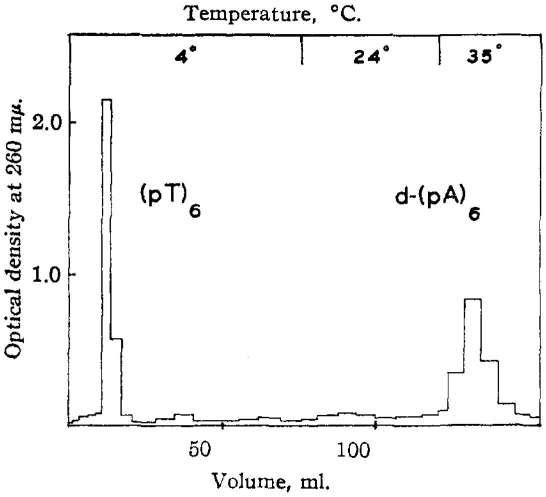

Fig. 1.

20 units long) connected at their 5′ phosphoryl ends to the cellulose by phosphodiester linkages. The cellulose was packed into a column (20 cm. × 1 cm. diam.) and washed extensively with 1 *M* NaCl-0.01 *M* NaH_2PO_4 (pH 7) solution. Ten optical density units each of $(pT)_6$ and d-$(pA)_6$ were passed slowly through the column in this salt solution at 4°. The elution diagram shows that the d-$(pA)_6$ was selectively bound to the column and could not be eluted until the temperature of the column had been raised to 35°. The separation was complete and the recovery quantitative. Preliminary experiments with *E. coli* amino acid transfer RNA on this column have resulted in a selective adsorption of 6% of the RNA. This fraction is now being examined for the presence of a consecutive adenosine sequence and for its specificity in accepting amino acids.

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YLID INTERMEDIATE IN THE REACTION OF TRIPHENYLPHOSPHINE WITH CARBON TETRACHLORIDE

Sir:

We wish to report an extremely simple, high yield route to prepare the ylid, triphenylphosphine dichloromethylene[1] [by the direct reaction of carbon tetrachloride with triphenylphosphine] and a convenient one-step synthesis for β,β-dihaloölefins.

When a concentrated solution of triphenylphosphine in carbon tetrachloride is allowed to stand at room temperature for 48 hours or is heated at 60° for 2–3 hours and then hydrolyzed, no triphenylphosphine is recovered.[2] This reaction was considered responsible for these observations

$$CCl_4 + 2(C_6H_5)_3P \longrightarrow (C_6H_5)_3PCl_2(I) + (C_6H_5)_3P{=}CCl_2(II)$$

In order to test this hypothesis, an equimolar amount of benzaldehyde was added to a mixture of triphenylphosphine in excess carbon tetrachloride which had been heated for 3 hours at 65°. Gas chromatographic analysis of the resulting solution indicated that most of the benzaldehyde was consumed and two new products, identified as β,β-dichlorostyrene and benzal chloride appeared. These lend support to the proposed intermediacy of triphenylphosphine dichloromethylene and triphenylphosphine dichloride.

$$(C_6H_5)_3P{=}CCl_2 + C_6H_5CHO \longrightarrow (C_6H_5)_3PO + C_6H_5CH{=}CCl_2$$

$$(C_6H_5)_3PCl_2 + C_6H_5CHO \longrightarrow (C_6H_5)_3PO + C_6H_5CHCl_2\;[3]$$

For synthetic utility it is convenient to conduct the entire reaction in one step by adding the carbonyl component to the initial mixture. For example, when a solution of 72.0 g. (0.274 mole) of triphenylphosphine and 29.0 g. (0.274 mole) of benzaldehyde in 150 ml. of carbon tetrachloride was heated at 60° for 2 hours, gas chromatographic analysis revealed that the benzaldehyde disappeared rapidly while benzal chloride and β,β-dichlorostyrene formed in equal quantities. Addition of 200 ml. of low boiling petroleum ether to the reaction mixture precipitated 69 g. (90%), m.p. 153–156°, of triphenylphosphine oxide. Fractional distillation of the filtrate gave less than 1 g. of unreacted benzaldehyde, 15.1 g. (72%) of benzal chloride, b.p. 121–3° (63 mm.) and 16.0 g. (72%) of β,β-dichlorostyrene,[4] b.p. 135–7° (63 mm.).

A careful study of the reaction of 32.7 g. (0.125 mole) of triphenylphosphine and 70 ml. of carbon tetrachloride in the presence of 22.8 g. (0.125 mole) of benzophenone at 60° was conducted and followed by quantitative gas chromatography. After 4 hours, the ratio of the peak area of the product, 1,1-diphenyldichloroethylene, to that of the benzophenone became constant. The solution contained 9.65 g. (0.052 mole) of benzophenone and 12.2 g. (0.049 mole) of 1,1-diphenyldichloroethylene (78% based on the stoichiometry):[5]

$$2(C_6H_5)_3P + 2(C_6H_5)_2CO + CCl_4 \longrightarrow 2(C_6H_5)_3PO + (C_6H_5)_2C{=}CCl_2 + (C_6H_5)_2CCl_2$$

However, *no* diphenyldichloromethane was observed, demonstrating that the triphenylphosphine dichloride produced in this reaction does not exchange with benzophenone. Addition of benzaldehyde to an aliquot of the reaction mixture produced benzal chloride almost immediately but, as anticipated, no β,β-dichlorostyrene was formed.

This shows that under special conditions and depending on the carbonyl component, considerable control of the product may be obtained. This type of reaction thus provides a potentially convenient route to otherwise difficultly accessible 1,1-dihaloölefins.

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(1) This ylid was first described by A. J. Speziale, G. L. Marco and K. W. Ratts, *J. Am. Chem. Soc.*, **82**, 1260 (1960).

(2) In the 60° case, 76% of triphenylphosphine oxide was obtained. An additional 12% of the triphenylphosphine was combined in a water soluble unidentified crystalline solid, m.p. 239–241° with an empirical formula of $C_{19}H_{16}Cl_2P$.

(3) L. Horner, H. Oediger and H. Hoffmann, *Ann.*, **626**, 26 (1959).

(4) *Anal.* Calculated for $C_8H_6Cl_2$: C, 55.5; H, 3.46; Cl, 41.0. Found: C, 55.9; H, 3.65; Cl, 41.23.

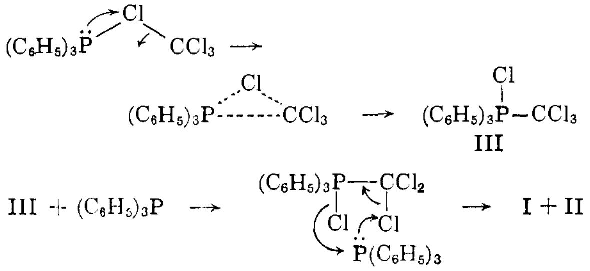
(5) The reaction mixture was conveniently worked up taking advantage of the insolubility of triphenylphosphine oxide in ethyl ether and the much greater solubility of benzophenone in methanol than that of 1,1-diphenyldichloroethylene. The latter, m.p. 78.0–78.5° was identified by comparison with an authentic sample.

The reactions of other polyhalomethanes with triphenylphosphine in the presence of benzaldehyde have been investigated in a preliminary manner. Thus with bromotrichloromethane, β,β-dichlorostyrene was observed, and with dichlorodifluoromethane and dibromodifluoromethane, β,β-difluorostyrene was noted. When the system tributylphosphine–carbon tetrachloride–benzaldehyde was studied, small amounts of benzal chloride and β,β-chlorostyrene were observed. A detailed examination of the above reactions and related systems is now under way.

Although insufficient data has been accumulated to delineate a detailed mechanism, certain experimental facts must be accommodated.

The reaction proceeds readily in total darkness and is not accelerated by azobisisobutyronitrile at 60° or by ultraviolet light at room temperature. Further, when the reaction was carried out in the presence of tetramethylethylene *none* of the corresponding dichlorocyclopropane derivative was detected, although this cyclopropane was observed in a competitive experiment in which dichlorocarbene was generated in the usual way[6,7] in the presence of *both* triphenylphosphine and tetramethylethylene.

The mechanism shown is consistent with the experimental observations:



Acknowledgment.—We wish to thank Dr. Richard W. Young of this Laboratory for his encouragement and helpful discussions.

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

[7] An authentic sample of 1,1-dichloro-2,2,3,3-tetramethylcyclopropane was supplied by Dr. W. A. Henderson, Jr., of this Laboratory, W. von E. Doering and W. A. Henderson, Jr., *J. Am. Chem. Soc.*, **80**, 5274 (1958).

CENTRAL RESEARCH DIVISION ROBERT RABINOWITZ
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RECEIVED JANUARY 16, 1962

ON d HYBRIDIZATION IN CHLORINE

Sir:

In a recent communication[1] Klemperer has argued "that the differences in chemical bonding of chlorine and fluorine cannot be naturally explained simply in terms of 3d hybridization." He cites the previously reported spectroscopic energies required to excite a p electron to the 3d level in these two atoms and then bases his argument on "the similarity in magnitude of 3d excitation in chlorine and fluorine" and on their "in each instance being slightly less than two e.v. below the ionization limit."

We question the argument that optical excitation energies for one electron in one center orbitals can be used directly to determine the stability of two electrons in two center orbitals. The argument applied to this particular case seems inappropriate for the following reasons:

(1) Excitation energies of the 3d electrons of *all* elements in the first two rows lie within two e.v. of their ionization energies.[2] For example, if one compares the second row element, sulfur, for which d orbital utilization in certain types of bonding is generally accepted, and the first row group member, oxygen, it is seen that these 3d excitation energies are 1.8 e.v. and 1.5 e.v., respectively, below the ionization energies. Further, there is even closer similarity in the magnitudes of these excitation energies between sulfur and oxygen, than between chlorine and fluorine.[3]

(2) Actually, comparing second to first row elements in the same group, the difference in this p to 3d excitation energy reaches a maximum, 4.7 e.v., for the pair chlorine to fluorine. In fact, it would seem that this particular difference, 108 kcal./mole, is significant because it is greater than the energy released in the formation of most covalent bonds.

(3) It is important to specify the type of bonding considered in discussing this subject. In general, there are two rather distinct ways in which d orbitals are utilized in covalent bonding: one, in added hybridization of atomic orbitals which are largely s and p in character and accommodate an octet of valence electrons (four bonds and/or unshared pairs); to our knowledge, no authors ascribe more than a few per cent. d character in this type of hybridization.[4] Two, given an octet of electrons which exhaust the s and p valence orbitals, it is apparent that second row non-metals can accept additional bonding electrons, either in forming new sigma bonds[5] or in stabilizing adjacent unshared pairs (pi bonding).[6] For this second type of utilization of an atomic orbital, it would seem that rather than optical excitation energy, it is the radius and angular concentration which is

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[1] W. Klemperer, *J. Am. Chem. Soc.*, **83**, 3910 (1961).

[2] C. E. Moore, "Atomic Energy Levels," Vol. I, United States Department of Commerce, 1949, Washington, D. C.

[3] Optical excitation energy related to the s to p promotion, which is the most common in first and second row atomic hybridization, can be readily estimated from Slater's one electron energy table (*Phys. Rev.*, **98**, 1039 (1955)), where it is seen that s to p excitation (even with the same principal quantum number) can require energy in excess of that required for ionization. For example, 2s to 2p for oxygen requires 16.5 e.v., while oxygen's ionization energy is only 13.6 e.v. Yet one would hardly argue on this basis that it is "arbitrary" or not "natural" to assign s character to the sigma bonding orbitals of oxygen.

[4] Some have even found it useful (*cf.*, L. Pauling, "The Nature of the Chemical Bond," 3rd Ed., Cornell University Press, Ithaca, N. Y., 1960, p. 126 ff.) to consider use of atomic orbitals of energy greater than d (f and g), even those of the energy continuum, in arriving at the hybridization of a bonding orbital.

[5] *Cf.* the numerous polyhalides of the second row non-metals; *e.g.*, ClF_3 and SF_6.

[6] One of the most interesting differences involving chlorine and fluorine, which can be naturally explained with d orbital resonance for the former, is the relatively greater stability of the $X_3C:^-$ ion when X is chlorine than when it is fluorine; for a leading reference see L. H. Slaugh and E. Bergmann, *J. Org. Chem.*, **26**, 3158 (1961). For a discussion of the nature of d orbital hybridization and multiple bond character in the halogen molecules themselves, see R. S. Mulliken, *J. Am. Chem. Soc.*, **77**, 884 (1955).