The authors believe that the power of the relaxation method, which has been widely applied to very fast reactions, is well illustrated by the application to the slow chromate–dichromate system. In many cases the technique has significant experimental advantages over various other methods. The simplification in interpretation, particularly for complex reactions, is enormous.

Acknowledgments.—The authors wish to thank Prof. R. G. Wilkins for his stimulating discussion on the use of relaxation techniques for studying slow reactions and Dr. M. Eigen for the use of his laboratory facilities. Both authors wish to acknowledge the support of NSF postdoctoral fellowships.

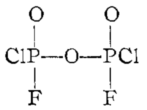
CONTRIBUTION FROM MONSANTO CHEMICAL COMPANY,
INORGANIC RESEARCH DEPARTMENT, ST. LOUIS 66, MISSOURI

Nuclear Magnetic Resonance Studies of $P_2O_3Cl_2F_2$ and Its Reorganization Products

BY M. M. CRUTCHFIELD, C. F. CALLIS AND J. R. VAN WAZER

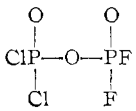
Received May 31, 1963

Preliminary P^{31} n.m.r. measurements made in our laboratory on a compound of empirical formula $P_2O_3Cl_2F_2$ identified it as the symmetrical compound diphosphoryl difluoride dichloride


$$\mathrm{Cl\overset{O}{\underset{F}{P}}{-}O{-}\overset{O}{\underset{F}{P}}Cl}$$

I

although details of spectral fine structure remained unexplained.[1] Subsequent heating in a sealed tube at 50° for several days led to the slow growth of reorganization products which were detected by the appearance of additional peaks in the 24.3 Mc. P^{31} spectrum. Under low resolution, the growth of an apparent 1:2:1 triplet with coupling constants appropriate for P–F bonds (*ca.* 1100 c.p.s.) suggested the formation of some of the asymmetrical isomer


$$\mathrm{Cl\overset{O}{\underset{Cl}{P}}{-}O{-}\overset{O}{\underset{F}{P}}F}$$

II

by halogen interchange.[2] The total spectrum was incompatible with the presence of a compound of this structure, however, since no additional P^{31} resonance peaks attributable to the chlorine-bonded phosphorus were observed and the separations of the apparent triplet peaks were not quite equal.

TABLE I

N.M.R. DATA FOR REORGANIZATION PRODUCTS OF $P_2O_3Cl_2F_2$

Fluorine spectra

	F^{19} chem. shift p.p.m. from CF_3COOH		P–F coupling $\lvert J_{P_1F_1}\rvert = \lvert J_{P_2F_2}\rvert$, c.p.s.		
Peaks	40.0 Mc.	24.3 Mc.	40.0 Mc.	24.3 Mc.	Assignment
A	−41.0	−41.8	1121	1123	$\mathrm{F\overset{O}{\underset{Cl}{P}}O}$— end groups
B	−70.2	−70.2	1172	1177	P(O)Cl_2F neso groups
C	−9.8	−10.1	1046	1060	$\mathrm{{-}O\overset{O}{\underset{F}{P}}O{-}}$ middle groups

Phosphorus spectra

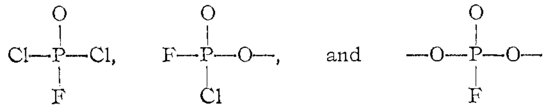
	P^{31} chem. shift p.p.m. from H_3PO_4		P–F coupling $\lvert J_{P_1F_1}\rvert = \lvert J_{P_2F_2}\rvert$, c.p.s.		
Peaks	24.3 Mc.	16.2 Mc.	24.3 Mc.	16.2 Mc.	Assignment
A	+19.0	+18.5	1116	1125	$\mathrm{F\overset{O}{\underset{Cl}{P}}O}$— end groups
B	−0.8	−1.7	1190	1175	P(O)Cl_2F neso groups
C	+44.0	+43.9	1057	1040	$\mathrm{{-}O\overset{O}{\underset{F}{P}}O{-}}$ middle groups

Average for all frequencies

	$\lvert J_{PF}\rvert$, c.p.s.	Std. dev., c.p.s.
A	1121	4
B	1179	8
C	1050	9

To resolve these apparent anomalies, additional P^{31} n.m.r. spectra have been taken at both 24.3 and 16.2 Mc., as well as F^{19} n.m.r. spectra at 40.0 and 24.3 Mc. Also, a double irradiation experiment[3] was performed in which the P^{31} spectrum was observed at 16.2 Mc., while simultaneously exciting the fluorine resonance at 37.6 Mc., in order to simplify the spin–spin interaction between phosphorus and fluorine.

The results of these experiments, summarized in Fig. 1 and Table I, demonstrate conclusively that the sealed tube reorganization of I at 50° (in the presence of possible catalytic traces of water) results not in fluorine redistribution but in the breaking of P–O–P bonds to form phosphoryl and polyphosphoryl halides containing, preferentially, one P–F bond per phosphorus. The P^{31} and F^{19} chemical shifts of the reorganization mixture at the four radiofrequencies can only be interpreted as arising from neso, end, and middle phosphoryl halide groups of the types


$$\mathrm{Cl{-}\overset{O}{\underset{F}{P}}{-}Cl,\quad F{-}\overset{O}{\underset{Cl}{P}}{-}O{-},\quad and\quad {-}O{-}\overset{O}{\underset{F}{P}}{-}O{-}}$$

respectively. If halogens are also undergoing positional exchange, the thermodynamics must be biased in favor of monofluoro substitution, since no trace of a signal from any –P(O)F_2 group could be detected in the phosphorus spectra. What previously appeared as an apparent large triplet in the 24.3 Mc. P^{31} spectrum

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[1] C. Stolzer and A. Simon, *Chem. Ber.*, **94**, 1976 (1961).

[2] L. C. D. Groenweghe and J. H. Payne, Jr., *J. Am. Chem. Soc.*, **81**, 6357 (1959).

[3] J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-resolution Nuclear Magnetic Resonance," McGraw-Hill Book Company, Inc., New York, N. Y., 1959, p. 160.

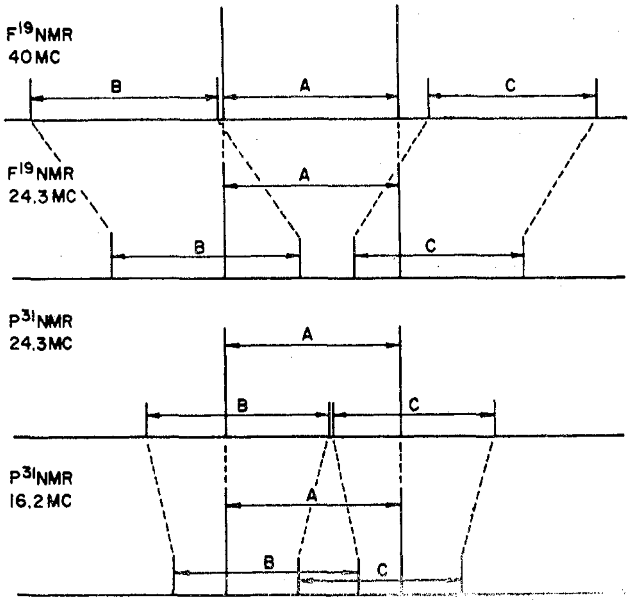
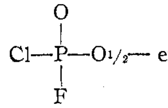
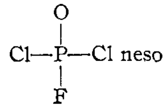
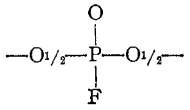


Fig. 1.—Schematic representation on a common frequency scale of n.m.r. spectra for reorganization products of $P_2O_3Cl_2F_2$.

A 
$\mathrm{Cl{-}\overset{O}{\underset{F}{P}}{-}O_{1/2}{-}}$ end groups

B 
$\mathrm{Cl{-}\overset{O}{\underset{F}{P}}{-}Cl}$ neso groups

C 
$\mathrm{{-}O_{1/2}{-}\overset{O}{\underset{F}{P}}{-}O_{1/2}{-}}$ middle groups

was due to the accidental overlap of two peaks from the doublets B and C shown in Fig. 1. This example re-emphasizes the need for caution in drawing structural conclusions based on n.m.r. measurements at a single radiofrequency.

Additional evidence is provided by the double resonance spectrum shown in Fig. 2. Here the three spin coupling doublets of the P^{31} spectrum at 16.2 Mc. have been decoupled[4] by simultaneous saturation of the fluorine resonances with a high radiofrequency power level at 37.6 Mc. The effect is that the three separate doublets each collapse into single peaks at the centers of the previous doublets. Since a slightly different decoupling frequency is required for each of the doublets, the spectrum in Fig. 2 does not represent a completely decoupled condition. By fine adjustment of the fluorine frequency it was possible, however, to satisfy the exact decoupling conditions for each of the three doublets in turn. From the data in Table I, it is apparent that as the number of oxygens bonded to phosphorus increases, the corresponding P^{31} and F^{19} chemical shifts both increase, while the absolute values of the strong P–F coupling constants, J_{PF}, decrease.

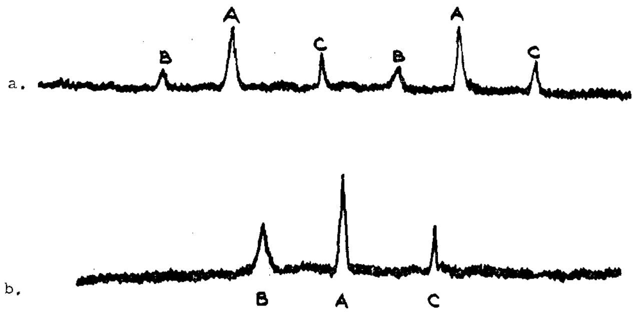


Fig. 2.—Phosphorus–fluorine decoupling mixture: a, normal P^{31} spectrum at 16.2 Mc.; b, decoupled P^{31} spectrum at 16.2 Mc., F irradiated at 37.6 Mc.

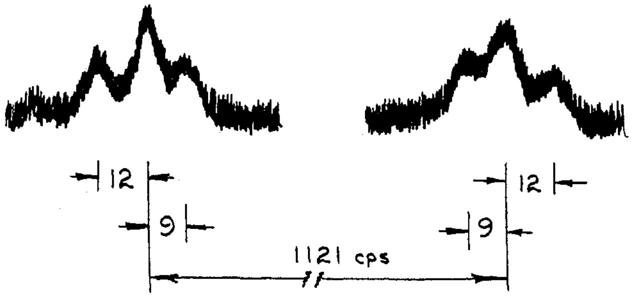
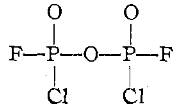


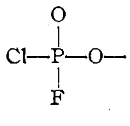
Fig. 3.—Asymmetrical fine structure on doublet peaks for


$\mathrm{F{-}\overset{O}{\underset{Cl}{P}}{-}O{-}\overset{O}{\underset{Cl}{P}}{-}F}$

in 24.3 Mc. P^{31} spectrum.

When examined under highest resolution, the individual peaks of the 24.3 Mc. P^{31} n.m.r. spectrum of pure I exhibit asymmetrical triplet fine structure as seen in Fig. 3. This is consistent with an A_2X_2 analysis[5] in terms of the following set of spin coupling constants: $|J_{P_1F_1}| = |J_{P_2F_2}| = 1121$ c.p.s., $|J_{P_1P_2}| = 21$ c.p.s., $|J_{P_1F_2}| = |J_{P_2F_1}| = 2$ c.p.s., 2 c.p.s. $> |J_{F_1F_2}| \geq 0$. The direction of the peak asymmetry requires that the constants $J_{P_1F_1} = J_{P_2F_2}$ be *opposite* in sign from $J_{P_1F_2} = J_{P_2F_1}$.

Although *dl* and *meso* diastereoisomers are to be expected for I, which contains two similarly substituted asymmetric phosphorus atoms, the nonbonding interactions are apparently of insufficient magnitude to produce observably different P^{31} chemical shifts for the *dl* and *meso* diastereoisomers. Such effects have been reported previously only for diastereoisomeric diphosphorus compounds containing a direct P–P bond.[6] The peaks shown in Fig. 3 changed into more complex multiplets with nonequivalent structure on heating at 50°. This was attributed to the superposition of new signals with slightly different chemical shifts arising from


$\mathrm{Cl{-}\overset{O}{\underset{F}{P}}{-}O{-}}$

end groups in longer chains.

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(4) W. A. Anderson, *Phys. Rev.*, **102**, 151 (1956).

(5) K. B. Wiberg and B. J. Nist, "The Interpretation of NMR Spectra," W. A. Benjamin, Inc., New York, N. Y., 1962, p. 309.

(6) L. Maier, *J. Inorg. Nucl. Chem.*, **24**, 275 (1962).

Peak intensity measurements were rather imprecise, but at equilibrium, the reorganization mixture consists of approximately 25% neso groups, 50% end groups, and 25% middle groups.

Experimental

Apparatus.—F^{19} and P^{31} n.m.r. measurements were made on a previously described spectrometer system[7] using a Varian Model V-4310 radiofrequency unit at 16.2 and 40.0 Mc. and a Model V-4311 radiofrequency unit at 24.3 Mc. Chemical shifts were measured with respect to CF_3COOH and 85% H_3PO_4 as reference standards using a tube interchange technique with audio sideband calibration of the field sweep. Upfield shifts are regarded as positive. Heteronuclear spin decoupling by double irradiation[2] was accomplished with a Varian spin decoupler, which provides a tunable excitation frequency at 37.6 Mc. for irradiation of F^{19} while one observes the P^{31} spectrum at 16.2 Mc. under low radiofrequency power.

Samples.—$P_2O_3Cl_2F_2$ was obtained as a pure liquid in a sealed test tube.[8] Preliminary examination by low-resolution P^{31} n.m.r. showed that it was better than 99% compound I. The tube was opened in a drybox and the sample transferred to a precision 5-mm. n.m.r. tube for examination under higher resolution. The sealed n.m.r. tube was then finally heated in a thermostated bath at 50° for several days to effect reorganization. Repeat measurements after 2 months assured that equilibrium had been reached.

Acknowledgment.—Messrs. J. T. Yoder and G. C. Roth assisted in making some of the n.m.r. measurements.

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[7] M. M. Crutchfield, C. F. Callis, R. R. Irani, and G. C. Roth, *Inorg. Chem.*, **1**, 813 (1962).

[8] The authors wish to thank Prof., Dr., Dr. Ing. E. h. A. Simon, Technische Hochschule, Dresden, for supplying us with an analyzed sample of $P_2O_3Cl_2F_2$. His average analytical data by two independent methods are as follows: *Anal.* Calcd.: P, 28.32; F, 17.36; Cl, 32.40; mol. wt., 218.9. Found: P, 28.76; F, 17.25; Cl, 32.29; mol. wt., 225 to 265.

CONTRIBUTION FROM THE ORGANICS DIVISION,
OLIN MATHIESON CHEMICAL CORPORATION,
NEW HAVEN, CONNECTICUT

Some Chemistry of Substituted Decaboranes

BY T. L. HEYING AND C. NAAR-COLIN

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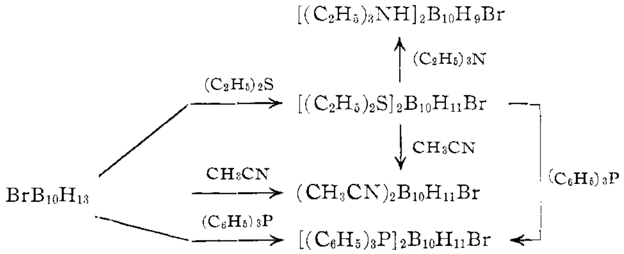
Although considerable chemistry of decaborane has been established, very few reports of reactions of substituted decaboranes have appeared. Therefore we conducted an investigation to determine whether some of the reactions characteristic of decaborane could be applied to its derivatives and to more thoroughly examine some reactions previously described. For example, numerous preparations[1] and reactions[2] of $B_{10}H_{12}$(ligand)$_2$ compounds have appeared but only recently has the first example of such a derivative of a substituted decaborane been reported[3]; we chose to prepare and study additional compounds of this type.

Acetonitrile reacted readily with 2-bromodecaborane[4] in refluxing benzene or excess nitrile to give bis(acetonitrile)-2-bromodecaborane. Due to its limited solubility in the more useful solvents, it was not practical to study its further reactions but the more useful bis(diethyl sulfide)-2-bromodecaborane also formed easily in benzene and had better solubility and infrared characteristics as well as a definitive melting point. A detailed ^{11}B n.m.r. study of this compound has been reported[3] and the same interpretation has been applied to all derivatives of this type herein described. Bis(triphenylphosphine)-2-bromodecaborane was also prepared by the spontaneous and rapid reaction of the phosphine with 2-bromodecaborane in ether.

The ligand displacement reaction in this series was demonstrated when bis(diethyl sulfide)-2-bromodecaborane was readily converted to the bis(triphenylphosphine) derivative on treatment with the phosphine at room temperature. On treatment with acetonitrile under the same conditions, bis(diethyl sulfide)-2-bromodecaborane was only slowly converted to the bis(acetonitrile) derivative. On the other hand, at room temperature in benzene, triethylamine reacted with bis(diethyl sulfide)-2-bromodecaborane to give bis(triethylammonium) bromononahydrodecaborate rather than the $B_{10}H_{11}Br$(ligand)$_2$ derivative. This would indicate that the $BrB_{10}H_{11}$ unit is more prone to rearrangement to the decaborate structure than the $B_{10}H_{12}$ unit, which does so only slowly in boiling benzene.[5] Other implications are discussed in more detail below.



Monoethyldecaborane[6] containing 60% 2-ethyldecaborane and 40% 1-ethyldecaborane was also readily converted to the analogous ligand derivatives. Mixed bis(triphenylphosphine)-1- and -2-ethyldecaborane was readily isolated and well defined but mixed bis(diethyl sulfide)-1- and -2-ethyldecaborane was slow to form and was an oil which would not crystallize, probably because of the mixed isomers. The ^{11}B n.m.r. spectrum readily indicated the structure and the mixture was efficiently converted to the mixed bis(triphenylphosphine) derivative by ligand displacement. Isomer distribution in the ligand derivatives similar to that of the starting mixed ethyldecaboranes was apparent from their ^{11}B n.m.r.

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[1] R. Schaeffer, *J. Am. Chem. Soc.*, **79**, 1006 (1957), as the original example.

[2] B. M. Graybill and M. F. Hawthorne, *ibid.*, **83**, 2673 (1961), and others.

[3] C. Naar-Colin and T. L. Heying, *Inorg. Chem.*, **2**, 659 (1963).

[4] R. Schaeffer, J. N. Shoolery, and R. Jones, *J. Am. Chem. Soc.*, **80**, 2670 (1958).

[5] M. F. Hawthorne and A. R. Pitochelli, *ibid.*, **81**, 5519 (1959).

[6] R. L. Williams, I. Dunstan, and N. J. Blay, *J. Chem. Soc.*, 430 (1960); E. R. Altwicker, A. B. Garrett, and E. A. Weilmuenster, U. S. Patent 2,999,117.