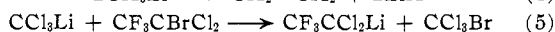
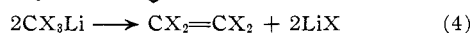
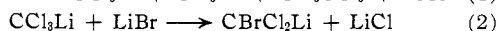
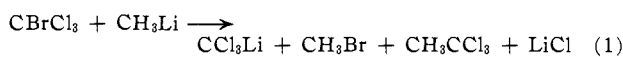


yield CCl_3Br and $\text{CF}_3\text{CCl}_2\text{Li}$ (D). The latter compound was also prepared directly from $\text{CF}_3\text{CBrCl}_2$ and CH_3Li (E). Its thermal decomposition yielded $\text{CCl}_2=\text{CF}_2$. No evidence was found for a significant reaction between CCl_3Li and CH_3Li which was present in excess during the addition of CBrCl_3 at -115° .

The following reactions are consistent with our results.



Reaction between CCl_3Li and an olefin without intermediate carbene formation was first indicated to us by the high yields of norcarane (to $\sim 90\%$) obtained by adding CBrCl_3 to cyclohexene and RLi (inverse addition).^{8,9} A highly selective reaction between CCl_2 and olefin in the presence of excess RLi appeared improbable. Other facts which are consistent with a direct reaction are the considerable stability of CCl_3^- ¹¹ and the large increase in electrophilic reactivity toward olefins and other nucleophiles caused by the introduction of α -halogen into methylzinc^{12,13} and -aluminum compounds.¹⁴ There appears to be no evidence to show that free carbenes are involved in the reactions of these compounds with olefins to form cyclopropanes.¹⁵

The properties of CCl_3Li make it unnecessary to invoke the initial formation of a carbene intermediate to account for the products formed when a 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).^{18,19} 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.¹⁰

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

(11) Base-catalyzed reactions of CHCl_3 in which the 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 Smith¹² (and Wittig and Schwartzenbach¹³) have favored a one-step reaction between the olefin and α -iodomethylzinc iodide, regarded as a methylene zinc iodide complex, in which zinc iodide is displaced. Hoberg¹⁴ has demonstrated the intermediate formation of olefin addition products with α -chloromethylaluminum compounds and has considered this type of mechanism general. We also note that Closs and Closs¹⁶ 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 phenyltrihalomercurys yield carbenes in refluxing benzene.^{9,17}

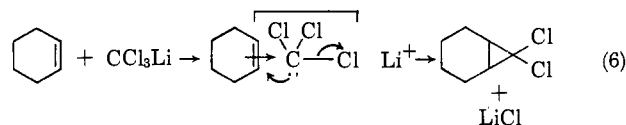
(16) G. L. Closs and L. E. Closs, *Angew. Chem. Intern. Ed. Engl.*, **1**, 334 (1962).

(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 RLi and LiX in aprotic solvents.

(19) No reaction products corresponding to the addition of CCl_3^- , as suggested by Hoberg, were found at -100° . Compare ref. 10.

is consistent with *cis* addition, as well as the lack of 1,4 addition to conjugated dienes,²⁰ an olefin reactivity order paralleling that for polar bromination and epoxidation,²¹ and the formation of carbene addition products (ylides) such as $(\text{C}_6\text{H}_5)_3\text{P}=\text{CCl}_2$ ²² which have been reported for dichlorocarbene.²³ 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 CCl_3Li in ether is applicable to other α -haloorganometallic compound-carbene systems under varying experimental conditions.^{26,29} We think that a spectrum of reaction mechanisms will be established ranging from concerted α -elimination³⁰ 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 carbylamine²⁴ and Reimer-Tiemann reactions²⁵ for which dichlorocarbene has been postulated as an intermediate also can be accounted for by nucleophilic displacements on 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.²⁷ Goldstein and Baum have noted the lack of evidence to exclude an α -chloroalkyl lithium as the reactive intermediate in a carbene insertion reaction.²⁸

(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 CF_2 ³⁰ from CHXF_2 's and for the reaction of CCl_3^- to yield 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 Bond¹

Sir:

Phosphinous chlorides undergo bimolecular reduction with metals²⁻⁴ 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).

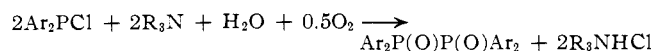
(3) K. Issleib and W. Seidel, *Ber.*, **92**, 2681 (1959).

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

phosphinous chlorides for the formation of the phosphorus-phosphorus bond. The method to be described uses quite mild conditions; in its present form, it has provided a synthesis of tetraaryldiphosphine dioxides in one step. Organic compounds containing the phosphorus-phosphorus bond are rare, and new synthetic approaches are needed.⁵ The method may prove to be adaptable to the preparation of other derivatives of diphosphine.

Exposure to the atmosphere of an ether solution of molar equivalents of a diarylphosphinous chloride and a tertiary amine results in the precipitation of the amine hydrochloride and the tetraaryldiphosphine dioxide. More of the latter can be recovered from the solution. The process is facilitated if a small amount (about 0.5 molar equiv.) of water is present initially, but excessive amounts cause hydrolysis of the chloride to the *sec*-phosphine oxide. Three different diphosphine dioxides have been obtained in 50–80% yield by this new reaction.

To account for the formation of diphosphine dioxides, it is necessary to assume that both hydrolysis and oxidation reactions are involved. No attempt has been



made yet to isolate intermediates of this complex process. The amine plays a vital role, as no coupling occurs in its absence. When either diphenylphosphine oxide or diphenylphosphinic chloride are included in the reaction mixtures, no improvement of the yield of diphosphine dioxide occurs, and when a mixture of the oxide and the phosphinic chloride is exposed to an amine in ether, a different reaction takes place.⁶ These observations suggest a process in which phosphorus-phosphorus bond formation precedes the hydrolysis and oxidation steps, with the amine involved in the coupling reaction. The amine cannot, however, act in a manner similar to metals in their coupling reaction, since it does not function as a reducing agent. Possibly an amine-phosphinous chloride complex, similar to that between amines and phosphorus trihalides,⁷ forms first and is susceptible to attack by a second molecule of phosphinous chloride, with displacement of the amine.⁸ These events would lead to an intermediate $[\text{Ar}_2\ddot{\text{P}}-\text{P}^+\text{Ar}_2\text{Cl}]\text{Cl}^-$, which is then stabilized by hydrolysis and oxidation. The over-all process is mechanistically unusual, involving first electrophilic and then nucleophilic behavior in the same kind of atom; substantiation is required and is now being sought.

The reaction has been conducted in ether, benzene, or tetrahydrofuran; the amine has been diethylaniline or triethylamine. The following procedure for tetraphenyldiphosphine dioxide is typical. A solution of 11.9 g. (0.0539 mole) of diphenylphosphinous chloride in 50 ml. of ether was added in 1 hr. to a chilled solution of 8.04 g. (0.0539 mole) of diethylaniline and 0.60 g. (0.0333 mole) of water in 60 ml. of ether. The mixture was stirred overnight unprotected from the atmosphere. A precipitate (10.4 g.) was washed with

200 ml. of water, leaving 4.64 g. of crude product. The ether filtrate left a solid on evaporation, which on washing with 100 ml. of water left 3.96 g. of crude diphosphine dioxide. The combined crude products (0.0214 mole, 79.4%) were thoroughly dried and recrystallized from dry acetone-ether (if water is present in this step, some hydrolysis occurs, and a precipitate of diphenylphosphinic acid results). The product had m.p. 167–169° (lit.⁹ m.p. 167°), the correct C, H, and P values, and an infrared spectrum in agreement with that reported.⁹ Heating in water caused cleavage to diphenylphosphinic acid and diphenylphosphine oxide in good yield. The dioxide is stable to air, but is readily oxidized by potassium permanganate or iodine solutions.

In similar fashion two new compounds were prepared: tetra(*p*-tolyl)diphosphine dioxide, 54%, m.p. 184–186° (*Anal.* Calcd. for $\text{C}_{28}\text{H}_{28}\text{O}_2\text{P}_2$: C, 73.35; H, 6.16; P, 13.51. Found: C, 73.58; H, 6.09; P, 13.61); 1,2-diphenyl-1,2-di(*p*-chlorophenyl)diphosphine dioxide, 63%, m.p. 155–156° (*Anal.* Calcd. for $\text{C}_{24}\text{H}_{18}\text{Cl}_2\text{O}_2\text{P}_2$: C, 61.16; H, 3.85; P, 13.15. Found: C, 61.45; H, 3.93; P, 12.99).

(9) W. Kuchen and H. Buchwald, *Ber.*, **91**, 2871 (1958).

(10) Philip Morris Research Assistant, 1962–1964.

DEPARTMENT OF CHEMISTRY
DUKE UNIVERSITY
DURHAM, NORTH CAROLINA

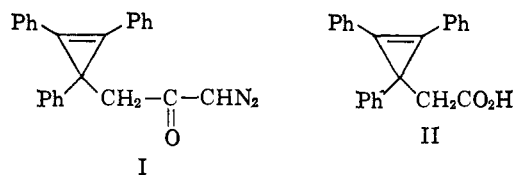
LOUIS D. QUIN
HARVEY G. ANDERSON¹⁰

RECEIVED MARCH 26, 1964

Rearrangements of 1-(1,2,3-Triphenylcyclopropenyl)-3-diazopropan-2-one

Sir:

The recent communication on the photolysis of 1,2-diphenyl-3-diazomethylketocyclopropene to give 4,5-diphenyltricyclo[1.1.1.0^{4,5}]pentan-2-one¹ has prompted us to report in preliminary form our studies on 1-(1,2,3-triphenylcyclopropenyl)-3-diazopropan-2-one (I). Compound II, (1,2,3-triphenylcyclopropenyl)acetic acid, precursor to I and prepared by hydrolysis of the crude reaction product from treatment of triphenyl-



cyclopropenyl bromide with ethyl bromoacetate in the presence of zinc in refluxing benzene-ether, had m.p. 181–183° dec. *Anal.* Calcd. for $\text{C}_{23}\text{H}_{18}\text{O}_2$: C, 84.63; H, 5.56. Found: C, 84.65; H, 5.55. Compound I, prepared from the acid chloride of II in the usual manner, had m.p. 119–122° dec. *Anal.* Calcd. for $\text{C}_{24}\text{H}_{18}\text{N}_2\text{O}$: C, 82.26; H, 5.18; N, 8.00. Found: C, 82.05; H, 5.21; N, 7.91. The n.m.r., ultraviolet, and infrared spectra were consistent with the structure.

When I was treated with copper powder in refluxing benzene for 1 hr. and the crude reaction product chromatographed on basic alumina, there was obtained after recrystallization a 57% yield of ketone III, 4,5,6-triphenyltricyclo[2.1.1.0^{6,6}]hexan-2-one,² m.p.

(1) S. Masamune, *J. Am. Chem. Soc.*, **86**, 735 (1964).

(2) The first example of such an intramolecular cyclization was reported by G. Stork and J. Ficini, *ibid.*, **83**, 4678 (1961).

(5) The subject has recently been reviewed: J. E. Huheey, *J. Chem. Educ.*, **40**, 153 (1963).

(6) L. D. Quin and H. G. Anderson, in preparation.

(7) R. R. Holmes, *J. Phys. Chem.*, **64**, 1295 (1960); *J. Am. Chem. Soc.*, **82**, 5285 (1960).

(8) Some analogy may be found in the synthesis of a diphosphine by displacement of an amine from an aminophosphine with a secondary phosphine: A. Burg, *ibid.*, **83**, 2226 (1961).