(11.4 barns/A H), which also possess a very low rotational barrier.[4,8] Moreover, recent theoretical calculations indicate that the cross-section slope for a methyl group freely rotating in one dimension is about 12,[9] again in agreement with the present results. The total cross-section technique is sensitive over a range of rotational barriers. For example, the slope for a methyl-group barrier of 1 kcal/mole is about 9 barns/A H.[4,6,9] From these comparisons, it appears certain that the methyl groups in $(CH_3)_2SnF_2$ are essentially freely rotating, with a barrier to rotation less than a few tenths of 1 kcal.

It would be interesting to extend these measurements to compounds with other than octahedral coordination, as well as to similar trimethyl compounds in which the methyl-group barrier might be considerably greater.

Acknowledgment.—The authors are indebted to P. S. Leung for performing the neutron transmission measurements on the Columbia spectrometer.

[9] P. S. Leung, J. J. Rush, and T. I. Taylor, unpublished work.

CONTRIBUTION FROM THE OLIN MATHIESON
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Reactions of Phosphonitrilic Chloride with *p*-Nitrophenol

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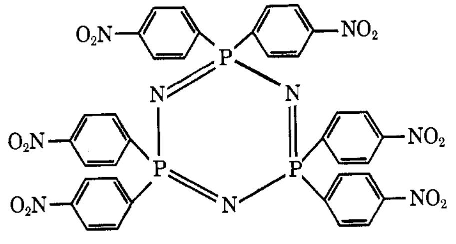
As reported by Brown,[1] attempts to synthesize nitrophenoxy-substituted phosphonitrilic chlorides by the reaction of trimeric phosphonitrilic chloride with sodium nitrophenoxides, prepared from nitrophenols and sodium, in a molar ratio of approximately 1:3 in boiling toluene failed to give any defined compound.



I

In search for hexakis(*p*-nitrophenoxy)phosphonitrile (I) we investigated the reaction of trimeric phosphonitrilic chloride with sodium *p*-nitrophenoxide in a 1:6 molar ratio. As did Brown, we obtained a dark brown, resinous reaction product from which small amounts of 2-chloro-2,4,4,6,6-pentakis(*p*-nitrophenoxy)-phosphonitrile (II) and 2,4,6-trichloro-2,4,6-tris(*p*-nitrophenoxy)phosphonitrile (III) were isolated after several extractions and recrystallizations. Structure III is supported by nuclear magnetic resonance spectroscopy. The proton-irradiated ^{31}P spectrum shows only one singlet at 17.4 ppm and, hence, indicates three equivalent phosphorus atoms. All efforts to isolate—besides II and III—the other yet unknown chloro(*p*-nitrophenoxy)phosphonitriles as well as compound I were futile. Attempts to synthesize tetrachlorobis(*p*-nitrophenoxy)phosphonitrile (IV) from 1 mole of $(PNCl_2)_3$ and 2 moles each of the phenol and triethylamine in refluxing toluene did not result in IV, but in substantial quantities of pure 2,4,4,6,6-pentachloro-2-(*p*-nitrophenoxy)phosphonitrile (V). Also isolated was a trace quantity of octakis(*p*-nitrophenoxy)-phosphonitrile (VI). Its formation was traced back to a small amount of $(PNCl_2)_4$ present in the starting material. The isolation of VI was facilitated by its low solubility in toluene and ether. Whereas the reaction of trimeric phosphonitrilic chloride with sodium *p*-nitrophenoxide had not afforded any amount of I, the corresponding reaction with the tetramer gave VI in 79% yield. Eventually, the trimeric compound I was obtained in 87% yield by reaction of $(PNCl_2)_3$ with excessive amounts of *p*-nitrophenol and potassium hydroxide in boiling xylene. Surprisingly, the melting point of 263–264°, recorded for the product obtained by this procedure, does not correspond with that of 212–214° found by Yokoyama,[2] who reported the preparation of I from $(PNCl_2)_3$ and sodium *p*-nitrophenoxide in undisclosed but apparently low yield.

Experimental Section

Melting points were determined in a modified Thiele Apparatus and are not corrected. The ^{31}P spectrum was obtained at 19.3 MHz with a Varian HR Type nmr spectrometer. Irradiation of H was done with an NMR Specialties HD-60 spin decoupler. The chemical shift was measured by the side-band technique relative to external 85% phosphoric acid. Melting points and results of the elemental analyses are compiled in Table I.

2,2,4,4,6,6-Hexakis(*p*-nitrophenoxy)phosphonitrile (I).—A mixture consisting of 209 g (1.5 moles) of *p*-nitrophenol, 94 g of potassium hydroxide, and 1000 ml of xylene was slowly heated with stirring to 80°. At this temperature, 70 g (0.2 mole) of $(PNCl_2)_3$ dissolved in 250 ml of xylene was added dropwise over a period of 1 hr. The mixture was then refluxed until 35 ml of water had collected in a Stark and Dean distilling trap (*ca.* 28 hr). The yellow precipitate was separated and washed with warm 10% aqueous potassium hydroxide and finally with water. Recrystallization of the dried solid from dimethylformamide and thereafter from cyclohexanone afforded 166 g of pure I.

2,2,4,4,6,6,8,8-Octakis(*p*-nitrophenoxy)phosphonitrile (VI).—To a stirred suspension of 36 g (1.5 moles) of sodium hydride in 250 ml of ether was added a solution of 209 g (1.5 moles) of *p*-nitrophenol in 350 ml of ether at such a rate that gentle refluxing resulted. The ether solvent was then replaced by 800 ml of xylene, and a solution of 70 g (0.15 mole) of $(PNCl_2)_4$ in 400 ml of xylene was added. After refluxing for 27 hr, the mixture was worked up as described for I. Recrystallization from dimethylformamide rendered 152 g of pure VI.

2,4,4,6,6-Pentachloro-2-(*p*-nitrophenoxy)phosphonitrile (V).—Solutions of 139.1 g (1 mole) of *p*-nitrophenol in 500 ml of toluene and 101.2 g (1 mole) of triethylamine in 500 ml of toluene were added dropwise and simultaneously to a boiling mixture of 173.8

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[1] C. J. Brown, *J. Polymer Sci.*, **5**, 465 (1950); see also D. Lipkin, U. S. Patent 2,192,921 (March 12, 1940).

[2] M. Yokoyama, *Nippon Kagaku Zasshi*, **81**, 481 (1960); *Chem. Abstr.*, **56**, 502 (1962).

TABLE I

p-NITROPHENOXY-SUBSTITUTED PHOSPHONITRILES

		Mp, °C	Yield, %	% calcd					% found					Mol wt	
				C	H	Cl	N	P	C	H	Cl	N	P	Calcd	Found
I	$(PN)_3(p\text{-}NO_2\cdot C_6H_4O)_6$	263–264	87	44.87	2.51	...	13.08	9.64	45.06	2.61	...	13.21	9.45	963.6	
II	$(PN)_3Cl(p\text{-}NO_2\cdot C_6H_4O)_5$	183–184	~0.7	41.80	2.35	...	13.02	10.80	41.97	2.50	...	13.11	10.90	861.0	
III	$(PN)_3Cl_3(p\text{-}NO_2\cdot C_6H_4O)_3$	225–226	~1.0	32.95	1.83	...	12.80	14.18	32.72	1.88	...	12.99	14.36	655.8	
V	$(PN)_3Cl_5\text{-}p\text{-}NO_2\cdot C_6H_4O$	95–97	17	16.00	0.90	39.36	12.44	20.64	16.20	0.89	39.40	12.54	20.48	450.6	
VI	$(PN)_4(p\text{-}NO_2\cdot C_6H_4O)_8$	299–301	79	44.87	2.51	...	13.08	9.64	45.09	2.31	...	13.10	9.54	1284	1275

g (0.5 mole) of $(PNCl_2)_3$ in 500 ml of toluene. After refluxing for 7 hr, the white precipitate was separated by filtration, and the filtrate was freed from solvent and fractionated. Compound V distilled at about 165° (0.02 mm). It was further purified by recrystallization from *n*-heptane to yield 38.3 g of pure V.

The filter cake—mostly triethylamine hydrochloride—was dissolved in water, and the insoluble portion was separated and dried. Recrystallization from dimethylformamide gave 12.8 g of pure VI.

2-Chloro-2,4,4,6,6-pentakis(*p*-nitrophenoxy)phosphonitrile (II) and 2,4,6-Trichloro-2,4,6-tris(*p*-nitrophenoxy)phosphonitrile (III).—An amount of 483.3 g (3.0 moles) of sodium *p*-nitrophenoxide was stirred in 1500 ml of refluxing xylene, and 138.9 g (0.40 mole) of trimeric phosphonitrilic chloride dissolved in 400 ml of xylene was added dropwise. Refluxing was continued for 31.5 hr after addition of the chloride was completed. The cooled product was washed with water. Removal of the xylene *in vacuo* rendered 183 g of a dark brown resinous material. This product was dissolved in 600 ml of warm toluene. A small amount of an undissolved white solid, mp 220–238°, was filtered off. The filtrate was concentrated to approximately half of its original volume. The concentrate deposited a small amount of solid, mp 177–216°, upon standing for 3 days. This product was recrystallized twice from toluene, once from 50% toluene–chloroform, and finally from toulene to give 2.1 g of pure II.

Small amounts of solids remained undissolved in each recrystallization of II. These were combined with the material melting at 220–238° and recrystallized from chloroform, in the presence of activated carbon, to give 2.9 g of pure III.

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Correspondence

The Role of ν(C–N) as Evidence for the Mode of Binding of Amides to Lewis Acids

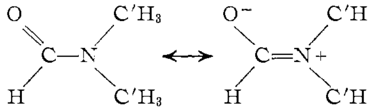
Sir:

While investigating the action of Lewis bases on the esterification of halides of elements in group IV,[1] we became interested in the application of evidence from infrared spectroscopy to the problem of determining whether, in amide adducts, the amide is coordinated through oxygen or nitrogen.

Nmr studies of amides show conclusively that the carbonyl oxygen is the stronger base toward the proton[2] and toward boron trichloride,[3] and a crystallographic study of formamide and acetamide complexes with bivalent metal ions has shown that the amide is bonded to the metal through oxygen.[4,5]

Apart from the studies mentioned above, other cases to be found in the literature are argued from infrared evidence, using ideas first put forward by Penland, Mizushima, Curran, and Quagliano in their definitive study of metal urea complexes.[6] Invariably the group frequency approximation has been applied. These ideas have found their way into a recently published textbook.[7] It is pointed out in the first part of the argument that the formation of oxygen-to-metal bonds will be accompanied by a decreased bond order for the carbonyl group and that this will result in a shift of the carbonyl stretching vibration (amide I band) to lower frequencies. This is found to be the case when complexes are formed by simple aldehydes and ketones,[8] and similar arguments have been put forward for coordination through oxygen in ligands containing the M–O group where M = S, P, As, or N.[9]

The second part of the argument relies on simple valence bond considerations, as illustrated in eq 1, to



I II (1)

dictate that the formation of the oxygen-to-metal bond will be accompanied by an increase in the order of the amide C—N bond and that this will result in a shift of ν(C—N) to higher frequencies. The test of the mode of binding of amides is then straightforward: a shift of ν(C═O) to lower frequencies and of ν(C—N)

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(4) M. Nardelli, *Gazz. Chim. Ital.*, **89**, 1616 (1959).

(5) The analogous thioacetamide complexes apparently bind likewise through the sulfur atom: L. Cavalca, M. Nardelli, and A. Braibanti, *ibid.*, **86**, 942 (1956).

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(7) R. S. Drago, "Physical Methods in Inorganic Chemistry," Reinhold Publishing Corp., New York, N. Y., 1965, pp 230, 231.

(8) L. J. Bellamy and R. F. Branch, *J. Chem. Soc.*, 4491 (1954).

(9) (a) J. Selbin, W. E. Bull, and L. H. Holmes, *J. Inorg. Nucl. Chem.*, **16**, 219 (1961); (b) F. A. Cotton, R. D. Barnes, E. Barnes, and E. Bannister, *J. Chem. Soc.*, 2199 (1960); (c) S. Horner and S. Y. Tyree, Jr., *Inorg. Chem.*, **1**, 122 (1962); (d) J. V. Quagliano, T. Fujita, G. Franz, D. J. Phillips, J. A. Walmsby, and S. Y. Tyree, Jr., *J. Am. Chem. Soc.*, **83**, 3770 (1961).