compound. In the immediate environment of the incipient chlorocarbenes is the chloride ion, held possibly in the crystal structure of the precipitated α -chloroalkyllithium compound.

As long as the chloride ion is constrained to the vicinity of the incipient carbene, the olefin fails to compete with it effectively for the divalent carbon fragment, and the reaction rate with the olefin remains very low, although the reader will note one would expect the same general reaction characteristics as the "free carbene" (electrophilic character, specificity, etc.). Most of the properties observed at low temperatures would appear to be those of the chloro carbanion structure (carbonation, nucleophilic addition to carbonyl groups,

(21) G. Wittig and K. Schwarzenbach, *Ann. Chem.*, **650**, 1 (1961).

(22) G. L. Closs and L. E. Closs, *Angew. Chem.*, **74**, 431 (1962).

(23) H. E. Simmons and R. D. Smith, *J. Am. Chem. Soc.*, **80**, 5323 (1958).

(24) That an equilibrium may exist between dihalocarbene and halide ion, *e.g.*, $\text{CCl}_2 + \text{Cl}^- \rightleftharpoons \text{CCl}_2^-$, has been demonstrated by Hine and Dowell.²⁵ Closs²⁶ has also suggested another possible equilibrium contributor involving a carbonium ion fragment $\text{Cl}_3\text{CLi} \rightleftharpoons \text{Cl}_2^+\text{CLi} \text{Cl}^-$.

(25) J. Hine and A. M. Dowell, *J. Am. Chem. Soc.*, **76**, 2688 (1954).

(26) G. Closs, personal communication.

nucleophilic displacement reactions). In contrast, as the constraint of temperature and the crystal structure is removed as the α -chloroalkyllithium compound dissolves on warming, the properties of the incipient carbene would become dominant. With the more nucleophilic olefins, the removal of chloride ion from the vicinity of the carbene fragment (facilitated possibly by electrophilic assistance of the lithium ion) would not have to proceed very far before bond formation to produce the cyclopropane would have started. With the more electrophilic olefins (like 1,1-diphenylethylene), chloride ion separation from the incipient carbene would have to progress further, approximating in the limit the free carbene mechanism.

This proposal appears compatible with much of the data presently available and, moreover, also extends the desirable feature of presenting a basis for a continuum of reaction structures between the wholly covalent organometallic compound on the one hand and the distinct free carbene on the other.

These new organolithium compounds described here and related structures are presently under continuing study; the elucidation of their reactions should provide new insight into the chemistry of divalent carbon.

Experimental

General Procedure. These reactions were carried out in glass equipment, generally a 300-ml. three-necked flask fitted with a stirrer and thermometer and accessory glass fittings. The equipment was thoroughly cleaned and dried. Immediately before use, the equipment was "flamed-out" and cooled under a purge of dry argon. All reagents were added through a rubber septum using hypodermic syringes. As in typical reactions of organometallic compounds, care was taken to avoid contamination with traces of moisture and carbon dioxide.

Materials. At regular intervals, the *n*-butyllithium stock solution (in hexane) was titrated by the method of Gilman and Haubein.²⁷ The tetrahydrofuran was purified before use by conventional procedures and after distillation under argon was stored over sodium ribbon before use.

Preparation and Carbonation of α,α -Dichlorobenzyl-lithium from Benzal Chloride. To 100 ml. of pure dry THF was added 7.34 g. of benzal chloride (45.6 mmoles, Eastman White Label). The reaction was cooled to -90° and 43 mmoles of *n*-butyllithium was added slowly over 10 min. After a total of 15 min. elapsed, the reaction was dumped into powdered Dry Ice. The Dry Ice was then allowed to vaporize and the THF layer partially evaporated. A mixture of equal volumes of benzene and water was added, anticipating separation of the lithium salt of the acid in the aqueous phase. We noted that, contrary to the usual carbonation of organolithium compounds, the aqueous phase became progressively more acid as we allowed the mixture to stand. We finally made the aqueous phase permanently basic with caustic and the aqueous phase was separated. The aqueous phase was then acidified and extracted twice with ethyl ether. The ether phases were combined and vacuum stripped to yield an orange liquid which was fractionally distilled. No more than

(27) H. Gilman and A. H. Haubein, *J. Am. Chem. Soc.*, **66**, 1515 (1944).

a drop or two of valeric acid may have been present. The first and only product isolated (2.7 g.) boiled at $131-133^\circ$ (6-7 mm.). This was collected as a very pale green liquid, which crystallized on standing a few moments to yield a white solid which was recrystallized from cyclohexane, m.p. $63-64.5^\circ$. The product was identified as phenylglyoxylic acid (lit. m.p. 66° , b.p. $147-151^\circ$ (12 mm.)). *Anal.* Calcd. for $C_8H_6O_3$: C, 64.0; H, 4.0; O, 32.0; neut. equiv., 150. Found: C, 63.99; H, 4.39; O, 31.6; neut. equiv. 148. The phenylhydrazone prepared from another preparation had m.p. 160° dec., lit. 160° dec. The yield of 2.7 g. is 42% of theory based on *n*-butyllithium used.

Preparation of α,α -Dichlorobenzyl-lithium from Benzotrichloride. α,α,α -Trichlorotoluene, 9.62 g. (49.2 mmoles, Eastman White Label), was dissolved in 100 ml. of pure dry THF and cooled to -100° . *n*-Butyllithium, 49 mmoles in 34 ml. of a hexane solution, was added slowly over a period of 45 min. After 1.25 hr. from the start, the reaction was dumped into stirred, powdered Dry Ice. The reaction was worked up as before (7.1 g. of acid fraction) to give 0.25 g. of an acid boiling between 73 and 109° at 0.3 mm., and 5.5 g. (75% yield) of phenylglyoxylic acid (b.p. $100-110^\circ$ at 0.3 mm.), crystallized, as usual, as it distilled.

Thermal Decomposition of α,α -Dichlorobenzyl-lithium. To 100 ml. of dry THF was added 7.76 g. (48.2 mmoles) of benzal chloride. The solution was cooled to -100° and 31.2 ml. (48.2 mmoles) of *n*-butyllithium in hexane was added over a period of 15 min. as before. After 15 min., the reaction was allowed to warm slowly to -70 or -65° . The reaction changes rapidly from a lavender slurry to a deep red solution and the temperature jumps an indefinite amount (10 or 20°). The change is irreversible (solution remains on cooling). A 60-ml. aliquot was carbonated, but no acid was isolated (no stable carbon-lithium bonds above ca. -60°). The remainder of the reaction was allowed to warm to room temperature. The solvent was evaporated to yield a deep red oil, which we unsuccessfully attempted to distill. No sharply defined fraction was obtained. We then attempted chromatography, but this also failed to yield pure fractions. A major amount of this material appeared to be polymeric (low degree of polymerization) of broad distribution, mainly soluble in benzene, but insoluble in petroleum ether and methanol.

Preparation of 1-Chloro-1-phenyltetramethylcyclopropane from α,α -Dichlorobenzyl-lithium (Benzal Chloride Derived). Benzal chloride, 9.47 g. (58.8 mmoles), was dissolved in 125 ml. of dry tetrahydrofuran and cooled to -100° ; *n*-butyllithium in hexane, 42 ml. (60 mmoles), was then added slowly over a period of 25 min. After the usual variety of dull colors, a pale lavender slurry was obtained, 45 min. after start. Tetramethylethylene, 40 ml., was then added slowly over ca. 15 min. There was no apparent reaction and the color remained the same. After a total of 1-hr. elapsed time since first start of butyllithium addition, the reaction was allowed to warm up slowly. Again, at about -65° , a spectacular jump in temperature occurred (to -40°), the precipitate disappeared, and a deep red solution formed. The reaction was poured into a beaker and the solvent evaporated. A crystalline residue was obtained, which dissolved in a 50:50 mixture of water-

ethyl ether. The ether phase was separated, dried, and stripped. An amber solid (wet with second component) was obtained. The solid dissolved readily in petroleum ether. On evaporating, beautiful prisms formed to yield 5.0 g. of product (m.p. 61–62°). The mother liquor was cooled, and 0.8 g. more was isolated (an infrared analysis later showed the latter to be the same compound). Evaporation of the mother liquor gave 2 g. of viscous yellow fluid. A sample of the crystalline solid was recrystallized from petroleum ether and identified as 1-chloro-1-phenyltetramethylcyclopropane m.p. (sharp) 65–66°, lit.²⁸ 66–67°. *Anal.* Calcd. for C₁₃H₁₇Cl: Cl, 17.0. Found: Cl, 17.2. An n.m.r. spectrum showed absorption at τ 8.96 and 8.63 assigned to methyl (2 pair) and at τ 2.7 (aromatic). The proton count (methyl (two types) to aromatic) was close to 6:6:6, as expected. The infrared spectrum also showed strong absorption at 1022 cm.⁻¹, indicative of the cyclopropane ring.²⁸ The yield of cyclopropane (5.8 g.) was 48%.

Preparation of 1-Chloro-1-phenyltetramethylcyclopropane from α,α -Dichlorobenzyl lithium (Benzotrichloride Derived). α,α,α -Trichlorotoluene, 10.4 g. (53 mmoles, benzotrichloride), was dissolved in 100 ml. of dry THF; *n*-butyllithium, 38 ml. of a hexane solution (53 mmoles), was added slowly over a period of 45 min. at -105°. A lavender slurry formed. Tetramethylethylene, 40 ml., was added, and the reaction was allowed to warm up slowly. Again, at about -65° a spectacular change occurred: the solid dissolved and the temperature jumped some 20 or 30°. The solution was a clear rose. The reaction mixture was evaporated and the crystalline residue dissolved in petroleum ether (the insoluble salt was discarded) and crystallized to give 4.4 g. of beautiful prisms, m.p. 63–65°. The mother liquor produced 3.5 g. more (an infrared analysis showed both to be identical). The total yield of the cyclopropane was 72% (pure). *Anal.* Calcd. for C₁₃H₁₇Cl: Cl, 17.0. Found: Cl, 17.0 (first crop), 16.4 (second crop). The infrared spectra of both were essentially the same and identical with that obtained from benzal chloride.

In a similar experiment, hydrolysis of the α,α -dichlorobenzyl lithium was accomplished by pouring the reaction mixture rapidly into 200 ml. of water. Distillation of the dried organic phase yielded benzal chloride (58% yield), which distilled at 72–75° (5 mm.). Additionally, solvolysis of the α,α -dichlorobenzyl lithium was accomplished by injecting a pre-cooled solution of methanol in tetrahydrofuran (4 ml.:15 ml. of THF) into the slurry of α,α -dichlorobenzyl lithium (73% yield of benzal chloride from the -100° reaction). With CH₃OD (Volk Chemical Co.) benzal chloride- α -d₁ was obtained and the infrared absorption spectrum was in agreement with the calculated CH vs. CD frequency shifts.

Reaction of α,α -Dichlorobenzyl lithium with Methyl Iodide. α,α -Dichlorobenzyl lithium in 100 ml. of tetrahydrofuran was prepared from 49.3 mmoles each of benzotrichloride and *n*-butyllithium as in previous preparations at -100°. To this mixture was added 5 ml. of methyl iodide (Fisher Certified Reagent) in 15 ml. of tetrahydrofuran over a 30-min. period. The lavender slurry became a brown color after 3 hr. The

reaction was yellowish. The reaction was quenched with 4 ml. of methanol in 10 ml. of tetrahydrofuran added dropwise. The reaction was then poured into 200 ml. of water and the organic phase was separated. The aqueous phase was washed three times with ethyl ether and separated. The organic phases were combined and dried over Na₂SO₄ and vacuum stripped. The liquid residue was fractionally distilled under vacuum to give 6.6 g. (77%) of a clear liquid identified as α,α -dichloroethylbenzene, b.p. 54° (0.4 mm.). *Anal.* Calcd. for C₈H₈Cl₂: Cl, 40.6. Found: Cl, 39.7.

The distillate was stirred overnight with refluxing water (50 ml.) to give acetophenone which was characterized as the 2,4-dinitrophenylhydrazone (9 g., 82%), m.p. 252–254° (no depression with authentic sample). The α,α -dichloroethylbenzene compound dehydrochlorinated on standing or gentle heating.

A similar preparation at -80° gave an 82% yield of α,α -dichloroethylbenzene. In contrast, no significant reaction of α,α -dichlorobenzyl lithium with *n*-butyl chloride was detected at -80°. In a similar experiment to that described above, 51.4% of the benzal chloride was recovered after quenching a 3-hr. reaction (essentially no reaction).

*Preparation of Trichloromethyl lithium from Chloroform and *n*-Butyllithium.* Chloroform, 12.46 g. (104 mmoles, Fisher Reagent Grade), was dissolved in 130 ml. of THF and cooled to -105°. *n*-Butyllithium in hexane, 73 ml. (104 mmoles), was then added very slowly over a 45-min. period. The reaction mixture darkened rapidly (after first few drops) and changed from purple finally to a greenish slurry. After 1.25 hr. from start of addition, the reaction was dumped onto stirred Dry Ice (amber-green color was not discharged). After evaporation of the Dry Ice and solvent on a steam bath, a semicrystalline brown residue remained. Water, 150 ml., was added and most of the residue dissolved. After extraction with ethyl ether, the aqueous phase was acidified and extracted with ethyl ether. The aqueous phase was re-extracted four times with ether. The ether phases were combined, dried, and vacuum stripped to yield 6.7 g. of a red oil, which was vacuum distilled.

The liquid gave a few drops of forerun on distillation and then yielded a clear liquid distillate (4.0 g.) boiling at 66–69° (0.6 mm.), which partially crystallized on standing. About half was pure white crystals and the other half clear liquid (which crystallized slightly below room temperature). The infrared spectra of both were very similar to a standard spectrum of trichloroacetic acid. The solid was deliquescent and identified as the trichloroacetic acid. *Anal.* Calcd. for C₂HO₂Cl₃: Cl, 65.1. Found: Cl, 63.9. The liquid fraction contained 55.3% Cl, which is close to theoretical for dichloroacetic acid, but its infrared spectrum showed it to be predominantly trichloroacetic acid, contaminated with lesser amounts of dichloroacetic acid (yield ca. 25%).

*Synthesis of Trichloromethyl lithium from CCl₄ and *n*-Butyllithium at -100°.* Carbon tetrachloride, 5.6 g. (36.5 mmoles, Fisher Certified Reagent), was dissolved in 100 ml. of pure THF and cooled to -105°. *n*-Butyllithium, 26 ml. (37 mmoles), was then added over a 30-min. period. There occurred a mild exotherm and a very gradual change from colorless to pale pink. After

(28) R. A. Moss, *J. Org. Chem.*, 27, 2683 (1962).

about half the butyllithium was added, a white precipitate became visible. After 1 hr. from the start, the reaction was a white slurry (very clean looking). After 1.5 hr., the reaction was dumped onto stirred powdered Dry Ice and worked up as before. All of the acid distilled at 69.5° (0.4 mm.) and crystallized in the condenser. We finally isolated 4.5 g. of acid. The infrared spectrum showed it to be identical with an authentic sample of trichloroacetic acid (76% yield).

Preparation of 7,7-Dichlorobicyclo[4.1.0]heptane (Dichloronorcarane) from Trichloromethylithium and Cyclohexene. Carbon tetrachloride, 7.98 g. (52 mmoles), was dissolved in 100 ml. of THF and cooled to -105°. *n*-Butyllithium-hexane solution, 35 ml. (52 mmoles), was then added slowly over a 45-min. period. To the gray precipitate of trichloromethylithium was added (15 min.) 30 ml. of cyclohexene (Eastman White Label). The reaction was then allowed to warm up slowly (by lowering cooling bath). At -65°, a color change was obvious; solution of the precipitate occurred as the temperature jumped from -63 to -38°. The solution was now very dark. The solvent was evaporated and the liquid-salt residue distilled to give 5.2 g. (60%) of a clear liquid identified as dichloronorcarane (b.p. 94-96° (30 mm.), n_D^{25} 1.5012; lit. b.p. 80.0-81.0° (15 mm.), n_D^{25} 1.5012). *Anal.* Calcd. for $C_7H_{10}Cl_2$: Cl, 43.0. Found: Cl, 43.6. An infrared spectrum confirmed the presence of cyclopropane ring (strong 1022-cm.⁻¹ absorption) and was identical with a standard spectrum of this compound.

Preparation of 1,1-Dichloro-2,2-diphenylcyclopropane from Trichloromethylithium and 1,1-Diphenylethylene. Carbon tetrachloride, 7.93 g. (51.4 mmoles), and 24 g. of 1,1-diphenylethylene (Eastman White Label) were dissolved in 100 ml. of THF and cooled to -100°. *n*-Butyllithium, 51 mmoles, in 34 ml. of a hexane solution, was added dropwise over a period of 45 min. After 1.5 hr. at -100°, the cooling bath was removed and the mixture was allowed to warm up. The exotherm occurred at about -60° and the slurry turned dark. After reaching room temperature, the reaction mixture was poured into 200 ml. of water, and the organic phase was separated. The aqueous phase was extracted several times with ethyl ether. The organic phases were combined, dried over Na_2SO_4 , and vacuum stripped. On stripping off the solvent, a solid crystallized out. This was recrystallized from petroleum ether to give 7.0 g. of beautiful, large prism-like crystals identified as 1,1-dichloro-2,2-diphenylcyclopropane, m.p. 113-114°. *Anal.* Calcd. for $C_{15}H_{12}Cl_2$: C, 68.4; H, 4.56; Cl, 27.0. Found: C, 68.5; H, 4.67; Cl, 27.0. The n.m.r. spectrum showed proton signals at τ 7.79 assigned to cyclopropane protons and a multiplet at τ 2.35-2.80 assigned to aromatic protons in the ratio of 2:10.

Preparation and Carbonation of Diphenylchloromethylithium. To 100 ml. of pure dry THF was added 6.84 g. (28.8 mmoles), of freshly distilled dichlorodiphenylmethane (Frinton Laboratories), and the reaction was cooled to -100°. *n*-Butyllithium, 27.5 mmoles in 19 ml. of hexane solution, was added slowly over a half-hour period. The reaction became a deep red color. After 1.25 hr. from the start, the reaction mixture was poured onto powdered Dry Ice and was stored overnight. The following morning water was added

but the white residue was only sparingly soluble. The water was made basic with sodium hydroxide and stirred for 1 hr. The mixture was filtered. The filtrate was extracted with ethyl ether and the aqueous layer was then separated and acidified. The aqueous layer was then extracted twice with ethyl ether, and the ether phase was separated and vacuum stripped. There was obtained 2.5 g. of a white, crystalline residue which was crystallized from hot water and identified as diphenylglycolic acid, m.p. 150-151°, lit. 150°. The infrared spectrum was the same as a standard sample and contained <0.1% chlorine. *Anal.* Calcd.: C, 73.68; H, 5.26; O, 21.2; neut. equiv., 228. Found: C, 73.70; H, 5.29; neut. equiv., 226. The crude yield of acid is 40% of theoretical based on *n*-butyllithium used. The mother liquor was condensed and distilled to give 1.13 g., clear liquid, b.p. 129° (0.7 mm.) of an as yet unknown structure.

Decomposition of Diphenylchloromethylithium in the Presence of Olefins. In a similar experiment as above, diphenylchloromethylithium was prepared from 29.2 mmoles of dichlorodiphenylmethane. After 1.5 hr., to this slurry was added 15 ml. of pure cyclohexene at -100° with no evidence of reaction; after 45 min., the reaction was allowed to warm up and gradually the color of the mixture changed to orange. The solvent was evaporated to give a solid-liquid residue. This was shaken with petroleum ether and filtered to give 1.64 g. of a white-to-pale-green powder (m.p. 210-220°) consisting predominantly of tetraphenylethylene (33% yield): analytical sample recrystallized from CCl_4 , m.p. 224-227°, identified by infrared and n.m.r. as tetraphenylethylene, aromatic proton signal centered at τ 2.82.

Preparation and Carbonation of Dichloromethylithium. To 100 ml. of pure dry THF was added 3.95 g. (46.5 mmoles) of methylene chloride and the reaction was cooled to -95°. *n*-Butyllithium, 46.5 mmoles in 31.5 ml. of a hexane solution, was added dropwise. No color formed until the addition was approximately half complete. Then, a white precipitate formed. After 2 hr., the reaction was poured onto Dry Ice and allowed to stand overnight. The acid product was isolated as in previous preparations and distilled to give a 60% yield of dichloroacetic acid, b.p. 90-91° (12 mm.). *Anal.* Calcd. for $C_2H_2O_2Cl_2$: Cl, 55. Found: Cl, 54. The infrared spectrum was the same as a standard sample of dichloroacetic acid; slight contamination with monochloroacetic acid was suspected.

Procedure for the Measurement of the Stability of α,α -Dichlorobenzylithium in the Presence of Tetramethylethylene. A. Control Runs. A 100-ml. quantity of purified THF was transferred by means of a syringe to a three-necked flask equipped with a low temperature thermometer, syringe cap, and motor-driven stirring rod. All glassware was predried and the flask was under a positive argon pressure. A 50-mmole (9.78 g.) quantity of benzotrichloride was then introduced into the reaction flask. The reaction flask was cooled with liquid nitrogen and adjusted such that the temperature of the reactant was -100 to -105°. A 50-mmole (ca. 33 ml. of 1.5 *M*) quantity of standardized butyllithium was added dropwise to the reactant solution over a 30-min. period. The reaction was then allowed

to proceed for 3 hr. at a temperature of -100° . At the end of the 3-hr. period, the reaction was quenched by preparing a solution of 4 ml. of methanol in 15 ml. of THF and precooling over Dry Ice prior to a dropwise addition to the reaction over a 15–20 min. period. The cold solution was then poured into 200 ml. of water and the THF layer separated. The water layer was then extracted three times with 75 ml. of ether, and the ether washings were combined with the THF layer. The ether was then stripped off and the liquid residue analyzed by vapor phase chromatography and then distilled under vacuum.

For runs at -78° , the reactants were mixed at -100° as above. The liquid nitrogen bath was then removed and replaced by a Dry Ice–acetone slurry, and the reaction was maintained between -76 and -80° for 3 hr. and then quenched and worked up as above. It was found desirable to maintain reasonably constant temperatures; this was done by inserting a mechanical stirrer in the refrigerant bath to maintain circulation of the refrigerant around the reaction flask.

B. With Tetramethylethylene. Immediately after butyllithium had been added to benzotrichloride, a fourfold molar excess (25 ml., ca. 200 mmoles) of pure tetramethylethylene was precooled over Dry Ice and added dropwise over a 30-min. period at -100° . The remaining procedure was as noted previously. For runs at -78° , the olefin was still added at -100° , and then the reaction was warmed to -80 to -76° . The cyclopropane formed was characterized in a small sample of the reaction mixture by vapor phase chromatography and then separated from the bulk reaction mixture by fractional distillation (b.p. 92° (0.7 mm.)). The crystals which formed in the condenser were recrystallized from petroleum ether (m.p. 64 – 66°).

As an alternate procedure, the olefin was added before the *n*-butyllithium with little change in results.

Procedure for the Measurement of the Stability of Trichloromethylithium in the Presence of Olefins. In a similar manner as described for α,α -dichlorobenzylithium, the stability of trichloromethylithium in the presence of various olefins was measured. After the 3-hr. reaction period, the reaction was dumped onto powdered Dry Ice and allowed to evaporate. The residue was dissolved in a mixture of ethyl ether and water. The aqueous phase was separated, acidified, and extracted with ethyl ether, which was then dried over sodium sulfate, vacuum stripped, and distilled to give trichloroacetic acid (b.p. 59 – 61° (0.5 mm.)), which crystallized. The yield of trichloroacetic acid was taken as a measure of the amount of unreacted trichloromethylithium.

The separated organic phase of the reaction was dried and carefully vacuum stripped. The solid residues were recrystallized. The liquids were vacuum distilled.

Preparation of 1,1-Dichlorotetramethylcyclopropane from Trichloromethylithium and Tetramethylethylene. A white slurry of trichloromethylithium was prepared

from 10.1 g. (65.4 mmoles) of carbon tetrachloride in 100 ml. of THF at -100° using 66 mmoles of *n*-butyllithium in 44 ml. of hexane solution. Tetramethylethylene, 20 ml., was then added slowly with no visual signs of reaction at -100° . The cooling bath was then removed and allowed to warm. At about -65° the precipitate dissolved and an exotherm occurred. The temperature jumped to -25° . After warming to room temperature, the reaction was poured into 250 ml. of water and the organic phase was separated. The aqueous phase was extracted with ethyl ether and the organic phases were then combined, dried over Na_2SO_4 , and distilled. A fraction was collected boiling at 164 – 166° ; this crystallized in the condenser, was removed, and was identified as 1,1-dichlorotetramethylcyclopropane (crystallized from methanol, m.p. 47 – 49° , lit. 49°). The pot residue also crystallized to give the same compound. A total of 6.4 g. (ca. 60%) of the cyclopropane was isolated. The n.m.r. spectrum showed one sharp peak at τ 8.75, consistent with equivalent methyl groups.

Preparation of 1,1-Dichloro-2-vinylcyclopropane from Trichloromethylithium and Butadiene. Again, a white-gray slurry of trichloromethylithium was prepared from 13.5 g. (87.8 mmoles) of carbon tetrachloride in 100 ml. of THF and 88 mmoles of *n*-butyllithium in 59 ml. of hexane. After 3 hr., 58 g. of butadiene was distilled into the reaction flask at -100° from a triisobutylaluminum–butadiene solution without visual signs of reaction. After 1 hr., the cooling bath was removed and the reaction allowed to warm. At about -65° , a marked exotherm occurred. The reaction mixture was then poured into 200 ml. of water. The organic phase was separated, the water phase was extracted three times with 75 ml. of ethyl ether, and the organic phases were combined, dried, and condensed to about 75 ml. (*via* vacuum stripping). The residue was then distilled yielding 5.74 g. (48%) of a clear liquid identified as 1,1-dichloro-2-vinylcyclopropane (b.p. 123 – 126° , lit. 123°). The n.m.r. spectrum showed two groups of multiplets, the first between τ 7.46 and 8.77 and the second between τ 3.88 and 4.82 in approximately a 1:1 ratio. The infrared spectrum appeared identical with that reported for this compound.¹⁹ *Anal.* Calcd. for $\text{C}_5\text{H}_6\text{Cl}_2$: Cl, 51.8. Found: Cl, 50.8.

Acknowledgment. We are pleased to acknowledge the aid of Mr. J. E. Forrette and C. Reagen in the interpretation of spectra (particularly n.m.r.) of several of the compounds described. We also wish to acknowledge helpful discussions of various aspects of this work with Drs. E. P. Goldberg, J. F. Pendleton, and F. Scardiglia, and Professors D. Seyferth and W. Moore, and in particular to unknown referees I and II of an earlier manuscript for several valuable comments.²⁹ Thanks are also due Mr. J. Devona and Mr. D. Mueller for checking several of these experiments.

(29) D. F. Hoeg, communication subsequently withdrawn for expansion to full-sized paper.