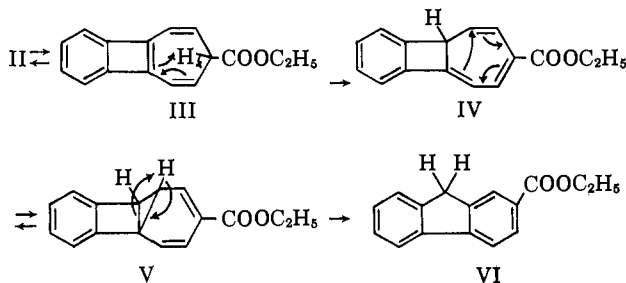


(log  $\epsilon$  4.54, 4.36, 4.34, 4.43, and 4.33) which gave analytical data consistent with adduct II (*Anal.* Found: C, 80.13; H, 6.05). The proton magnetic resonance spectrum of this ester in  $\text{CDCl}_3$  showed, in addition to the ethoxyl protons, a two-proton singlet at  $\tau$  6.16 and a seven-proton complex of bands in the region  $\tau$  1.8 to 2.8. These features immediately excluded any norcaradiene structure (such as II) and were also in disagreement with a tautomeric cycloheptatriene formulation (e.g., III), since spin-spin coupling between protons on saturated carbon and the olefinic protons would be expected.<sup>9</sup> However, the unsplit  $\text{CH}_2$  resonance at  $\tau$  6.16 was reminiscent of the  $\text{CH}_2$  resonance of fluorene, which appears at  $\tau$  6.19,<sup>10</sup> and indeed the properties of the ester were consistent with its formulation as ethyl fluorene-2-carboxylate (VI), reported<sup>11</sup> to melt at 83–84°. Synthesis of the authentic ester by oxidation of 2-acetylfluorene<sup>12</sup> left no doubt as to the nature of the carbethoxycarbene product; the mixture melting point, ultraviolet, and n.m.r. spectra were identical.

Although isolation of the fluorene VI from addition of carbethoxycarbene to biphenylene is at first surprising, its formation can be understood in terms of known processes of tropilidene chemistry.<sup>13</sup> Thus the primary adduct II should be in tautomeric equilibrium with cycloheptatriene III, which in turn could undergo thermal 1,5-hydrogen transfer<sup>14</sup> to the isomeric triene IV.



The latter should exist in equilibrium with a second norcaradiene, V, which contains the elements of a highly strained bicyclopentane system. Criegee and Rimmelin have observed<sup>15</sup> that bicyclopentane itself undergoes thermal isomerization at 330° to give cyclopentene; the analogous rearrangement of diene V would be expected to proceed even more readily and lead directly to the observed fluorene ester VI.

It is apparent that the remarkable chain of isomerizations represented by the postulated reaction sequence could seriously interfere with syntheses of molecules containing cyclobutenes fused to actual or potential cycloheptatriene rings. We are currently examining the possibility of intercepting some of the proposed

(9) In cycloheptatriene the coupling constant between  $\text{CH}_2$  and adjacent olefinic CH is ca. 7 c.p.s. (NMR Spectra Catalog, Varian Associates, 1962, spectrum 158).

(10) Value given by G. V. D. Tiers, in "Characteristic NMR Shielding Values," Vol. II, Minnesota Mining and Manufacturing Co., St. Paul, Minn., 1958, p. 12.

(11) D. C. Morrison, *J. Org. Chem.*, **23**, 1772 (1958).

(12) M. D. Barnett, G. H. Daub, F. N. Hayes, and G. D. Ott, *J. Am. Chem. Soc.*, **82**, 2282 (1960). The intermediate fluorene-2-carboxylic acid melts with decomposition at 275° and is thus probably the acid isolated by Baker and McOmie.<sup>7</sup>

(13) Tautomerism in the cycloheptatriene-norcaradiene system has been reviewed by E. Vogel, *Angew. Chem.*, **72**, 6 (1960); **74**, 829 (1962).

(14) A. P. ter Borg, H. Kloosterziel, and N. von Meurs, *Proc. Chem. Soc.*, 359 (1962).

(15) R. Criegee and A. Rimmelin, *Chem. Ber.*, **90**, 414 (1957).

tropilidene intermediates by effecting the addition of the appropriate carbenes to biphenylene derivatives at lower temperatures.

ORGANIC CHEMICAL RESEARCH SECTION      ANDREW S. KENDE  
LEDERLE LABORATORIES DIVISION          PAUL T. MACGREGOR  
AMERICAN CYANAMID COMPANY  
PEARL RIVER, NEW YORK

RECEIVED MARCH 20, 1964


### Trichloromethylithium, an Electrophilic Reagent

Sir:

We wish to report the preparation of trichloromethylithium and its reaction with cyclohexene at low temperature to produce 7,7-dichloronorcarane in high yield.<sup>1</sup> Our results point to  $\alpha$ -halogenated<sup>3</sup> organometallic compounds of the alkali metals as highly reactive electrophilic reaction intermediates which are distinguishable from the carbenes. The accessibility of such substances for study and as specific reagents is demonstrated.<sup>4</sup>

Experimental results are summarized in Table I. Trichloromethylithium was prepared by adding  $\text{CBrCl}_3$  to  $\text{CH}_3\text{Li}$  slurry in ether at  $-115^\circ$ . Reaction with

TABLE I<sup>a</sup>

	$\text{CH}_2\text{Br}$	$\text{CHCl}_2$	$\text{CHBrCl}$	$\text{CH}_2=\text{CCl}_2$	$\text{CCl}_2=\text{CCl}_2$	Other products
A	87	65	11	6	5	77 
B <sup>b,c</sup>	82	3	0	7	1	
C <sup>b</sup>	88	56	16	8	5	
D <sup>d</sup>	88	30	6	5	4	{ 13 $\text{CHCl}_2\text{CF}_3$ { 24 $\text{CCl}_2=\text{CF}_2$ { 67 $\text{CHCl}_2\text{CF}_3$ { 12 $\text{CCl}_2=\text{CF}_2$ { 4 $\text{CH}_3\text{Cl}$
E	81					

<sup>a</sup> The values given are percentages based on  $\text{CH}_3\text{Li}$ . In each case ca. 0.04 mole of  $\text{CCl}_3\text{Li}$  ( $\text{CF}_3\text{CCl}_2\text{Li}$ ) was prepared in 150 ml. of ether by adding 5% excess  $\text{CBrCl}_3$  ( $\text{CF}_3\text{CBrCl}_2$ ) to  $\text{CH}_3\text{Li}$  at  $-115^\circ$  during 2 hr. All analyses are by g.l.c. on fractions separated after treatment with ethereal HCl. Other identified products such as  $\text{CH}_3\text{Cl}$ ,  $\text{CCl}_4$ ,  $\text{CH}_2=\text{CHCl}$ ,  $\text{CCl}_2=\text{CBrCl}$ ,  $\text{CH}_3\text{CBrCl}_2$ , and  $\text{CH}_3\text{CH}=\text{CH}_2$  total less than 5% per reaction. <sup>b</sup> Warmed (10 min.) to  $-100^\circ$  for 1 hr., recooled to  $-115^\circ$ , and HCl added. <sup>c</sup> Partial reaction to form dichloronorcarane was observed at  $-115^\circ$ . <sup>d</sup> Six hours at  $-115^\circ$  with 0.05 mole  $\text{CF}_3\text{CBrCl}_2$ .

ethereal HCl yielded 65%  $\text{CHCl}_3$  and 11%  $\text{CHBrCl}_2$  (A). With 2 equiv. of cyclohexene present and warming to  $-100^\circ$ , 77% dichloronorcarane was formed (B). Under the same conditions (1 hr. at  $-100^\circ$ ),  $\text{CCl}_3\text{Li}$  was thermally stable but yielded additional  $\text{CBrCl}_2\text{Li}$  by exchange with  $\text{LiBr}$  (C).<sup>7</sup> On warming to  $-80^\circ$  the  $\text{CCl}_3\text{Li}$  reagent decomposed exothermally to form a mixture of tetrahaloethylenes. With  $\text{CF}_3\text{CBrCl}_2$  at  $-115^\circ$  partial exchange took place to

(1) The intermediate formation of dichlorocarbene was originally postulated for this synthesis. Initial attempts to demonstrate the formation of  $\text{CCl}_2\text{Li}$  were unsuccessful.<sup>2</sup>

(2) W. T. Miller, Jr., and C. S. Y. Kim, *J. Am. Chem. Soc.*, **81**, 5008 (1959).

(3) Excluding fluorine.

(4) Nucleophilic reactions of  $\alpha$ -chloro alkali metal compounds as transient intermediates<sup>5,11</sup> and as reagents of the type ( $p$ -R— $\text{C}_6\text{H}_4$ ) $_2\text{C}=\text{CClLi}$ <sup>6</sup> have been shown.

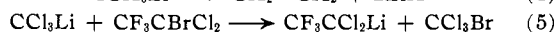
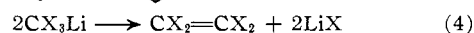
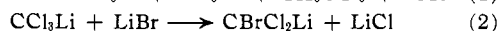
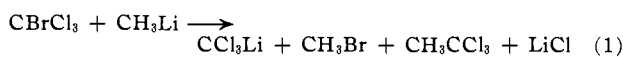
(5) D. F. Hoeg and D. I. Lusk, *J. Am. Chem. Soc.*, **86**, 928 (1964); C. R. Hauser, W. R. Braser, P. S. Skell, S. W. Kantor, and A. E. Brodhag, *ibid.*, **78**, 1653 (1956); M. S. Kharasch, W. Nudenberg, and E. K. Fields, *ibid.*, **66**, 1276 (1944); W. T. Miller, Jr., and R. Becker, Abstracts, 145th National Meeting of the American Chemical Society, New York, N. Y., Sept., 1963, p. 14M.

(6) G. Kölblich and H. Trapp, *Z. Naturforsch.*, **18b**, 1125 (1963).

(7) The  $\text{CH}_3\text{Li}$  was prepared from  $\text{CH}_3\text{Br}$  and lithium metal.

yield  $\text{CCl}_3\text{Br}$  and  $\text{CF}_3\text{CCl}_2\text{Li}$  (D). The latter compound was also prepared directly from  $\text{CF}_3\text{CBrCl}_2$  and  $\text{CH}_3\text{Li}$  (E). Its thermal decomposition yielded  $\text{CCl}_2=\text{CF}_2$ . No evidence was found for a significant reaction between  $\text{CCl}_3\text{Li}$  and  $\text{CH}_3\text{Li}$  which was present in excess during the addition of  $\text{CBrCl}_3$  at  $-115^\circ$ .

The following reactions are consistent with our results.



Reaction between  $\text{CCl}_3\text{Li}$  and an olefin without intermediate carbene formation was first indicated to us by the high yields of norcarane (to  $\sim 90\%$ ) obtained by adding  $\text{CBrCl}_3$  to cyclohexene and  $\text{RLi}$  (inverse addition).<sup>8,9</sup> A highly selective reaction between  $\text{CCl}_2$  and olefin in the presence of excess  $\text{RLi}$  appeared improbable. Other facts which are consistent with a direct reaction are the considerable stability of  $\text{CCl}_3^-$ <sup>11</sup> and the large increase in electrophilic reactivity toward olefins and other nucleophiles caused by the introduction of  $\alpha$ -halogen into methylzinc<sup>12,13</sup> and -aluminum compounds.<sup>14</sup> There appears to be no evidence to show that free carbenes are involved in the reactions of these compounds with olefins to form cyclopropanes.<sup>15</sup>

The properties of  $\text{CCl}_3\text{Li}$  make it unnecessary to invoke the initial formation of a carbene intermediate to account for the products formed when a  $\text{CCl}_3^-$  (trihalomethyl alkali metal compound) is generated in the presence of an olefin or other nucleophile. We postulate that such reactions take place by nucleophilic attack on carbon with concerted (and, in ether, cation-assisted) elimination of halide ion. This type mechanism is shown with cyclohexene (eq. 6).<sup>18,19</sup> It

(8) C. S. Y. Kim, Ph.D. Thesis, Cornell University, 1960.

(9) The formation of dihalocyclopropanes from olefins has been the accepted criterion for postulating carbene intermediates since Doering and Hoffman's important discovery of the cyclopropane synthesis.<sup>10</sup>

(10) W. von E. Doering and A. K. Hoffman, *J. Am. Chem. Soc.*, **76**, 6162 (1954).

(11) Base-catalyzed reactions of  $\text{CHCl}_3$  in which the  $\text{CCl}_3$  group persists are especially significant. For example, see: Ch. Weizmann, E. Bergmann, and M. Sulzbacher, *ibid.*, **70**, 1189 (1948); D. Seyferth and J. M. Burlitch, *ibid.*, **84**, 1757 (1962); J. Hine, R. C. Peck, Jr., and B. D. Oakes, *ibid.*, **76**, 827 (1954), and the references which are cited to earlier work.

(12) H. F. Simmons and R. D. Smith, *ibid.*, **81**, 4256 (1959).

(13) G. Wittig and K. Schwartzenbach, *Ann.*, **650**, 1 (1961).

(14) H. Hoberg, *ibid.*, **656**, 1 (1962).

(15) Simmons and Smith<sup>12</sup> (and Wittig and Schwartzenbach<sup>14</sup>) have favored a one-step reaction between the olefin and  $\alpha$ -iodomethylzinc iodide, regarded as a methylene zinc iodide complex, in which zinc iodide is displaced. Hoberg<sup>14</sup> has demonstrated the intermediate formation of olefin addition products with  $\alpha$ -chloromethylaluminum compounds and has considered this type of mechanism general. We also note that Closs and Closs<sup>16</sup> have proposed a nucleophilic substitution mechanism with a complex of diphenylmethylene and lithium bromide to explain unexpected stereochemical results. Seyferth, Burlitch, and Heeren have concluded that phenyltrihalomercurs yield carbenes in refluxing benzene.<sup>9,17</sup>

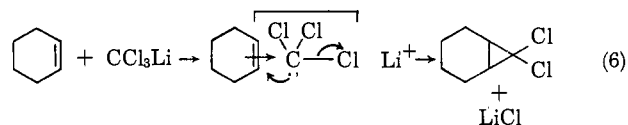
(16) G. L. Closs and L. E. Closs, *Angew. Chem. Intern. Ed. Engl.*, **1**, 334 (1962).

(17) D. Seyferth, J. M. Burlitch, and J. K. Heeren, *J. Org. Chem.*, **27**, 1491 (1962).

(18) Equation 6 is intended only to represent the essential features of the process. More information regarding the reaction species, which will be solvent dependent, is required to formulate a model for the transition state. Most probably, association is an important factor, particularly for reactions with other polar species such as  $\text{RLi}$  and  $\text{LiX}$  in aprotic solvents.

(19) No reaction products corresponding to the addition of  $\text{CCl}_3^-$ , as suggested by Hoberg, were found at  $-100^\circ$ . Compare ref. 10.

is consistent with *cis* addition, as well as the lack of 1,4 addition to conjugated dienes,<sup>20</sup> an olefin reactivity order paralleling that for polar bromination and epoxidation,<sup>21</sup> and the formation of carbene addition products (ylides) such as  $(\text{C}_6\text{H}_5)_3\text{P}=\text{CCl}_2$ <sup>22</sup> which have been reported for dichlorocarbene.<sup>23</sup> Charge type is presumed to be an important factor in determining reagent selectivity. The formation of two new carbon-carbon bonds provides an unusually large driving force for the olefin reaction.



Much more work will be required to determine how widely the reaction pattern found for  $\text{CCl}_3\text{Li}$  in ether is applicable to other  $\alpha$ -haloorganometallic compound-carbene systems under varying experimental conditions.<sup>26,29</sup> We think that a spectrum of reaction mechanisms will be established ranging from concerted  $\alpha$ -elimination<sup>30</sup> to bimolecular nucleophilic substitution (eq. 6).

**Acknowledgment.**—This work was supported by a grant from the National Science Foundation for which grateful acknowledgment is made. We also wish to acknowledge the importance of experiments carried out by Dr. C. S. Y. Kim which provided a basis for this work.

(20) R. C. Woodworth and P. S. Skell, *J. Am. Chem. Soc.*, **79**, 2542 (1957); M. Orchin and E. C. Herrick, *J. Org. Chem.*, **24**, 139 (1959).

(21) W. von E. Doering and W. A. Henderson, Jr., *J. Am. Chem. Soc.*, **80**, 5274 (1958).

(22) A. J. Speziale, G. J. Marco, and K. W. Ratts, *ibid.*, **82**, 1260 (1960). Compare Seyferth and Burlitch, ref. 11.

(23) Other processes such as the carbylamine<sup>24</sup> and Reimer-Tiemann reactions<sup>25</sup> for which dichlorocarbene has been postulated as an intermediate also can be accounted for by nucleophilic displacements on  $\text{CCl}_3^-$ .

(24) M. Saunders and R. W. Murray, *Tetrahedron*, **6**, 88 (1959); M. B. Frankel, H. Feuer, and J. Bank, *Tetrahedron Letters*, No. 7, 5 (1959).

(25) H. Wynberg, *Chem. Rev.*, **60**, 169 (1960).

(26) Recently, although considering carbene intermediates most likely, Closs and Closs have pointed out the circumstantial nature of the evidence for carbenes as true intermediates and that the organolithium compounds postulated as carbene precursors can also be used to formulate the observed transformations.<sup>27</sup> Goldstein and Baum have noted the lack of evidence to exclude an  $\alpha$ -chloroalkyl lithium as the reactive intermediate in a carbene insertion reaction.<sup>28</sup>

(27) G. L. Closs and L. E. Closs, *J. Am. Chem. Soc.*, **85**, 99 (1963).

(28) M. J. Goldstein and S. J. Baum, *ibid.*, **85**, 1885 (1963).

(29) Hine, in his pioneering work on the chemistry of the polyhalomethanes, has presented convincing evidence for the concerted production of  $\text{CF}_2$ <sup>30</sup> from  $\text{CHXF}_2$ 's and for the reaction of  $\text{CCl}_3^-$  to yield  $\text{CCl}_2$ : in aqueous solutions. For the latter reaction, our results suggest the participation of a solvent molecule or other nucleophilic species (see Mechanism II, J. Hine, *J. Am. Chem. Soc.*, **72**, 2438 (1950).

(30) J. Hine and P. B. Langford, *ibid.*, **79**, 5497 (1957).

DEPARTMENT OF CHEMISTRY  
CORNELL UNIVERSITY  
ITHACA, NEW YORK

WILLIAM T. MILLER, JR.  
DAVID M. WHALEN

RECEIVED MARCH 25, 1964

## A New Method for the Formation of the Phosphorus-Phosphorus Bond<sup>1</sup>

Sir:

Phosphinous chlorides undergo bimolecular reduction with metals<sup>2-4</sup> to form tetrasubstituted diphosphines. We have discovered another way to utilize

(1) Supported in part by Research Grant CA-05507 from the National Cancer Institute, Public Health Service.

(2) F. A. Hart and F. G. Mann, *J. Chem. Soc.*, 3939 (1957).

(3) K. Issleib and W. Seidel, *Ber.*, **92**, 2681 (1959).

(4) W. Hewerton and H. R. Watson, *J. Chem. Soc.*, 1490 (1962).