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UNIVERSITY OF ILLINOIS, URBANA, ILLINOIS

The Preparation and Properties of the Phenyl Phosphonitrilic Bromides[1]

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The reaction between phenylphosphorus(III) dibromide, bromine, and ammonium bromide in *sym*-tetrabromoethane yields the phosphonitrilic compounds $[NP(C_6H_5)Br]_{3 \text{ and } 4}$, together with a mixture of the higher oily homologs. Both *cis*- and *trans*-$[NP(C_6H_5)Br]_3$ are characterized in terms of their dipole moments, nuclear magnetic resonance spectra, infrared spectra, X-ray diffraction patterns, solubilities, chemical reactions, and properties of their reaction products. *cis–trans* Isomerism is also characteristic of a series of ammonolysis and aminolysis products of the trimeric phenyl phosphonitrilic bromides.

The possible synthesis of compounds of the type $[NP(Ar)X]_n$ (Ar = aryl) was first investigated by Bode and Bach,[2] who obtained the substance $N_3P_3(C_6H_5)_3(OH)_2Cl$ by heating a mixture of phenylphosphorus(V) tetrachloride and ammonium chloride in *sym*-tetrachloroethane and ultimately recrystallizing from dioxane. Shaw and Stratton[3] applied the same procedure to the synthesis of the trimer, $[NP(C_6H_5)Cl]_3$ (m.p. 188°), and three isomeric forms of the corresponding tetramer. Humiec and Bezman[4] used the same fundamental reaction to obtain trimeric phenylphosphonitrilic chloride (m.p. 161–163°) but only in low yields.

Although it was recognized that all of these compounds could exist in isomeric forms, no definitive proof for their configurations was offered. More recently, it has been shown,[5,6] however, that the mixed chlorobromophenyltriphosphonitriles obtained from the reaction of phenylphosphorus(III) dibromide with bromine and ammonium bromide in *sym*-tetrachloroethane yield *cis* and *trans* aminolysis products and that pure bromophenyltriphosphonitrile obtained by a similar preparative reaction in *sym*-tetrabromoethane exists as *cis* and *trans* isomers. This report is concerned with the more detailed chemistry of these interesting *geometrical* isomers.

The bromophenyltriphosphonitriles are obtained by the same general procedure as the phosphonitrilic bromides,[7] but with some modifications to obtain yields (*ca.* 30% of the trimer–tetramer mixture) that are comparable to the best reported for the simple bromides[7] or chlorides.[8,9] Unfortunately, the yields are seriously reduced as a consequence of the difficulties experienced in the separation of the desired cyclic compounds from the oily higher homologs and from the decomposition products of *sym*-tetrabromoethane. Optimum conditions, as determined by a systematic study of variables, involve reaction of approximately stoichiometric quantities of phenylphosphorus(III) dibromide and bromine with a large excess of ammonium bromide (1:8 mole ratio) at 168–170° for 6 days. The loss of bromine is negligible. Extraction of the reaction product with boiling *n*-heptane then removes the trimer and subsequent treatment of the residue with hot toluene removes the tetramer. Further separation techniques do not give the other homologs in states of purity. With *sym*-tetrachloroethane as the reaction medium, however, it is possible to obtain the reddish crystalline compound $NP(C_6H_5)BrP(C_6H_5)Br_4$ in large quantities. This resembles closely its completely brominated analog.[7]

Separation of *cis*-$N_3P_3(C_6H_5)_3Br_3$ from its *trans* isomer is readily effected by fractional crystallization from *n*-heptane. Although the solubilities of the two isomers are essentially identical at 25° (Table I), the *cis* compound crystallizes much more rapidly than the *trans* when a hot concentrated solution is cooled. Fractional crystallization of the tetrameric product from toluene gives no indication of the separation of stereoisomers. Instead, a product melting at 227–229° is recovered uniformly. It cannot yet be said with certainty that this is one of the various possible isomeric products or that it is a mixture of isomers.

Both dipole moment and phosphorus-31 nuclear magnetic resonance data indicate clearly that the bromophenyltriphosphonitrile melting at 194–195° has the *cis* configuration and that the isomer melting at 152–153° has the *trans* configuration. Dipole moments of 5.27 and 2.36 D. for the higher and lower melting compounds, respectively, are consistent with *cis*–

TABLE I

SOLUBILITY DATA FOR *cis*- AND *trans*-$N_3P_3(C_6H_5)_3Br_3$ AT 25°

Solvent	Solubility, g./100 g. of solvent *cis*	*trans*
Benzene	12.63	. . .
Diethyl ether	5.98	5.50
Carbon tetrachloride	4.75	8.83
Cyclohexane	1.46	2.59
Petroleum ether (90–110°)	0.58	. . .
n-Heptane	0.26	0.25

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[1] Ring Index nomenclature would require substitution of the term azaphosphorine for phosphonitrile, Thus the compound $N_3P_3(C_6H_5)_3Br_3$ could be named triphenyltribromotriazatriphosphorine rather than tribromotriphenyltriphosphonitrile, as has been done in this manuscript.

[2] H. Bode and H. Bach, *Ber.*, **75B**, 215 (1942).

[3] (a) R. A. Shaw and C. Stratton, *Chem. Ind.* (London), 52 (1959); (b) R. A. Shaw and C. Stratton, *J. Chem. Soc.*, 5004 (1962).

[4] F. S. Humiec and I. I. Bezman, *J. Am. Chem. Soc.*, **83**, 2210 (1961).

[5] T. Moeller and P. Nannelli, *Inorg. Chem.*, **1**, 721 (1962).

[6] T. Moeller and P. Nannelli, *ibid.*, **2**, 659 (1963).

[7] K. John and T. Moeller, *J. Inorg. Nucl. Chem.*, **22**, 199 (1961).

[8] L. G. Lund, N. L. Paddock, J. E. Proctor, and H. T. Searle, *J. Chem. Soc.*, 2542 (1960).

[9] M. L. Nielsen and G. Cranford, *Inorg. Syn.*, **6**, 94 (1960).

TABLE II

DIPOLE MOMENT DATA FOR *cis*- AND *trans*-$N_3P_3(C_6H_5)_3Br_3$ IN BENZENE AT 25°

Compound	α	β	γ	P_2, cm.^{3}	MR, cm.^{3}	μ, D.
cis-$N_3P_3(C_6H_5)_3Br_3$	5.333	−0.60	0.34	706.55	136.08	5.27
trans-$N_3P_3(C_6H_5)_3Br_3$	1.333	−0.60	0.34	250.38	136.08	2.36

trans isomerism (Table II). The existence of a single resonance peak at −16.4 p.p.m. for the higher melting compound, as opposed to two peaks at −20.1 and −18.0 p.p.m. for the other,[6] is another direct indication that the former compound is the *cis* isomer.

trans-$N_3P_3(C_6H_5)_3Br_3$, melting at 152–153°, can be converted to a second crystalline modification melting at 162–163° by careful crystallization from a dilute *n*-heptane solution. The lower melting of the two is a triclinic species, but difficulty in obtaining suitable crystals of the other modification has thus far precluded assignment of a definite crystal system. The triclinic form is obtained either by crystallization from more concentrated solutions in *n*-heptane or from acetonitrile. Only the triclinic crystals deposit from the latter solvent, irrespective of conditions. The infrared spectra of the two solids are identical (Table III), but their X-ray diffraction patterns are different (Table IV).

TABLE III

INFRARED SPECTRA OF $[NP(C_6H_5)Br]_{3,4}$ AND DERIVATIVES (NaCl REGION)

Compound	P–N frequency, cm.$^{-1}$	P–C_6H_5 frequency, cm.$^{-1}$	Medium
cis-$N_3P_3(C_6H_5)_3Br_3$	1180, 1126	1443	CCl_4
	1180, 1126	1444	KBr
trans-$N_3P_3(C_6H_5)_3Br_3$	1183, 1117	1443	CCl_4
	1180, 1117	1440	KBr
cis-$N_3P_3(C_6H_5)_3(NH_2)_3$	1180, 1126	1440	KBr
trans-$N_3P_3(C_6H_5)_3(NH_2)_3$	1180, 1120	1438	KBr
cis-$N_3P_3(C_6H_5)_3(NHCH_3)_3$	1185, 1125	1438	KBr
trans-$N_3P_3(C_6H_5)_3(NHCH_3)_3$	1185, 1122	1441	KBr
cis-$N_3P_3(C_6H_5)_3(NHC_2H_5)_3$	1175, 1122	1442	KBr
trans-$N_3P_3(C_6H_5)_3(NHC_2H_5)_3$	1180, 1117	1440	KBr
cis-$N_3P_3(C_6H_5)_3(NH\textit{n}-C_3H_7)_3$	1190, 1128	1442	CCl_4
trans-$N_3P_3(C_6H_5)_3(NH\textit{n}-C_3H_7)_3$	1190, 1120	1440	CCl_4
cis-$N_3P_3(C_6H_5)_3(NH\textit{n}-C_4H_9)_3$	1186, 1125	1440	CCl_4
trans-$N_3P_3(C_6H_5)_3(NH\textit{n}-C_4H_9)_3$	1185, 1123	1440	CCl_4
$N_4P_4(C_6H_5)_4Br_4$	1295	1443	KBr

Isomeric amido derivatives are readily obtained from *cis*- and *trans*-$N_3P_3(C_6H_5)_3Br_3$ by treating with an excess of liquid ammonia and extracting with ethyl acetate (for the *cis*) or benzene (for the *trans*). These compounds are purified by recrystallizing from the same solvents. Correspondingly, *n*-alkylamino derivatives are obtained by treating the isomeric bromides with an excess of the amine in benzene as a solvent,[10] evaporating, and recrystallizing from *n*-heptane. Both forms of the *n*-propylamino and *n*-butylamino derivatives were identical with those previously reported as aminolysis products of the chlorobromophenyltriphosphonitriles.[5]

Certain of the properties of the compounds prepared are summarized in Table V.

TABLE IV

X-RAY DIFFRACTION POWDER DATA (2*d* IN CM.)

	trans-$N_3P_3(C_6H_5)_3Br_3$	
cis-$N_3P_3(C_6H_5)_3Br_3$	M.p. 152–153°	M.p. 162–163°
1.99 w[a]	2.58 w	2.16 m
2.20 vw	2.92 s	2.56 s
2.51 s	3.26 w	2.90 s
2.79 s	3.54 vw	3.44 m
3.02 vw	4.08 vw	3.80 m
3.32 m	4.30 w	4.12 m
4.03 m	4.54 m	4.32 m
4.46 m	4.86 s	4.58 s
4.79 m	5.00 w	4.76 m
5.29 m	5.32 vw	5.10 s
5.61 m	5.62 m	5.24 w
6.24 m	5.92 m	5.44 w
6.62 vw	6.42 m	5.68 m
6.93 m	6.78 w	6.00 s
7.17 w	7.00 vw	6.28 s
7.42 m	7.30 w	6.60 m
7.90 w	7.50 vw	6.92 m
8.82 w	7.76 w	7.40 m
9.46 vw	8.38 w	7.60 m
9.84 w	8.88 w	7.80 m
10.34 w	9.14 vw	8.16 vw
	9.44 vw	8.40 w
	10.04 w	8.98 m
	10.78 w	9.56 w
	12.12 vw	9.92 w
	12.96 vw	10.70 m
	13.94 vw	11.12 w
		11.56 w
		11.94 m
		12.34 w

[a] vw, very weak; w, weak; m, medium; s, strong.

Experimental

Materials.—All chemicals were of the best quality commercially available. Bromine, phosphorus(III) bromide, phenylphosphorus(III) dichloride, ethyl acetate, and the various amines were used directly and without further treatment. Ammonium bromide was first ground to 100–150 mesh in a ball mill, then dried at 110° for 2 days and stored over phosphorus(V) oxide until used. *sym*-Tetrabromoethane was dried over phosphorus(V) oxide and distilled. Benzene, toluene, and *n*-heptane were dried with sodium. Acetonitrile was distilled twice from phosphorus(V) oxide. All solvents used for solubility studies were redistilled after drying. Benzene used for dipole moment measurements was dried with sodium, distilled from phosphorus(V) oxide, and redried with fresh sodium.

Analyses.—Microanalytical data were obtained by standard procedures. Trimeric and tetrameric compositions were established by infrared measurements and molecular weight determinations.

Solubility Measurements.—Saturated solutions were obtained by equilibration of excess solid with solvent for 2 days at 25 ± 0.02°. Solvent was removed from measured aliquots by vacuum evaporation and the residues weighed directly.

Instrumental Studies.—All infrared spectra were obtained with a Model 21 Perkin-Elmer spectrometer, using sodium chloride optics. The X-ray diffraction powder patterns were obtained with a Hayes unit using nickel-filtered Cu Kα radiation and a camera of 7.0-cm. radius. The crystal systems of the *cis*- and

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[10] K. John, T. Moeller, and L. F. Audrieth, *J. Am. Chem. Soc.*, **82**, 5616 (1960).

TABLE V

PROPERTIES OF $[NP(C_6H_5)Br]_{3,4}$ AND DERIVATIVES

Compound	M.p.,[a] °C.	Mol. wt.[b,c]	Analysis, %[c]				
			C	H	N	P	Br
$N_3P_3(C_6H_5)_3Br_3$		606	35.67	2.49	6.93	15.33	39.57
cis	194–195	622	35.74	2.53	6.87	15.30	39.59
trans	152–153; 162–163	621	35.92	2.58	6.94	15.25	39.31
$N_3P_3(C_6H_5)_3(NH_2)_3$			52.18	5.09	20.28	22.43	
cis	274		52.28	5.07	20.12	22.37	
trans	202–203		52.35	5.08	20.00	22.33	
$N_3P_3(C_6H_5)_3(NHCH_3)_3$			55.26	5.96	18.41	20.37	
cis	167		55.26	5.92	18.60	20.64	
trans	112–113[d]		55.14	6.01	18.28	20.10	
$N_3P_3(C_6H_5)_3(NHC_2H_5)_3$			57.82	6.67	16.86	18.64	
cis	126–127		57.82	6.63	16.92	18.38	
trans	91–92[d]		57.63	6.64	16.69	18.55	
$N_3P_3(C_6H_5)_3(NH\textit{n}\text{-}C_3H_7)_3$			59.98	7.27	15.54	17.19	
cis	128–129		59.95	7.10	15.35	17.02	
trans	92–93		60.01	7.36	15.63	17.03	
$N_3P_3(C_6H_5)_3(NH\textit{n}\text{-}C_4H_9)_3$			61.83	7.78	14.42	15.95	
cis	97–98		61.74	7.63	14.44	15.70	
trans	78–79		61.96	7.90	14.35	16.18	
$N_4P_4(C_6H_5)_4Br_4$		808	35.67	2.49	6.93	15.33	39.57
	227–229	803	35.59	2.47	6.98	15.09	39.75

[a] Uncorrected. [b] By vapor pressure lowering in benzene. [c] First line for each substance calculated, others found. [d] Fresh sample.

trans-tribromotriphenyltriphosphonitriles were established from single-crystal photographs obtained with a precession camera.

Dipole Moments.—Dielectric constants were measured with a heterodyne beat apparatus of conventional design.[11] Refractive indices were obtained with a differential refractometer at the 436 mμ line of mercury.[12] Specific volumes were measured with a 4.5-ml. Lippincott pycnometer. Weight fractions used were in the range 0.002–0.02. Dipole moments were then calculated according to the method of Halverstadt and Kumler.[13] No allowance was made for atom polarization.

Synthesis and Separation of Compounds.—Only typical syntheses are described. Parallel reactions were used for the preparation of related substances.

Phenylphosphorus(III) Dibromide, $P(C_6H_5)Br_2$.—Phenylphosphorus(III) dichloride (250 g.) and phosphorus(III) bromide (500 g.) were placed in a 500-ml., 3-necked flask equipped with a reflux condenser. The mixture was then treated with anhydrous hydrogen bromide for 24 hr. while being stirred magnetically and refluxed. The product was then distilled and the fraction boiling at 259–261° (lit.[14] 255–257°) collected as an oily, moisture-sensitive liquid; yield, *ca.* 300 g. (80%). Alternatively, collecting a fraction boiling at 85° (0.5 mm.) gave a yield of 330 g. (88%).

Anal. Calcd. for $P(C_6H_5)Br_2$: C, 26.89; H, 1.88; P, 11.56; Br, 59.61. Found: C, 26.94; H, 1.87; P, 11.77; Br, 59.62.

Bromophenylphosphonitriles, $[NP(C_6H_5)Br]_{3,4}$.—To a mixture of 450 g. (4.59 moles) of ammonium bromide and 150 g. (0.559 mole) of phenylphosphorus(III) dibromide in *ca.* 350 ml. of *sym*-tetrabromoethane, 90 g. (0.562 mole) of bromine dissolved in *ca.* 50 ml. of *sym*-tetrabromoethane was added slowly with vigorous stirring and cooling in an ice bath. The temperature was then raised over a 24-hr. period to 168–170° (oil bath temperature) and maintained in this range for 6 days. No further addition of bromine was necessary. After the system was cooled, the unreacted ammonium bromide was removed by filtration, washed with benzene, dried, and weighed. The quantity consumed was essentially theoretical. The solvent was removed from the filtered solution by distillation *in vacuo* at *ca.* 80–90° (oil bath temperature), and the black, oily residue produced was extracted with five *ca.* 300-ml. volumes of boiling *n*-heptane. When cooled, the heptane solutions deposited the crude crystalline product, together with an oily material that slowly solidified on standing under heptane. Purification was effected by repeated recrystallization from *n*-heptane, with charcoal added. A total of 27.1 g. (24%) of trimeric bromophenylphosphonitrile, *ca.* 60% of which was the *trans* isomer, was obtained.

The remaining reaction residue was treated with 300 ml. of hot toluene. Several recrystallizations from toluene of the product obtained when this solution was cooled gave 6.9 g. (6%) of the tetramer.

Separation of *cis*- and *trans*-$N_3P_3(C_6H_5)_3Br_3$.—This was effected by fractional crystallization from *n*-heptane. Hot, concentrated solutions of the mixture deposited the *cis* isomer first as beautiful, colorless, monoclinic crystals. The *trans* modification then separated both as colorless triclinic crystals melting at 152–153° and as crystals of an unidentified type melting at 162–163°. The latter modification was obtained preferentially from dilute solutions and was converted to the triclinic by recrystallization from more concentrated solutions in *n*-heptane or from any solution in acetonitrile. Recrystallization from acetonitrile may result in partial isomerization to the *cis* compound unless the initial substance is pure.

***cis*-Amidophenyltriphosphonitrile, $N_3P_3(C_6H_5)_3(NH_2)_3$.**—A 3.03-g. (0.005 mole) quantity of *cis*-$N_3P_3(C_6H_5)_3Br_3$ was treated with a large excess of liquid ammonia and the mixture was evaporated slowly while being stirred. The operation was then repeated twice. The solid residue was extracted with ethyl acetate in a Soxhlet apparatus and the product that crystallized from the extract was purified by recrystallization from the same solvent. The yield was 1.75 g. (87%).

***cis*-Methylaminophenyltriphosphonitrile, $N_3P_3(C_6H_5)_3(NHCH_3)_3$.**—To 3.03 g. (0.005 mole) of *cis*-$N_3P_3(C_6H_5)_3Br_3$ dissolved in 150 ml. of benzene, anhydrous methylamine was added *via* a gas inlet tube until no more reaction was observed. The reaction mixture was then stirred overnight. The precipitated methylamine hydrobromide was removed and the benzene evaporated. Recrystallization of the product from *n*-heptane gave 1.9 g. (83%) of the pure compound.

***trans*-*n*-Propylaminophenyltriphosphonitrile, $N_3P_3(C_6H_5)_3(NH\textit{n}\text{-}C_3H_7)_3$.**—To a solution of 2.95 g. (0.05 mole) of *n*-propylamine in *ca.* 50 ml. of benzene, 3.03 g. (0.005 mole) of *trans*-$N_3P_3(C_6H_5)_3Br_3$ dissolved in 100 ml. of benzene was added slowly with stirring. The mixture was refluxed for several hours and then filtered.

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(11) A. W. Cordes, Doctoral Dissertation, University of Illinois, 1960.

(12) B. A. Brice and M. Halver, *J. Opt. Soc. Am.*, **41**, 1033 (1951).

(13) I. F. Halverstadt and W. D. Kumler, *J. Am. Chem. Soc.*, **64**, 2988 (1942).

(14) G. M. Kosolapoff, "Organophosphorus Compounds," John Wiley and Sons, Inc., New York, N. Y., 1950, p. 49.

The clear solution was evaporated and the solid produced recrystallized from *n*-heptane. The pure product weighed 2.2 g. (81%).

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Some Characteristics of the Cyclic Trimeric Sulfanuric Chlorides

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The dipole moments in benzene solution of cyclic trimeric α- and β-sulfanuric chlorides are 3.88 and 1.91 D., respectively. Correlations of the dipole moments and infrared spectra support assignment of a second chair-type configuration to the β isomer. The β compound is converted rapidly to the α isomer in polar solvents such as acetonitrile and diethyl ether but is more stable in nonpolar media and stable in the solid state. Cleavage of the sulfur–nitrogen bond rather than substitution on the ring appears to characterize reactions of the α compound with solvolytic reagents.

Among the cyclic inorganic systems, those represented by the sulfanuric chlorides, although of considerable potential interest, have been only incompletely investigated. Except for data on the synthesis of the trimers[1–3] and on the structure of the α isomer,[4] essentially no information is available. Yet even formal analogies with other related cyclic systems (*e.g.*, the phosphonitrilic systems) suggest the importance of extensive investigations of isomerism and chemical reactivity.

The trimeric sulfanuric chlorides are best prepared by the thermal cleavage of trichlorophosphazosulfonyl chloride.[1] This procedure yields a mixture of configurational isomers, of which only the α and β forms are sufficiently stable to permit ready isolation. The pyrolytic decomposition is best effected at 118–120° under a pressure of 2.5–5 mm. with a slow purge of dry nitrogen[5] to remove liberated phosphorus(V) oxytrichloride. Separation of the α and β forms is effected by extracting the pyrolysis residue with boiling *n*-heptane and either fractionally crystallizing the resulting solution or evaporating it and fractionally subliming *in vacuo*. At least one additional isomer has been detected in admixture with the β form recovered by vacuum sublimation, but the ease with which it decomposes to a red oil in most solvents has thus far prevented its recovery in a state of purity. In the light of subsequent discussions, it is reasonable to assume that other isomers may also be present in the pyrolysis product.

The α isomer melts at 144–145°; the β isomer at 46–47°. α-Sulfanuric chloride is much less soluble in general than its β isomer (Table I). Each gives a characteristic X-ray powder diffraction pattern (Table II). Recent X-ray studies[4] have shown crystals of the α compound to be orthorhombic and to contain four molecules to the unit cell. The distribution of bonds about each sulfur atom is roughly tetrahedral, and the chlorine atoms are arranged axially. The ring is in a chair configuration.

TABLE I
SOLUBILITY DATA FOR α-$[NS(O)Cl]_3$ AT 25°[a]

Solvent	Solubility, g./100 g. of solvent
Benzene	22.50
Acetonitrile	13.15
Carbon disulfide	4.10
Carbon tetrachloride	2.95
Petroleum ether (90–110°)	2.32
Cyclohexane	1.63
n-Heptane	1.56

[a] β-$[NS(O)Cl]_3$ much more soluble in each solvent. Solubility too large to permit accurate measurement.

The α compound is stable with respect to conversion to any other isomer either in the solid state or in solution in any solvent that does not effect its chemical decomposition. The β compound is stable in the solid state and in nonpolar media such as cyclohexane or benzene. However, isomerization to the α compound is rapid in more polar solvents such as acetonitrile or diethyl ether. That this conversion involves an equilibrium in solution between the two forms is suggested by the changes with time of the infrared absorption spectrum of the β compound in acetonitrile. The infrared spectra of freshly prepared equimolar acetonitrile solutions of both isomers have absorption bands at 665, 700, and 820 cm.$^{-1}$, but intensities vary between the two. On standing, the spectrum of the α compound

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(1) A. V. Kirsanov, *J. Gen. Chem. USSR*, **22**, 93 (1952).

(2) M. Goehring, J. Heinke, H. Malz, and G. Roos, *Z. anorg. allgem. Chem.*, **273**, 200 (1953).

(3) M. Goehring and H. Malz, *Z. Naturforsch.*, **9b**, 567 (1954).

(4) (a) A. J. Banister and A. C. Hazell, *Proc. Chem. Soc.*, 282 (1962); (b) G. A. Wiegers and A. Vos, *ibid.*, 387 (1962).

(5) Kirsanov used dry air. Any dry, chemically inert gas may be used.