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Some Tetra- and Octasubstituted Aminolysis Products of Tetrameric Phosphonitrilic Chloride

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Contrary to general belief, it is shown that complete aminolysis of tetrameric phosphonitrilic chloride can be effected with a variety of amines. It is shown, further, that by use of the proper ratio of reactants tetrasubstituted derivatives can be obtained also. If the amine is sufficiently sterically hindered, only the tetrasubstituted derivative can be obtained. Nuclear magnetic resonance data suggest that in such tetrasubstituted materials each phosphorus atom is bonded to only one amine substituent.

It is well known that removal of the chlorine atoms from the phosphonitrilic chlorides can be effected by such solvolytic reagents as ammonia, amines, hydrazine and alcohols.[1] With amines, reported studies have been restricted largely to reactions of the trimer with the lower aliphatic compounds,[2] although a number of disubstituted derivatives of the tetramer have been described recently.[3] On the basis of the variable chloride content of the small quantities of products obtained, earlier workers reported that complete aminolysis is difficult to achieve. Preparation of larger quantities of materials has shown, however, that complete aminolysis does occur except with amines of low basicity or of such size that steric inhibition exists. Any chloride present is as unremoved amine hydrochloride. Although many amine hydrochlorides are nearly completely insoluble in organic solvents, solubility is apparently enhanced by the phosphonitrilic species present. Dissolved hydrochlorides remain after evaporation of reaction solvent and cannot then be removed readily by recrystallization. Excess amine increases solubility.

Amine hydrochlorides are most effectively removed from the phosphonitrilic derivatives by washing the organic phase with water. Prior neutralization of any excess unreacted amine with hydrochloric acid is essential for complete purification. Extraction of the crude material with liquid ammonia, particularly in an apparatus like that described by Goehring and Niedenzu,[4] is effective where the solubility of the phosphonitrilic compound is small. Remaining small quantities of amine hydrochloride can then be removed by extraction with N,N-dimethylformamide.

Synthesis of tetrasubstituted derivatives of tetrameric phosphonitrilic chloride requires stoichiometric quantities of reactants and mild reaction conditions. Thus, tetrapiperidinotetrachlorotetraphosphonitrile results at room temperature from reaction of the tetrameric chloride with piperidine in a 1:8 mole ratio in anhydrous benzene. With a larger amine, however, tetrasubstituted products result even with excess amine and at elevated temperatures. Thus, the tetrameric chloride and N-methylaniline give only the tetrasubstituted product even in mole ratios up to 1:20

Although several structural possibilities exist for tetrasubstituted derivatives of the tetramer, direct formation of such derivatives with hindered amines suggests symmetrical structures in which one amine group is bonded to each phosphorus atom. The presence of but a single line in the nuclear magnetic resonance spectra of these compounds (Table I) suggests only one phosphorus environment and is in agreement with this type of structure.

TABLE I

NUCLEAR MAGNETIC RESONANCE SPECTRA

Compound	Chemical shift p.p.m. (reference H_3PO_4)	Solvent	R.f. frequency, Mc.
$P_4N_4Cl_4[N(CH_3)C_6H_5]_4$	+1.1	CS_2	16.2
$P_4N_4Cl_4(NC_5H_{10})_4$	−1.7	$CHCl_3$	16.2

The infrared spectra of aminolysis products of the tetrameric chloride (Table II) are characterized by multiple bands in the regions assigned[3,5,6] to the P_4N_4 ring system. The single band in the 1300–1325 cm.$^{-1}$ region shown by derivatives of aromatic and heterocyclic amines corresponds closely to the 1315 cm.$^{-1}$ band of the unsubstituted tetrameric chloride. Derivatives of aliphatic

TABLE II

INFRARED SPECTRA FOR AMINOLYSIS PRODUCTS

Compound	Solvent	Frequency, cm.$^{-1}$
$P_4N_4(NHCH_3)_8$	KBr	1383, 1215, 1088
$P_4N_4(NHC_2H_5)_8$	CS_2	1392, 1262, 1118
$P_4N_4[NH(CH_2)_2CH_3]_8$	CS_2	1394, 1266, 1108
$P_4N_4[NH(CH_2)_3CH_3]_8$	CS_2	1395, 1260, 1122
$P_4N_4[NH(CH_2)_4CH_3]_8$	CS_2	1395, 1265, 1120
$P_4N_4[NH(CH_2)_5CH_3]_8$	CS_2	1395, 1265, 1120
$P_4N_4(NHCH_2C_6H_5)_8$	CS_2	1300
$P_4N_4(o\text{-}NHC_6H_4CH_3)_8$	CS_2	1315[a], 1292
$P_4N_4(m\text{-}NHC_6H_4CH_3)_8$	CS_2	1328, 1270
$P_4N_4(p\text{-}NHC_6H_4CH_3)_8$	CS_2	1325, 1265
$P_4N_4(NC_5H_{10})_8$	CS_2	1326, 1281
$P_4N_4[N(CH_2CH_2)_2O]_8$	KBr	1325, 1288
$P_4N_4Cl_4[N(CH_3)C_6H_5]_4$	CS_2	1330, 1275
$P_4N_4Cl_4[NC_5H_{10}]_4$	CS_2	1305

[a] Weak.

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(2) (a) M. Becke-Goehring and K. John, *Angew. Chem.*, **70**, 657 (1958); (b) S. K. Ray and R. A. Shaw, *Chem. and Ind. (London)*, 53 (1959); (c) M. Becke-Goehring, K. John and E. Fluck, *Z. anorg. allgem. Chem.*, **302**, 103 (1959); (d) S. K. Ray and R. A. Shaw, *Proc. Chem. Soc.*, 26 (1960); (e) M. Becke-Goehring and K. John, *Z. anorg. allgem. Chem.*, **304**, 127 (1960).

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TABLE III

CHARACTERISTICS OF OCTASUBSTITUTED AMINOLYSIS PRODUCTS

Compound	Yield, %	M.p., °C.		Analyses C	H	N	P	Cl
$P_4N_4(NHCH_3)_8$	84	201	Calcd.	22.86	7.67	39.99	29.48	...
			Found	23.23	7.75	39.77	29.50	...
$P_4N_4(NHC_2H_5)_8$	80	122	Calcd.	36.08	9.08	31.56	23.27	...
			Found	36.61	9.13	31.49	23.19	...
$P_4N_4[NH(CH_2)_2CH_3]_8$	74	96	Calcd.	44.70	10.01	26.07	19.22	...
			Found	44.50	9.97	25.81	18.90	...
$P_4N_4[NH(CH_2)_3CH_3]_8$	74	86	Calcd.	50.77	10.65	22.21	16.37	...
			Found	50.87	10.85	22.00	16.61	...
$P_4N_4[NH(CH_2)_4CH_3]_8$	65	79	Calcd.	55.27	11.13	19.34	14.26	...
			Found	55.51	11.40	19.16	14.54	...
$P_4N_4[NH(CH_2)_5CH_3]_8$	80	70	Calcd.	58.74	11.50	17.13	12.63	...
			Found	59.02	11.52	17.09	12.89	...
$P_4N_4(o\text{-}NHC_6H_4CH_3)_8$	80	229 dec.	Calcd.	65.35	6.27	16.34	12.04	...
			Found	65.69	6.19	16.53	12.05	...
$P_4N_4(m\text{-}NHC_6H_4CH_3)_8$	69	199	Calcd.	65.35	6.27	16.34	12.04	...
			Found	65.00	6.51	16.56	12.25	...
$P_4N_4(p\text{-}NHC_6H_4CH_3)_8$	83	207	Calcd.	65.35	6.27	16.34	12.04	...
			Found	65.29	6.29	16.50	12.32	...
$P_4N_4(NHCH_2C_6H_5)_8$	48	121.5	Calcd.	65.35	6.27	16.34	12.04	...
			Found	65.46	6.52	16.68	11.82	...
$P_4N_4(N(CH_2CH_2)_2NCH_2CH_2)_8$	58	>230 dec.	Calcd.	56.31	9.45	19.71	14.53	...
			Found	56.07	9.52	19.44	14.49	...
$P_4N_4(N(CH_2CH_2)_2OCH_2CH_2)_8$	42	>230 dec.	Calcd.	44.23	7.43	19.35	14.26	...
			Found	44.61	7.34	19.25	14.73	.....
$P_4N_4Cl_4[N(CH_3)(C_6H_5)]_4$	55	146	Calcd.	45.06	4.32	15.02	16.60	19.00
			Found	45.26	4.04	14.90	16.58	18.77
$P_4N_4Cl_4(N(CH_2CH_2)_2NCH_3)_4$	50	204	Calcd.	36.49	6.13	17.02	18.82	21.54
			Found	37.01	6.01	17.00	19.12	21.61

amines, however, show multiple banding at 1392–1395 cm.$^{-1}$ and 1260–1266 cm.$^{-1}$, except for the methylamine compound where these bands are displaced to 1383 and 1215 cm.$^{-1}$, respectively.

Experimental

Only typical syntheses are described to illustrate the general procedures followed. Pertinent data for all compounds prepared are summarized in Table III.

Octa-*m*-toluidino-tetraphosphonitrile.—46.36 g. (0.1 mole) of tetrameric phosphonitrilic chloride[7] was dissolved in 250 ml. of anhydrous benzene.[8] This solution was added slowly and at room temperature to a well-stirred solution of 171.44 g. (1.6 moles) of freshly distilled *m*-toluidine in 1200 ml. of anhydrous benzene. The mixture then was refluxed for 60 hr. Precipitated amine hydrochloride (102.35 g.; theoretical, 114.89 g.) was removed by filtration. The remaining hydrochloride was taken out by 8-10 washings with 500 ml. of water.[9] The benzene layer was dried over calcium chloride for 12 hr. and then evaporated to dryness. The product obtained was recrystallized repeatedly from a 1:1 mixture of *n*-heptane and toluene.

(7) Obtained from Albright and Wilson Mfg. Ltd., Oldbury, Birmingham, England, and purified by repeated distillation in vacuum: $(PNCl_2)_4$, 188° (12 mm.), m.p. 124°.

(8) Except for the methylamine compound where chloroform was used to enhance solubility, octasubstituted compounds are best prepared in benzene as solvent.

(9) In comparable reactions where excess amine was employed, neutralization was effected with dilute hydrochloric acid prior to the extraction step.

Tetra-N-methylanilino-tetrachloro-tetraphosphonitrile.—46.36 g. (0.1 mole) of tetrameric phosphonitrilic chloride was dissolved in 250 ml. of anhydrous benzene. This solution was added at room temperature to a well stirred solution of 214.30 g. (2.0 moles) of N-methylaniline in 1200 ml. of anhydrous benzene. The resulting solution then was refluxed for 60 hr., during which time no precipitate formed, but the solution turned yellow. When cooled, the solution became brown, and *ca.* 42.0 g. of amine hydrochloride precipitated. The filtered solution now was treated with water to extract remaining amine hydrochloride. After drying over calcium chloride for 12 hr., the excess N-methylaniline and the solvent were evaporated. The remaining gray crude material was recrystallized from petroleum ether (b.p. 90–110°) with the aid of activated charcoal.

Tetrapiperidino-tetrachloro-tetraphosphonitrile.—A solution of 46.36 g. (0.1 mole) of tetrameric phosphonitrilic chloride in 250 ml. of anhydrous benzene was added with stirring to a cooled (*ca.* 0°) solution of 68.12 g. (0.8 mole) of freshly distilled piperidine in 800 ml. of anhydrous benzene. The mixture then was warmed to room temperature and stirred at this temperature for 4 hr. After removal of precipitated amine hydrochloride, the solution was evaporated and the resulting oily crude material recrystallized first from acetonitrile and finally from ether.

Instrumental Studies.—All infrared spectra were obtained with a Model 21 Perkin–Elmer spectrometer, using a sodium chloride prism. The nuclear magnetic resonance spectra of phosphorus-31 were measured with a Model V-4300B Varian instrument, employing a Model V-4012-HR Varian magnet, with a 16.2 mc. radiofrequency oscillator and a field of 9395 gauss. Microanalyses for phosphorus and chlorine were carried out by the Clark Microanalyses Laboratory, Urban, Illinois.

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Stereospecific Influences in Metal Complexes Containing Optically Active Ligands.[1] Part V. Absolute Stereospecificity in Metal Complexes of Optically Active Polyaminocarboxylic Acids

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Metal complexes of the optically active 1,2-propylenediamine- and *trans* 1,2-cyclohexanediaminetetraacetic acids, in which the ligand is sexadentate and quinquedentate in function, have been prepared. One form only, *e.g.*, D*l* in the cobalt(III) sexadentate complexes, could be isolated. The other isomer, (D*d*), appeared to be very small in amount or excluded, *i.e.*, $K > 99$ and $-\Delta F^0 > 3$ kcal./g. mole. The quinquedentate rhodium complex of *l*-propylenediaminetetraacetic acid, obtained in a single isomeric form, mutarotated to a low value in the light, but the rotation was regained in the dark. None of the complexes, even those containing Cu(II) and Cr(III) could be isomerized by heating in aqueous solution or in the presence of charcoal. From Courtauld atomic models one optical isomer of the complex, whether the ligand is sexadentate or quinquedentate in function, appeared to be sterically hindered. Atom crowding due to the methyl group of the asymmetric carbon does not appear sufficient to exclude completely the strained isomer, but its concentration in the equilibrium mixture would be small. On the other hand, it was evident from models that one of the isomers of the metal complexes of *l*-cyclohexanediaminetetraacetic acid involved considerable distortion of the cyclohexane ring, and would appear to be excluded.

The "inert" metal complexes of optically active 1,2-propylenediamine and *trans*-1,2-cyclohexanediamine tetraacetic acids provide simple stable systems for the study of stereospecific influences, since only two optical isomers, *e.g.*, D*d*, D*l*, may arise from one optical form of the polyaminocarboxylic acid. The optical isomers of the former acid have been obtained by direct synthesis from active 1,2-propylenediamine or by decomposition of the resolved cobalt(III) complex.[2] Commercial 1,2-cyclohexanediaminetetraacetic acid (H_4CDTA) is considered to exist in the le;2e, *trans* form,[3,4] and the *cis*-isomer (1e;2a) seems to have defied all attempts at preparation.[5] Resolution of the acid with *d*-phenylethylamine, *l*-quinine,[6] and in the present work, with *d*-cinchonine was fruitless. The optical isomers ($[\alpha]_D = \pm 53°$) were obtained ultimately by the decomposition of the cobalt(III) complex which had been resolved through the *cis*-dinitrobis-(ethylenediamine)-cobalt(III) salt.

Though previous work with *cis*-dinitro-ethylenediamine-propylenediamine cobalt(III) and bis-(ethylenediamine)-*d*-(cyclopentanediamine)-cobalt-(III) ions[7,8] suggested that little stereospecificity would be expected, especially in the $[Co(PDTA)]^-$ ion, complete stereospecificity, ($K > 99$, $-\Delta F^0 >$ 3 kcal./g. mole), was found. No trace of a second isomer was detected when active barium *l*-propylenediaminetetraacetatocobaltate(III), prepared from the pure levo acid, was fractionally crystallised from aqueous alcohol. The diastereoisomer with *cis*-$[Coen_2(NO_2)_2]^+$ ion was then prepared and recrystallized several times, but the rotation of the recovered barium salt was unchanged. The high solubility of salts of the optically active $[Co(CDTA)]^-$ ion prevented similar studies. However, unlike the active $[Co(EDTA)]^-$ ion, which racemized slowly[9] (half-life = 168 min., 100°), no rotational change occurred when solutions of salts of the $[Co(PDTA)]^-$ and $[Co(CDTA)]^-$ ions were kept at 98° for several hours. Similarly, although the $[Co(EDTA)]^-$ ion racemized completely in aqueous solution in the presence of activated charcoal, no rotational change occurred in 2 hr. with the $[Co(PDTA)]^-$ and $[Co(CDTA)]^-$ ions.

Quinquedentate Complexes.—No evidence was found other than for a single geometrical or optical isomer in the quinquedentate cobalt(III) complexes of optically active propylenediaminetetraacetic acid with chloro or nitro groups occupying the unique coördination position. Each optical configuration of the organic moiety permits the formation of four geometrical isomers depending on the position of the nitro (or chloro) group with respect to the methyl group and the two nitrogen atoms. The resolution of DL-K[Co(*dl*-H·PDTA)-Cl] yielded only two isomers, D*d* and L*l*, identical with the isomers prepared from the optically active complexing agent. Both isomers were transformed with complete retention of configuration to the pure sexadentate complexes discussed above. Similarly, the blue chloro complex could be prepared in almost 100% yield from the sexadentate

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