CONTRIBUTION FROM THE MELLON INSTITUTE,
PITTSBURGH, PENNSYLVANIA 15213

Phenoxylation and Aminolysis of Diphenyltetrachlorotriphosphonitrile. The Use of Nuclear Magnetic Resonance for Structural Determination

BY C. T. FORD, JEAN M. BARR, F. E. DICKSON, AND I. I. BEZMAN

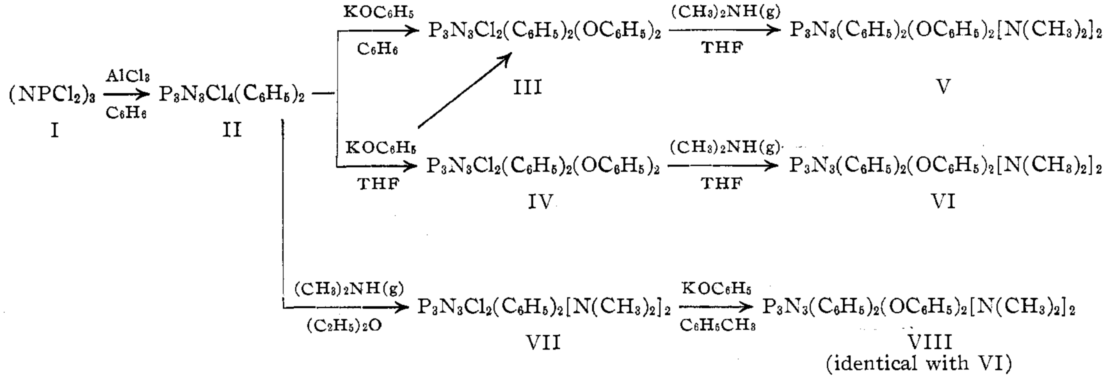
Received August 23, 1965

Treatment of $P_3N_3Cl_4(C_6H_5)_2$ with restricted amounts of phenol has given two of the three possible isomeric $P_3N_3Cl_2(C_6H_5)_2(OC_6H_5)_2$ derivatives. Both P^{31} nmr spectra of these compounds and H^1 nmr spectra of their $-[N(CH_3)_2]$ and $-(NHCH_3)$ derivatives show that the $-OC_6H_5$ groups in each compound are attached to separate phosphorus atoms.

We have previously[1,2] demonstrated that proton magnetic resonance spectra can be used to determine both positional and *cis–trans* configurations of various N,N′-dimethylamino- and N-methylaminotriphosphonitriles. We have also applied this procedure[3] to delineation of the substitution pattern in the formation of phenoxy esters of $(NPCl_2)_3$ (I) and found it to be nongeminal.

As part of a general study of functionality reduction of I by replacement of four of the six chlorine atoms by nonreactive or less reactive groups, we have synthesized dichlorodiphenyldiphenoxytriphosphonitrile, $P_3N_3Cl_2(C_6H_5)_2(OC_6H_5)_2$, and obtained it in two isomeric forms, III and IV. P^{31} nmr spectra of III and IV and H^1 nmr spectra of their N,N′-dimethylamino derivatives, $P_3N_3(C_6H_5)_2(OC_6H_5)_2[N(CH_3)_2]_2$, V and VI, showed that partial phenoxylation of diphenyltetrachlorotriphosphonitrile, $P_3N_3Cl_4(C_6H_5)_2$ (II), takes place nongeminally and that compounds III and IV are *cis* and *trans* isomers. The data did not indicate which was *cis* or *trans*. Further confirmation of the structure of IV was obtained by phenoxylation of dichlorodiphenyldi-N,N′-dimethylaminotriphosphonitrile, $P_3N_3Cl_2(C_6H_5)_2[N(CH_3)_2]_2$ (VII), in which it had been previously established[2a] that the chlorine atoms are attached to separate phosphorus atoms. The product of this reaction was compound VIII. A summary of the reactions is given in Scheme I.

SCHEME I



Experimental Section

Benzene, toluene, diethyl ether, petroleum ether (bp 30–60°), and *n*-hexane were dried over freshly extruded sodium wire. Tetrahydrofuran (THF) was dried overnight over molecular sieves 4A. Reagent grade phenol and KOH were used as received. Trimeric phosphonitrilic chloride (I) was obtained commercially and recrystallized to constant melting point from petroleum ether before use. Molecular weights were determined cryoscopically in benzene. Melting points were taken in capillary tubes and are uncorrected.

$P_3N_3Cl_4(C_6H_5)_2$ (II).—This compound was prepared by refluxing I in benzene in the presence of 4 moles of $AlCl_3$ per mole of I and purifying the product as described previously.[2a]

$P_3N_3Cl_2(C_6H_5)_2(OC_6H_5)_2$ (III and IV).—The isomeric products were made by allowing potassium phenoxide and II to react in a 2:1 mole ratio. The KOC_6H_5 was formed by the reaction of KOH pellets and phenol *in situ*. When the phenoxylation of II was effected in THF solution, both III and IV were obtained; when a hydrocarbon solvent, benzene or toluene, was used, only III could be isolated from the reaction mixture. Following are procedures for each solvent.

(A) **In THF.**—Potassium phenoxide was prepared by refluxing for 1 hr a mixture of 25.4 g (0.45 mole) of KOH and 42.6 g (0.45 mole) of phenol in 1150 ml of THF. To this at room temperature was added, over a period of 5 min, a solution of 97.6 g (0.23 mole) of II in 250 ml of THF. The resulting pale yellow heterogeneous reaction mixture was stirred for about 1 hr at room temperature, heated slowly to reflux, maintained there for 4.5 hr, and then cooled. The insoluble KCl by-product was removed by filtration, and the filtrate was concentrated by distillation. Addition of 500 ml of benzene followed by fractional distillation resulted in removal of residual THF. The benzene solution was washed with 0.5 *N* NaOH and distilled water, dried, and concentrated to approximately 250 ml. To this solution was added 750 ml of petroleum ether, and the mixture was allowed to stand several days at room temperature, giving 22.2 g of a white crystalline product, mp 97–136°. Re-

---

(1) I. I. Bezman and C. T. Ford, *Chem. Ind.* (London), 163 (1963).

(2) (a) C. T. Ford, F. E. Dickson, and I. I. Bezman, *Inorg. Chem.*, **3**, 177 (1964); (b) *ibid.*, **4**, 890 (1965).

(3) C. T. Ford, F. E. Dickson, and I. I. Bezman, *ibid.*, **4**, 419 (1965).

crystallization from *n*-hexane gave, as a first crystalline crop, 11.0 g (8.9% yield) of III, mp 143°.

Concentration of the residual hexane solution gave several subsequent fractions of crystalline material, all melting within the temperature range 98–103° and constituting a total weight of 8.1 g.

From the original benzene–petroleum ether filtrate was obtained 95.3 g of solid material. This was dissolved in 600 ml of *n*-hexane at reflux, and the solution was concentrated gradually to give several fractions, the first of which, 34.3 g, melted at 98–103°. Combination of this with the previously isolated 8.1 g of product melting within the same range gave a total weight of 42.3 g (34.1% yield) of crude IV, mp 98–103°. Two recrystallizations from *n*-hexane gave 18.8 g (15.2% yield) of IV, mp 104°.

Anal. Calcd. for $C_{24}H_{20}O_2Cl_2N_3P_3$: C, 52.76; H, 3.69; Cl, 12.98; N, 7.69; P, 17.01; mol wt, 546. Found (compound III, mp 143°): C, 52.97; H, 3.91; Cl, 12.91; N, 7.58; P, 17.13; mol wt, 514; (compound IV, mp 104°): C, 52.98; H, 3.85; Cl, 12.73; N, 7.49; P, 17.19; mol wt, 521.

(B) **In Benzene.**—A mixture of 43.1 g (0.10 mole) of II, 11.2 g (0.20 mole) of KOH, and 19.5 g (0.21 mole) of phenol was refluxed for 17 hr in 500 ml of C_6H_6. Water was azeotroped from the mixture and collected in a Dean–Stark trap. The reaction mixture was washed twice with equal amounts of 5% aqueous KOH, twice with distilled water, and dried overnight over $CaSO_4$. After removing the $CaSO_4$ by filtration, the filtrate was evaporated to dryness, leaving an oil which crystallized slowly from a diethyl ether–petroleum ether solution. Compound III, mp 143°, was obtained in 25% yield. A melting point of a mixture of this product and a sample of III prepared by the THF reaction (above) showed no depression. The infrared spectra of both of these materials were superimposable. No trace was found of compound IV. When toluene was used as solvent, or reflux time was doubled, or the reaction was scaled up significantly, the yield of III decreased to 10% or less, again with no IV obtained.

$P_3N_3(C_6H_5)_2(OC_6H_5)_2[N(CH_3)_2]_2$ (V).—Gaseous $(CH_3)_2NH$ was bubbled slowly into a 2% solution of III in THF at reflux for 48 hr. After cooling, the by-product $(CH_3)_2NH \cdot HCl$ was removed by filtration and the filtrate was evaporated to dryness, leaving an oily residue. This was dissolved in a mixture of $(C_2H_5)_2O$ and *n*-hexane and crystallization took place after 3 days. The product was recrystallized from the same solvent mixture to give V in 35% yield, mp 96°. *Anal.* Calcd for $C_{28}H_{32}O_2N_5P_3$: Cl, 0; N, 12.43; mol wt, 564. Found: Cl, 0.23; N, 12.30; mol wt, 556.

$P_3N_3(C_6H_5)_2(OC_6H_5)_2[N(CH_3)_2]_2$ (VI).—Gaseous $(CH_3)_2NH$ was bubbled slowly into a 2% solution of IV for 5 hr. After cooling, the by-product $(CH_3)_2NH \cdot HCl$ was removed by filtration and the filtrate was evaporated to dryness. The residue was crystallized and recrystallized from $(C_2H_5)_2O$ to give VI in 90% yield, mp 108°. *Anal.* Calcd for $C_{28}H_{32}O_2N_5P_3$: C, 59.68; H, 5.72; Cl, 0; N, 12.43; P, 16.49; mol wt, 564. Found: C, 59.80; H, 5.74; Cl, 0.04; N, 12.24; P, 16.65; mol wt, 532.

$P_3N_3(C_6H_5)_2(OC_6H_5)_2[N(CH_3)_2]_2$ (VIII).—A mixture of 16.0 g (0.036 mole) of VII, 4.7 g (0.084 mole) of KOH, and 7.8 g (0.083 mole) of phenol in 250 ml of toluene was maintained at reflux for 7 days. Water was azeotroped from the mixture and collected in a Dean–Stark trap. The reaction mixture was washed twice with equal amounts of 5% aqueous KOH, twice with distilled water, and dried overnight over $CaSO_4$. After removing the $CaSO_4$ by filtration, the filtrate was evaporated to dryness, leaving an oily residue which crystallized from $(C_2H_5)_2O$ over a period of several days. Recrystallization from the same solvent gave VIII in 30% yield, mp 108°. *Anal.* Calcd for $C_{28}H_{32}O_2N_5P_3$: C, 59.68; H, 5.72; N, 12.43; P, 16.49. Found: C, 59.95; H, 5.81; N, 12.28; P, 16.61. The melting point of a mixture of VI and VIII showed no depression and their infrared spectra were superimposable.

P^{31} nmr spectra were obtained for compounds III and IV on a Varian HR 100 spectrometer system operating at 40.5 Mc/sec. External trimethyl phosphite was used for calibration, employing a Hewlit-Packard Model 200CD oscillator and Model 524C counter for side-band generation and frequency counting. Chemical shifts are expressed relative to 85% H_3PO_4. Proton nmr spectra were obtained for compounds V, VI, and VIII on a Varian A-60 nmr spectrometer system operating at 60 Mc/sec with tetramethylsilane employed as an internal reference. All samples were prepared as 20% solutions (w/v) in $CDCl_3$.

Discussion

Because both phenyl groups in II are known to be attached to the same phosphorus atom[2b] and the P–N ring is planar[4,5] with the chlorine atoms lying above and below the plane of the ring, replacement of two of the four chlorine atoms by phenoxy groups can give the compound $P_3N_3Cl_2(C_6H_5)_2(OC_6H_5)_2$ in three isomeric forms. In one of these, both phenoxy groups are attached to the same phosphorus atom; in each of the others the phenoxy groups are attached to separate phosphorus atoms, the difference between them being *cis* and *trans* configurations.

As indicated above, when phenoxylation was carried out in benzene, only one isomer (III) was isolated in crystalline form; in THF, two isomers (III and IV) were obtained. These reactions were repeated several times with the same results. Additionally, we have carried out partial phenoxylation of a tetrameric phosphonitrile and also obtained only one isomer when a hydrocarbon solvent was used, but two isomers with THF. It should be noted that in benzene or toluene, by-product water is azeotroped out of the system as the KOC_6H_5 forms. In THF, the water remains in the system throughout the reaction. Further, KOC_6H_5 is substantially insoluble in hydrocarbon solvents but was completely soluble in refluxing THF at the concentrations used.

No reason can be offered for the difference in results as related to reaction medium. However, it should be noted that phosphonitrilic esters, particularly when not all the chlorine atoms are replaced by –OR groups, often are formed as oils, and isolation of crystalline products may be difficult. The initial oily products are formed in high yield and, after isolation of as much crystalline material as possible, the residual oils appear to have substantially the same composition as the former as indicated by chemical analysis and infrared spectra. In some cases, storage of the residual oils at room temperature or below for long periods of time (as much as a year) has given more crystalline product.

The P^{31} nmr spectra of III and IV are identical and, as shown in Figure 1, consist of a doublet and a second, broad, diffuse absorption, indicating the presence of only two phosphorus environments. If both phenoxy groups were attached to the same phosphorus atom in either III or IV, the P^{31} nmr spectra would be dissimilar, and, in fact, one of these would indicate the presence of three P^{31} environments, *i.e.*, $\equiv P(C_6H_5)_2$, $\equiv PCl_2$, and $\equiv P(OC_6H_5)_2$. The spectra are, however, consistent with the interpretation that the doublet

---

(4) A. Wilson and D. F. Carroll, *Chem. Ind.* (London), 1558 (1958).

(5) F. Pompa and A. Ripamonti, *Ric. Sci.*, **29**, 1516 (1959).

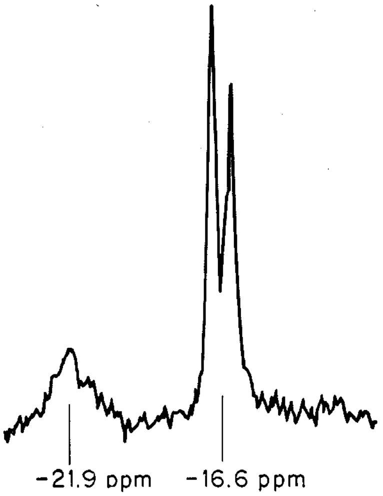


Figure 1.—P^{31} nmr spectrum of $P_3N_3Cl_2(C_6H_5)_2(OC_6H_5)_2$.

represents two identical phosphorus atoms, $\equiv P(Cl)(OC_6H_5)$, and the broad absorption represents the $\equiv P(C_6H_5)_2$ grouping. The broad absorption should theoretically be a triplet but in actuality is typically broadened by coupling to the protons of the adjacent phenyl rings. Further confirmation of the above interpretation is given by the fact that the integrated area of the doublet is twice that of the broad diffuse absorption.

Further indication of the structures of III and IV came from the H^1 spectra of their $-N(CH_3)_2$ derivatives, V and VI. The spectra were almost identical, each consisting of a doublet broadened by long-range phosphorus coupling.[6,7] The apparent[2a] coupling constants, J'_{PH}, and chemical shifts (from TMS) obtained from the spectra were 12.5 cps, 2.74 ppm and 12.4 cps, 2.52 ppm for V and VI, respectively. We have previously shown[3] that, in cyclic triphosphonitriles, the $\equiv P(OC_6H_5)[N(CH_3)_2]$ structure has a J'_{PH} value of 12.5 ± 0.3 cps. The agreement of the observed J'_{PH} values for V and VI with this is taken as evidence that the phenoxy groups are each in a $\equiv P(OC_6H_5)[N(CH_3)_2]$ grouping and, therefore, are attached to separate phosphorus atoms. We have also shown previously[2a] that J'_{PH} for the $\equiv P[N(CH_3)_2]_2$ grouping is only approximately 11.8 cps, further evidence contradicting this structure for V or VI.

Finally, additional confirmation of the structure of VI was afforded by isolation of VIII by phenoxylation of VII and finding, as indicated in the Experimental Section, that VI and VIII were identical. Compound VII was reported previously[2a] to be a mixture of *cis* and *trans* isomers of the structure in which the $-N(CH_3)_2$ groups are attached to separate phosphorus atoms also carrying chlorine atoms. Thus, unless there are unusual group migrations during phenoxylation, the phenoxy groups in VI must be attached to separate phosphorus atoms. It was surprising to find that, despite the fact that VII was a mixture of *cis* and *trans* isomers, only VIII could be obtained in crystalline form from the phenoxylation product.

Some efforts were also made to establish the structures of III and IV by degradative hydrolysis. Isolation of either phenyl or diphenyl phosphate, together with diphenylphosphinic acid from the $\equiv P(C_6H_5)_2$ group, would have been pertinent in determining the location of the phenoxy groups. However, the conditions employed (heating the compounds with an excess of aqueous HCl in sealed tubes at 155–200° for 24–48 hr) gave only the diphenylphosphinic acid. A strong odor of phenol was noted when the tubes were opened, indicating probable concurrent hydrolysis of the phenyl phosphate.

By treatment of III and IV with CH_3NH_2 and processing as for the N,N′-dimethylamino derivatives, V and VI, the corresponding N-methylamino compounds $P_3N_3(C_6H_5)_2(OC_6H_5)_2(NHCH_3)_2$ (IX and X) were obtained from III and IV, respectively. Chemical analyses were in accord with calculated values for both compounds; IX, mp 162°, was obtained in 10% yield; X, mp 140°, was obtained in 60% yield. The H^1 nmr spectra were substantially the same as for compounds V and VI; apparent coupling constants and chemical shifts obtained from the spectra were 13.3 cps, 2.67 ppm for IX and 13.2 cps, 2.47 ppm for X. Thus, a $\equiv P(OC_6H_5)(NHCH_3)$ grouping in a cyclic triphosphonitrile is characterized by $J'_{PH} = 13.3$ cps. It is interesting to note that for both pairs of *cis–trans* isomers, V and VI as well as IX and X, the difference in chemical shift between *cis* and *trans* configurations is the same, 0.2 ppm.

Some difference in reactivity of the chlorine atoms in III and IV was indicated by the aminolysis reactions. Thus, aminolysis of III to form V and IX took 48 hr, while VI and X were obtained after only 5 hr. Also, the yields of VI and X (as pure, crystalline materials) were substantially higher than those of V and IX. When aminolysis of III was carried out for only 5 hr, only one of the two chlorine atoms was replaced. Thus, $P_3N_3Cl(C_6H_5)_2(OC_6H_5)_2[N(CH_3)_2]$ (XI), mp 76°, was obtained in 55% yield. When CH_3NH_2 was used, $P_3N_3Cl(C_6H_5)_2(OC_6H_5)_2(NHCH_3)$ (XII), mp 110°, was obtained in 95% yield.

Acknowledgment.—This work was carried out for the Armstrong Cork Company, Lancaster, Pa., to whom we are indebted for long-term financial support. We also appreciate the assistance of Mr. H. A. Bomberger with some of the syntheses and experimental measurements.

---

(6) R. R. Holmes and J. A. Forstner, *Inorg. Chem.*, **2**, 377 (1963).

(7) G. Allen, D. J. Oldfield, N. L. Paddock, F. Rallo, J. Serregi, and S. M. Todd, *Chem. Ind.* (London), 1032 (1965).