converted rapidly to polymeric materials, but in the gas phase it has been recovered partially after several weeks. In certain instances, *e.g.*, in the presence of boron trifluoride or hydrogen fluoride, cyanogen fluoride has undergone violent reaction, and accordingly precautions should be taken in working with this compound.

Cyanogen fluoride, like cyanogen chloride, reacted with benzene in the presence of aluminum chloride to form benzonitrile in 20% conversion.

We are indebted to Drs. W. C. Smith, J. E. Castle, and D. D. Coffman for helpful discussions and suggestions during the course of this investigation. A more detailed account of the syntheses, properties, and chemistry of cyanogen fluoride will be given in forthcoming publications.

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THE PREPARATION AND PROPERTIES OF ReF_7[1]

Sir:

In the course of an attempt to prepare the compound ReF_6, certain observations were made which lead us to believe that we have succeeded in preparing the hitherto unknown compound ReF_7. In addition we have succeeded in obtaining a considerably purer preparation of ReF_6 than those reported previously.[2-4]

Our original preparation, made by the action of fluorine on rhenium metal at 400°, exhibited a vapor pressure of 68 mm. at 0°. This differed from vapor pressures reported in the literature for ReF_6. Moreover, it was much lower than the vapor pressure observed for samples of ReF_6 that had been prepared previously at this laboratory.

Upon further treatment with fluorine at several atmospheres and 400° the compound absorbed fluorine and became less volatile (vapor pressure 25 mm. at 0°).

Experiments were carried out to determine the nature of this compound and the results are listed below: (1) only fluorine and rhenium are present. (2) Chemical analysis implies an empirical formula of $ReF_{6.9}$ (Given, 1.929 g. compound: Found: 1.106 g. Re, 0.771 g. F; Calculated for ReF_7: 1.126 g. Re, 0.804 g. F). (3) Measurement of fluorine absorption by authentic ReF_6 at 400° shows that approximately $^1/_2$ mole of fluorine is absorbed per mole of ReF_6 to yield ReF_7. (4) Reaction of ReF_7 with Re metal at 400° results in the formation of ReF_6. (5) Vapor density determinations on both compounds give molecular weights of 322.7 for ReF_7 and 300.9 for ReF_6. (6) The infrared spectrum of ReF_7 exhibits markedly different features from the spectrum of ReF_6 over the region studied, 600 cm.$^{-1}$ to 2000 cm.$^{-1}$ The two strong combination bands, $\nu_2 + \nu_3$, and $\nu_1 + \nu_3$, which are observed at 1316 cm.$^{-1}$ and 1469 cm.$^{-1}$ in the ReF_6 spectrum[4] are absent in the ReF_7 spectrum and are replaced by four less intense absorption bands in this region. ReF_7 has a very intense absorption band, presumably a fundamental, that coincides with the fundamental, ν_3, observed for ReF_6 at 716 cm.$^{-1}$.

The melting points of ReF_7 and ReF_6 have been determined on gram amounts of these compounds. Preliminary vapor pressure measurements were made on both compounds using a high sensitivity quartz sickle gauge.

ReF_7 is a pale yellow solid with a melting point of 48.3°. ReF_6 is a yellow solid, melting at 18.6°. Some preliminary vapor pressure measurements for solid ReF_7 and for liquid and solid ReF_6 are shown in Table I.

TABLE I

VAPOR PRESSURES OF ReF_6 AND ReF_7

t, °C.	Pressure, mm.	t, °C.	Pressure, mm.
Vapor pressure of ReF_6		Vapor pressure of ReF_7	
Solid		Solid	
0.0	167	0.0	25
9.4	272	10.1	46
14.9	356	15.2	61
Liquid		25.2	106
20.3	454	34.2	165
26.9	590		
30.9	686		

Comparison of the infrared spectra[4] as well as the wide variations in properties reported for ReF_6,[2-4] and the ease with which both ReF_6 and ReF_7 can be prepared lead us to believe that previous workers have been working with mixtures of these two compounds.

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[1] Based on work performed under the auspices of the U. S. Atomic Energy Commission.

[2] O. Ruff, W. Kwasnick and E. Ascher, *Z. anorg. allgem. Chem.*, **209**, 113 (1932).

[3] O. Ruff and W. Kwasnick, *ibid.*, **219**, 65 (1934).

[4] J. Gaunt, *Trans. Faraday Soc.*, **50**, 209 (1954).

A NEW PREPARATION OF TRIPHENYLPHOSPHINEMETHYLENES BY THE REACTION OF CARBENES WITH TRIPHENYLPHOSPHINE[1]

Sir:

Many examples of the reaction of halocarbenes with olefins, which yields halogen-substituted cyclopropanes, have been reported since the first communication on this subject by Doering and Hoffmann.[2] Also, the kinetics of the reaction of halocarbenes with halide ions, hydroxide ion and water have been studied.[3] The electrophilic nature of the carbenes in these reactions has been clearly demonstrated.[3,4] Accepting the description[4] of halocarbenes in terms of carbon in the singlet state in which an electron pair fills one orbital, leaving one orbital unoccupied, one might expect to find reactions of halocarbenes with other nucleophiles besides olefins and halide ions.

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[1] Presented in part at the Fifteenth Southwest Regional Meeting of the American Chemical Society, Baton Rouge, December 4, 1959.

[2] W. v. E. Doering and A. K. Hoffmann, THIS JOURNAL, **76**, 6162 (1954).

[3] J. Hine and A. M. Dowell, Jr., *ibid.*, **76**, 2688 (1954).

[4] P. S. Skell and A. Y. Garner, *ibid.*, **78**, 5430 (1956); W. v. E. Doering and W. A. Henderson, *ibid.*, **80**, 5274 (1958).

We report here such a reaction and its utility in organic syntheses. The donor properties of triphenylphosphine are well known, and we have found that the preparation of halocarbenes from halomethanes, either by the alkoxide method[2] or by the alkyllithium method,[5] when carried out in the presence of triphenylphosphine, gives triphenylphosphinehalomethylene reagents[6], *e.g.*

$$CH_2Cl_2 + n\text{-BuLi} + (C_6H_5)_3P \longrightarrow (C_6H_5)_3P{=}CHCl + LiCl + C_4H_{10}$$

Addition of hydrogen bromide to the yellow solution of triphenylphosphinechloromethylene, prepared by adding 0.1 mole of *n*-butyllithium in ether to 0.11 mole of triphenylphosphine and 0.13 mole of methylene chloride in ether at −30°, precipitated a mixture of $[(C_6H_5)_3PH]Br$ and $[(C_6H_5)_3PCH_2Cl]Br$. The precipitated solids were dissolved in water, causing quantitative decomposition of triphenylphosphonium bromide to HBr and triphenylphosphine. Filtration of the latter was followed by precipitation of $[(C_6H_5)_3PCH_2Cl][B(C_6H_5)_4]$, m.p. 189–192° (dec.) (Calcd. for $C_{43}H_{37}ClPB$: C, 81.84; H, 5.91; Cl, 5.62. Found: C, 82.03; H, 6.17; Cl, 5.37) by addition of aqueous sodium tetraphenylborate to the filtrate. It was determined in this manner that triphenylphosphinechloromethylene had been formed in about 65% yield. A separate experiment using $[(C_6H_5)_3PCH_2Cl]Br$, purified by recrystallization from 2-propanol–ether (m.p. 209–211°. Calcd. for $C_{19}H_{17}ClBrP$: C, 58.26; H, 4.38; Cl, 9.05; Br, 20.40. Found: C, 58.47; H, 4.31; Cl, 8.6; Br, 20.3. Picrate, m.p. 192–194°. Calcd. for $C_{25}H_{19}O_7N_3ClP$: C, 55.61; H, 3.55; Cl, 6.56. Found: C, 55.60; H, 3.76; Cl, 6.32) in aqueous solution at comparable *p*H showed that the $[(C_6H_5)_3PCH_2Cl]^+$ ion is precipitated quantitatively by sodium tetraphenylborate. When phenyllithium was used as the base in the chlorocarbene generation, triphenylphosphinechloromethylene resulted in yields of *ca.* 40%. Dibromo- and dichlorocarbene could also be trapped in this manner to give triphenylphosphinedihalomethylene reagents.

Triphenylphosphinehalomethylenes undergo the Wittig reaction,[7] thus providing a new general synthesis of substituted vinyl chlorides and vinylidene chlorides and bromides. Treatment of solutions of triphenylphosphinechloromethylene with aldehydes and ketones using standard Wittig reaction conditions resulted in the expected substituted vinyl chlorides. A mixture of the *cis* and *trans* isomers was obtained when an aldehyde or unsymmetrical ketone was used. As an example may be given the preparation of 1-chloro-2-phenyl-1-propene[8] in 46% yield, based on methylene chloride, by the reaction of $(C_6H_5)_3P{=}CHCl$ with acetophenone. Gas chromatographic analysis showed that both possible geometrical isomers were present in 1:1.15 ratio; no assignment of structure was attempted. Triphenylphosphinechloromethylene may also be prepared by treatment of the triphenylchloromethylphosphonium bromide described above with phenyllithium in ether. The reagent prepared in this manner reacted with acetophenone to give 1-chloro-2-phenyl-1-propene in yields of 80–90%. The lower yield of the chloroölefin obtained when $(C_6H_5)_3P{=}CHCl$ was used in the solution in which it was generated by trapping of chloromethylene may be due to the presence of unreacted triphenylphosphine which interferes in isolation of the chloroolefin by distillation.

Some of the other conversions carried out include: cyclohexanone to chloromethylenecyclohexane; methyl isobutyl ketone to 1-chloro-2,4-dimethyl-1-pentene; diethyl ketone to 1-chloro-2-ethyl-1-butene and acetophenone to 1,1-dibromo-2-phenyl-1-propene (*via* CBr_2 generated using potassium *tert*-butoxide).

Extension of this reaction to the preparation of other phosphinemethylene reagents and the application of these reagents in organometallic syntheses such as those we have reported recently[9] is in progress.

We are grateful to the National Science Foundation for a predoctoral fellowship awarded to one of us (S.O.G.) and to the Quartermaster Research and Engineering Command for support of this work.

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[5] G. L. Closs and L. E. Closs, THIS JOURNAL, **81**, 4996 (1959); W. T. Miller, Jr., and C. S. Y. Kim, *ibid.*, **81**, 5008 (1959).

[6] G. Wittig and W. Haag, *Chem. Ber.*, **88**, 1654 (1955), with this end in mind, added diazomethane to triphenylphosphine in ether solution, but stable $(C_6H_5)_3P{=}N{-}N{=}CH_2$ was formed instead of $(C_6H_5)_3P{=}CH_2$.

[7] G. Wittig and U. Schöllkopf, *Chem. Ber.*, **87**, 1318 (1954); see also U. Schöllkopf, *Angew. Chem.*, **71**, 260 (1959).

[8] B.p. 102–105° at 14 mm. Calcd. for C_9H_9Cl: C, 70.82; H, 5.94. Found: C, 70.81; H, 5.95.

[9] S. O. Grim and D. Seyferth, *Chem. and Ind. (London)*, 849 (1959).

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CONDITIONS FOR STEREOSPECIFIC OLEFIN-MERCAPTAN RADICAL ADDITIONS

Sir:

Non-stereospecificity in radical-olefin addition reactions is the generally accepted pattern, certain additions involving hydrogen bromide being the only established exceptions.[1,2,3,4,5] Although mercaptans add to alkenes with high specific reaction velocities[6] (10^6 l. mole^{-1} sec.$^{-1}$), there have been a number of reports on non-stereospecificity for olefin-mercaptan additions.[7,8,9] We confirm this pattern for the reaction of CH_3SD with the *cis*- and *trans*-2-butenes at −70°. Under reaction conditions producing only minor amounts of olefin

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[1] For reviews of the earlier literature, C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957; and P. S. Skell, R. C. Woodworth and J. H. McNamara, THIS JOURNAL, **79**, 1253 (1957).

[2] P. S. Skell and R. G. Allen, *ibid.*, **80**, 5997 (1958).

[3] P. S. Skell and R. G. Allen, *ibid.*, **81**, 5383 (1959).

[4] H. L. Goering and D. W. Larsen, *ibid.*, **81**, 5937 (1959).

[5] N. A. Le Bel (Abstracts Boston Meeting 1959, 4-O) described non-stereospecific reaction of HBr with norbornene. Also, private communication from Prof. P. I. Abell indicates that in the 1-bromo-1-cycloalkenes (C_4,C_6,C_7), additions of hydrogen bromide are not stereospecific.

[6] C. Sivertz, *J. Phys. Chem.*, **63**, 34 (1959).

[7] F. G. Bordwell and W. A. Hewett, THIS JOURNAL, **79**, 3493 (1957).

[8] H. L. Goering, D. I. Relyea and D. W. Larsen, *ibid.*, **78**, 348 (1956).

[9] S. J. Cristol and R. P. Arganbright, *ibid.*, **79**, 6039 (1957).