centration, as indicated in Fig. 4. The formation constant for the completely mixed compounds from the end members according to the reaction

$$PCl_3 + PBr_3 + P(OC_6H_5)_3 \rightleftharpoons 3PClBr(OC_6H_5) \qquad (6)$$

can then be calculated by the equation

$$K_f = K_5(K_f'K_f''K_f''')^{1/3} = 1.5 \times 10^3 \qquad (7)$$

in which K_5 is the equilibrium constant for equation 5 and K_f', K_f'' and K_f''' are the three formation constants for the reactants in equation 5 whose values are given in Table I. Because of accumulated errors, the value of the formation constant is considered rather inaccurate. It is given only to indicate that its order of magnitude is significantly greater than that calculated for a completely random system which would be 216.

Although there are not sufficient data on which to reach firm conclusions, it appears that deviations from ideal randomness are more pronounced in systems based on triply connected phosphorus than in equivalent systems based on quadruply connected phosphorus. This conclusion is in accord with the wide variations in chemical shifts observed in nuclear magnetic resonance studies on compounds based on triply connected phosphorus as compared to those based on quadruply connected phosphorus. These findings can be explained qualitatively by the difference between the way significant intramolecular electrical charge differences are avoided in compounds based on triply connected phosphorus as compared to compounds based on quadruply connected phosphorus.[6] When three ligands are attached to a phosphorus atom, avoidance of charge unbalance between them and the phosphorus is achieved by changing the bond angles and hence the type of hybridization; whereas feedback of the charge appears to be accomplished in compounds based on quadruply connected phosphorus by π-bonding, utilizing the d orbitals of the phosphorus.[7]

Although detailed rate measurements were not made, our studies indicate that exchange of ligands between molecules based on triply connected phosphorus proceeds at a considerably faster rate than exchange of the same ligands between molecules based on quadruply connected phosphorus. Presumably the exchange for the molecules based on triply connected phosphorus occurs *via* a Walden inversion which might be expected to be a lower energy process than the one involved in the exchange of ligands between molecules based on quadruply connected phosphorus. In this latter case, the activated complex may well involve the utilization of a d orbital of the phosphorus in its σ-bond base structure, so that the activated complex would be based on sp^3d hydridization of the phosphorus.

Acknowledgments.—We wish to thank Dr. Donald P. Ames for carrying out some nuclear magnetic resonance measurements reported herein and for his help in interpreting the nuclear magnetic resonance data. Mr. George Brautigam also made a number of the nuclear magnetic resonance determinations and measured some of the resulting resonance peak areas.

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[6] J. R. Van Wazer, "Phosphorus and Its Compounds: Chemistry," Interscience Publishers, Inc., New York, N. Y., 1958, Chapter 2; J. R. Van Wazer, THIS JOURNAL, **78**, 5709 (1956).

[7] H. H. Jaffé, *J. Inorg. Nuclear Chem.*, **4**, 372 (1957).

[CONTRIBUTION FROM MONSANTO CHEMICAL COMPANY, RESEARCH DEPARTMENT, INORGANIC CHEMICALS DIVISION]

Principles of Phosphorus Chemistry. IX. Reorganization of Triply and Quadruply Connected Monophosphorus Compounds[1]

BY EINHARD SCHWARZMANN[2] AND JOHN R. VAN WAZER

RECEIVED MAY 6, 1959

In simple reorganization between triply and quadruply connected monophosphorus compounds, eight molecular species are involved. In addition to the two dissociation constants of the mixed triply connected molecules and the two dissociation constants of the mixed quadruply connected molecules, a fifth equilibrium constant is needed to describe the system. The systems $OPCl_3$–PBr_3 and $OPBr_3$–PCl_3 are compared and found to have the same set of five equilibrium constants, as would be expected. Some preliminary data on the system $OPCl_3$–$P(OC_6H_5)_3$ also are given.

To round out the work reported in the previous four papers[3] of this series, a study was made of reorganization between triply and quadruply connected compounds based on a single phosphorus atom. The major amount of work was done on the systems $OPCl_3$–PBr_3 and $OPBr_3$–PCl_3. Less precise measurements were made on the $OPCl_3$–$P(OC_6H_5)_3$ system.

Experimental Results

The reagents and method of study were the same as those described in preceding papers of this series.[3] The reorganization between $OPCl_3$–PBr_3 was carried out at temperatures of 200 and 110°. Measurements on the 200° samples were made after eight weeks, but trial experiments indicated that equilibrium was reached in several days. The measurements on the 110° samples were made after four weeks. It is interesting to note that, after two months at 25°, essentially no reaction was found. The system $OPBr_3$–PCl_3 was measured after one week at 200°. All of the tubes contained clear colored liquids at the end of the heating period, and there was no indication of side reactions.

The system $OPCl_3$–$P(OC_6H_5)_3$ was measured after one week at 200°, and another set of tubes was heated to 300° for several weeks. At 200°, no decomposition was observed. However, the liquids in the tubes stored at 300° exhibited a licorice-brown color, and the n.m.r. measurements gave

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[1] A preliminary investigation of this subject was made by Dr. Ekkehard Fluck shortly before he left our laboratory to return to Heidelberg University.

[2] On leave of absence during the 1958–1959 academic year from Göttingen University, Germany.

[3] L. C. D. Groenweghe and J. H. Payne, Jr., THIS JOURNAL, **81**, 6357 (1959); J. R. Van Wazer, and E. Fluck *ibid.*, **81**, 6360 (1959); L. C. D. Groenweghe, J. H. Payne and J. R. Van Wazer, unpublished.

indications of side reactions (at least one unidentified organophosphorus compound).

Since eight species are involved in the equilibria between triply and quadruply connected phosphorus compounds, it is extremely important to obtain precise n.m.r. results in this type of investigation. The quantitative data reported for the systems $OPCl_3$–PBr_3 and $OPBr_3$–PCl_3 were obtained during a period when the n.m.r. spectrograph was operating very satisfactorily with good high resolution.

Results and Conclusions

Reorganization between triply and quadruply connected phosphorus compounds is shown graphically in Fig. 1 for the system $OPCl_3$–PBr_3. Generally speaking, Fig. 1 is typical of the type of results obtained when a triply connected monophosphorus compound is reorganized with a quadruply connected one. Within experimental error, the same quantitative results were found for the system at 110 and 200°. It should be noted that all possible species—$OPCl_3$, $OPCl_2Br$, $OPClBr_2$, $OPBr_3$, PBr_3, PBr_2Cl, $PBrCl_2$ and PCl_3—are found in Fig. 1. With all of the phosphorus being triply connected on the left side of the diagram and none of this type of phosphorus on the right side of the diagram, the sum of the phosphorus present in the various triply connected species linearly decreases from 100 to 0% of the total phosphorus when going from the left to the right side of the diagram. The reverse is true of the quadruply connected phosphorus. From the quantitative measurement of the eight species, it is possible to obtain the two equilibrium constants of the type shown in eq. 1 below, and the two equilibrium constants of the type shown in eq. 2.

$$K_{\mathrm{d,T}} = \frac{[PX_3][PXY_2]}{[PX_2Y]^2} \tag{1}$$

$$K_{\mathrm{d,Q}} = \frac{[OPX_3][OPXY_2]}{[OPX_2Y]^2} \tag{2}$$

where X is either Cl or Br. These constants have been determined previously in our laboratory.[3] In addition, there must be a constant relating the equilibrium between the triply and the quadruply connected phosphorus compounds. In its simplest form, this type of constant can be written in fourteen different ways, ignoring reciprocals, as indicated by eq. 3 below. The fourteen different expressions are related to each other through the four expressions corresponding to eq. 1 and 2 above.

$$K_{\mathrm{I}} = \frac{[PX_iY_{3-i}][OPX_jY_{3-j}]}{[PX_nY_{3-n}][OPX_{i+j-n}Y_{3-(i+j-n)}]} \tag{3}$$

where X is either Cl or Br, and $0 \leqslant i + j - n \leqslant 3$, with i and j assuming any fixed integer value between 0 and 3. For completely random reorganization, all of the forms of K_{I} should be equal to unity, since no particular combination of X and Y would be preferred in either the triply or quadruply connected systems. Although the form of K_{I} involving PBr_3, $OPCl_3$, PCl_3 and $OPBr_3$ would—at first glance—appear to be the best one to use, these four species are only measurably present at a value of the composition parameter $R = 1.5$, where the PCl_3 and $OPBr_3$ are found only in small amounts, as shown by Fig. 1. Therefore, the form of K_{I} chosen to represent the results of this investigation has PBr_2Cl and $OPBrCl_2$ in the numerator, with $PBrCl_2$ and $OPBr_2Cl$ in the denominator.

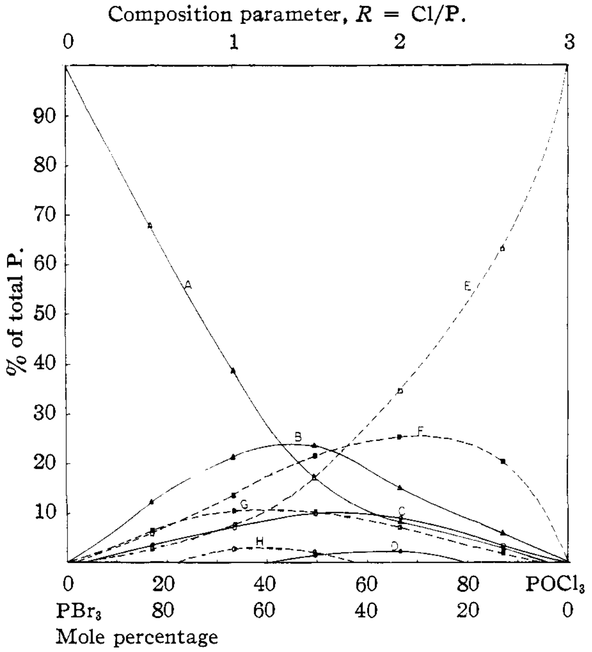

Fig. 1.—Equilibrium in the system PBr_3–$OPCl_3$; A = PBr_3, B = PBr_2Cl, C = $PBrCl_2$, and D = PCl_3; E = $OPCl_3$, F = $OPBrCl_2$, G = $OPBr_2Cl$, and H = $OPBr_3$.

The equilibrium constants found for the $OPCl_3$–PBr_3, and $OPBr_3$–PCl_3 systems are listed in Table I where they are given to only one significant figure. Higher accuracy is not found because of the number of species present in the system. Within experimental error, both systems gave the same constants at the two temperatures investigated. It should be noted that, when K_1, K_2, K_3 and K_4 are not equal to the value of one-third which corresponds to completely random reorganization, the various forms of K_{I} will have widely different values.

TABLE I

CONSTANTS FOR REORGANIZATION EQUILIBRIA IN THE SYSTEM $OPCl_3$–$OPBr_3$–PCl_3–PBr_3

Constant	Value from this work	Our previously reported[3] value
$K_1 = \frac{[PBr_3][PBrCl_2]}{[PBr_2Cl]^2}$	0.6	0.7
$K_2 = \frac{[PCl_3][PBr_2Cl]}{[PBrCl_2]^2}$	.4	.2
$K_3 = \frac{[OPBr_3][OPBrCl_2]}{[OPBr_2Cl]^2}$	.3	.34
$K_4 = \frac{[OPCl_3][OPBr_2Cl]}{[OPBrCl_2]^2}$	.5	.41
$K_5 = \frac{[PBr_2Cl][OPBrCl_2]}{[PBrCl_2][OPBr_2Cl]}$	5	..

Because of this, there is no meaning in comparing the experimental value of $K_5 = 5$ given in Table I, to the value of unity which this constant would have in a completely random system. Therefore, the non-ideality of equilibrium between the triply and quadruply connected species cannot be presented succinctly in terms of a free energy difference as was done for the systems based on all triply connected phosphorus in Paper VIII of this series.[3]

In the system obtained by reorganizing triphenyl phosphite with phosphorus oxychloride, two species are present for which n.m.r. data were not previously available. We find that phenyl dichlorophosphate, $OPCl_2(OC_6H_5)$, exhibits a chemical shift[4] of -1.5 p.p.m. with respect to 85% H_3PO_4. This means that the resonance peak for this compound can be resolved from the peak corresponding to $OPCl_3$ with only the utmost difficulty. Diphenyl monochlorophosphate, $OPCl(OC_6H_5)_2$, exhibits a chemical shift of $+6.2$ p.p.m. with respect to 85% H_3PO_4.

When plotted in the same manner as Fig. 1, the system $OPCl_3$–$P(OC_6H_5)_3$ appears appreciably different from the system $OPCl_3$–PBr_3. Completely random reorganization at R = Cl/P = 1.50 should lead to 6.25% of the total phosphorus in each of the four simple compounds and 18.75% in each of the four mixed species. The experiment showed these various percentages of total phosphorus in the simple compounds: PCl_3, 6.5; $P(OC_6H_5)_3$, 0; $OPCl_3$, 1.8; and $OP(OC_6H_5)_3$, 12.3—with the mixed species giving: $PCl_2(OC_6H_5)$, 30.6; $PCl(OC_6H_5)_2$, 12.6; $OPCl_2(OC_6H_5)$, 16.0; and $OPCl(OC_6H_5)_2$, 20.2. From these data, a value was obtained for the form of K_I shown in eq. 4

$$K = \frac{[PCl(OC_6H_5)_2][OPCl_2(OC_6H_5)]}{[PCl_2(OC_6H_5)][OPCl(OC_6H_5)_2]} = 0.3 \qquad (4)$$

Within the accuracy of measurement, the values of the dissociation constants of monophenyl dichlorophosphate and diphenyl monochlorophosphate cannot be differentiated from the theoretical value[3] of one-third, corresponding to completely random reorganization.

Acknowledgments.—We wish to thank George Brautigam for carrying out the n.m.r. measurements which form the basis of this paper. We are also indebted to Ekkehard Fluck for his preliminary study of the reorganization between triphenyl phosphate and phosphorus oxychloride. John R. Parks calculated the conditions to be met in eq. 3, in order to get the set of independent constants.

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[4] J. R. Van Wazer, C. F. Callis, J. N. Shoolery and R. C. Jones, THIS JOURNAL, **78**, 5715 (1956).

[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY AND THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO]

Diboron Tetrachloride and Tetrafluoride as Reagents for the Synthesis of Organoboron Compounds. II. The Behavior of the Diboron Tetrahalides toward Unsaturated Organic Compounds[1]

BY P. CERON, A. FINCH, J. FREY, J. KERRIGAN, T. PARSONS, G. URRY AND H. I. SCHLESINGER

RECEIVED OCTOBER 13, 1958

The study of the reactions of diboron tetrachloride with unsaturated hydrocarbons has been extended to the corresponding reactions of diboron tetrafluoride and to those of vinyl halides and other halogen derivatives of ethylene, to propene, to cyclopropane, to butene-2, to acetylene, to allyl halides, to butadiene and to 4-chlorobutene-1. Several new compounds are described and the effect of substitution of halogen atoms for the hydrogen atoms of unsaturated hydrocarbons is pointed out and discussed briefly.

It has been shown[2] previously that diboron tetrachloride reacts with ethylene at low temperature ($-80°$) to form 1,2-bisdichloroborylethane $Cl_2BC_2H_4BCl_2$.[3] The present paper shows that diboron tetrachloride reacts in similar fashion with propene, cyclopropane, butene-2, acetylene, butadiene, allyl halides and 4-chlorobutene-1. But the corresponding reaction with vinyl halides or other haloethylenes does not occur even at temperatures well over 25°. It is further noteworthy that the adducts[4] of diboron tetrahalides and vinyl halides are far less stable than the adducts involving the unsubstituted unsaturated hydrocarbons or that involving 4-chlorobutene-1. The failure of the haloethylenes to undergo the reaction in question is analogous to the relatively low reactivity of these compounds toward electrophilic reagents in general, as is also the renewed reactivity when the substituting BCl_2 group is not attached to a carbon atom directly adjacent to the double bond.

One mole of acetylene adds only one mole of diboron tetrachloride, although the resulting "adduct" $Cl_2BC_2H_2BCl_2$ still contains doubly bonded carbon atoms. One mole of butadiene may, on the other hand, add either one or two moles of B_2Cl_4. Evidently the presence of BCl_2 groups attached to carbon atoms adjacent to double bonds has the same effect in decreasing the reactivity of the double bond as do halogen atoms similarly located; as in the case of halogen atoms the inhibiting effect of BCl_2 groups is either lacking or is much less pronounced if the substituting groups are attached to carbon atoms not adjacent to double bonds.

The corresponding reactions of diboron tetrafluoride[5] are in general similar to those of the

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[1] This paper is based largely on Annual Reports submitted to the Office of Naval Research in connection with Contracts N6-ori-020100 Project NR356-255 and Nonr2121(02) Project NR052-255. These reports cover the years ending June 30 or July 31, 1954, 1956 and 1957, and are entitled "Hydrides and Borohydrides of Light Weight Elements and Related Compounds." In addition certain parts have been taken from a thesis submitted to the Department of Chemistry, University of Chicago, by John Frey in part fulfillment of the requirements for the degree of Doctor of Philosophy.

[2] G. Urry, J. Kerrigan, T. D. Parsons and H. I. Schlesinger, THIS JOURNAL, **76**, 5299 (1954).

[3] The structure indicated by this formula was originally based on chemical evidence; it has since been confirmed by E. B. Moore and W. W. Lipscomb, *Acta Cryst.*, **9**, 688 (1956).

[4] The products of the reactions herein described are, strictly speaking, not adducts, since in their formation the boron to boron bonds of the tetrahalides are severed. The term is nevertheless used as a matter of convenience.

[5] A. Finch and H. I. Schlesinger, THIS JOURNAL, **80**, 3573 (1958).