bustion analyses were determined by Schwartzkoff Microanalytical Laboratory, Woodside, N.Y.

 2α -Chloro- 1α , 9α -methano- 2β , 8, 8, 10α -tetramethyldecalin (2). -)-Thujopsene (102 g, 0.5 mol) was cooled to 5° and vigorously agitated while anhydrous hydrogen chloride was passed in over 1.7 hr. Gas absorption ceased when 1 molar equiv had been added and the reaction mixture crystallized with an attendant temperature rise to 25°. Ice-cold hexane (100 ml) was added and the mixture was rapidly filtered through a cold sintered glass funnel to afford 63 g of solid material, mp $40-43^{\circ}$ dec. A sample recrystallized from hexane at -50° exhibited mp $42-45^{\circ}$ dec: ir (CCl₄, 0°) 1255, 1160, 1150, 1030, 1000, 827 cm⁻¹; nmr (CDCl₃, -10°) δ 0.55, 1.00, 1.12, 1.81 (s, 3 each); $[\alpha]^{\circ}D - 95^{\circ}$ (c 20%, $CHCl_3$).

A crystalline sample stored under nitrogen at -20° for 10 days showed little signs of decomposition.

Anal. Calcd for $C_{15}H_{25}Cl$: C, 74.81; H, 10.46; Cl, 14.72. Found: C, 74.91; H, 10.48; Cl, 14.53.

 9α -Chloromethyl-2,8,8,10 α -tetramethyl-1-octalin (3).—The nmr sample (at -10°) of tertiary chloride 2 was warmed to 20° for 0.4 hr and the spectra were recorded. The major component showed the following nmr resonances: δ 1.00, 1.04, 1.08 (s, 3 each), 1.70 (s, 3, vinyl CH₃), 3.59 (s, 2), 5.05 (s, 1, $W_{h/2} = 4$ Hz); ir (CCl₄) 1080, 845, 648 cm⁻¹.

 4α -Chloro- 4β , 7α , 11, 11-tetramethylbicyclo [5, 4, 0] undec-1-ene (4).—The above nmr sample was warmed to 40° for an additional 1.0 hr and the spectra were recorded. The major component showed the following nmr resonances: 1.08 (s, 6), 1.22, 1.59 (s, 3 each), 2.27 (d, d, 1, J = 14, 9 Hz), 2.95 (d, d, 1, J = 14, 6 Hz), 5.48 (d, d, 1, J = 9, 6 Hz); ir (CCl₄) 1230, 672 cm⁻¹.

 2α -Chloromethyl- 2β , 8, 8, 10α -tetramethyl-1(9)-octalin (5). Continued warming of the above nmr sample at 40° for an additional 20 hr gave the stable neopentyl chloride 5 with the following nmr resonances: $\delta 1.05$ (s, 6), 1.08, 1.17 (s, 3 each), 3.31 (s, 2), 5.11 (s, 1, $W_{h/2} = 2.5 \text{ Hz}$); ir (CCl₄) 1020, 925, 860, 718, 662 cm⁻¹; $[\alpha]^{25}D + 75^{\circ}$ (c 20%, CDCl₃). These data are identical with those reported by Friedrich¹⁰ for chloride 5

Treatment of neopentyl chloride 5 at reflux for 6 hr with 10%aqueous sodium carbonate gave recovered unchanged starting material.

 4β , 7α ,11,11-Tetramethylbicyclo [5.4.0] undec-1-en-4\alpha-o1 (Widdrol) (6).—An 18-g sample of crystalline chloride 2 was heated to 60° for 2.0 hr. The nmr spectrum showed that the products at this point were approximately an equimolar mixture of chlorides 3 and 4 with only trace amounts of chlorides 2 and 5. Water (150 ml) and sodium carbonate (10 g) were added and the mixture was allowed to reflux for 6 hr. The mixture was cooled and the organic layer was separated. Analysis by gas chromatography showed three peaks identified as thujopsene (1, 57%), an unidentified hydrocarbon (18%), and widdrol (6, 25%). Distillation on a micro-still head afforded 12.2 g of liquid fractions, bp 100-110° (1.5 mm), with an infrared spectrum virtually identical with that of thujopsene (1). The fractions boiling at $125-135^{\circ}$ (1.5 mm) (4.0 g) crystallized and were recrystallized from methanol to afford widdrol (6): mp 89-90°; nmr (CDCl₃) & 1.08, 1.22 (s, 6 each), 1.94 (d, d, 1, J = 14, 9 Hz), 2.48 (d, d, 1, J = 14, 6 Hz), 5.48 (d, d, 1, J = 9, 6 Hz). The infrared spectrum was identical with that reported by Enzell¹² for widdrol.

The same products were also obtained in a similar ratio when the crystalline hydrochloride 2 was treated directly with 10%aqueous sodium carbonate at reflux for 3 hr.

Treatment of Thujopsene with Anhydrous Hydrogen Bromide. (-)-Thujopsene (51 g, 0.25 mol) was cooled to 0° and vigorously agitated while anhydrous hydrogen bromide was passed in. Absorption was slow and the theoretical amount was consumed in 4.5 hr. The dark colored mixture did not crystallize as had been the case for the chloride analog. Hexane (50 ml) was added and the mixture was washed neutral with cold 10% aqueous sodium (s, 6), 1.08, 1.17 (s, 3 each), 3.25 (s, 2), 5.10 (s, 1). The spectral data are identical with those reported by Itô¹⁶ and coworkers for the bromide analog of chloride 5.

Registry No.-1, 470-40-6; 2, 34905-90-3; 3, 34905-91-4; 4, 34905-92-5; 5, 32540-35-5; 5 bromide analog, 34905-94-7; 6, 6892-80-4.

Aniline Derivatives of Tetrakis(hydroxymethyl)phosphonium Chloride

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The development of flame-retardant finishes for cotton based on the reaction of tetrakis(hydroxymethyl)phosphonium chloride (1) with polyfunctional amines such as melamine² has led to the investigation of many other nitrogen compounds as resin-forming substrates.^{3,4} Secondary amines give well-defined monomeric products,^{5,6} but primary amines, such as cetylamine,⁷⁻⁹ have thus far given only polymeric products.⁷⁻¹² In this paper we report our investigation of the reaction of 1 and some of its derivatives with aniline, which led to a series of well-defined crystalline compounds.

Aniline reacts readily with 1 in ethanol or acetone at room temperature, displacing all four hydroxyl groups (Scheme I).¹³ The product, tetrakis(anilino-



(1) One of the laboratories of the Southern Marketing and Nutrition Research Division, Agricultural Research Service, U. S. Department of Agriculture.

(2) W. A. Reeves and J. D. Guthrie, Text. World, 104 (2), 101 (1954).

(3) G. L. Drake, Jr., "Encyclopedia of Chemical Technology," Vol. 9, 2nd ed, Wiley, New York, N. Y., 1966, p 300.
(4) K. A. Petrov and V. A. Parshina, Usp. Khim., 37, 1218 (1968) (Engl.

transl., 532). (5) H. Coates and P. A. T. Hoye [to Albright & Wilson (Mfg.) Ltd.], British Patent 842,593 (1960); Chem. Abstr., 55, 4363 (1961).

(6) D. J. Daigle, W. A. Reeves, and D. J. Donaldson, Text. Res. J., 40, 580 (1970).

(7) W. A. Reeves and J. D. Guthrie, Ind. Eng. Chem., 48, 64 (1956). (8) W. A. Reeves and J. D. Guthrie (to United States of America as represented by the Secretary of Agriculture), U. S. Patent 2,809,941 (1957);

Chem. Abstr., 52, 2421 (1958). (9) J. G. Evans, G. Landelle, J. R. W. Perfect, B. Topley, and H. Coates [to Bradford Dyers' Assoc. Ltd. and Albright & Wilson (Mfg.) Ltd.],

British Patent 761,985 (1956); Chem. Abstr., 51, 9178 (1957). (10) W. A. Reeves and J. D. Guthrie (to United States of America as

represented by the Secretary of Agriculture), U. S. Patent 2,668.096 (1954); Chem. Abstr., 48, 6710 (1954).

Chem. Abstr., 40, 6110 (1994).
 (11) Anon. [to Albright & Wilson (Mfg.) Ltd.], Belgian Patent 626,626
 (1963); Chem. Abstr., 61, 7144 (1964).

(12) E. V. Kuznetsov, R. K. Valetdinov, Ts. Ya. Roitburd, and L. B. Zakharova, Tr. Kazan. Khim.-Tekhnol. Inst., 29, 20 (1960); Chem. Abstr., 58, 547 (1963).

(13) A 1:1 molar ratio of aniline to 1 is reported to give a yellow polymer (ref 9, example 18).

methyl)phosphonium chloride (2), is unaffected by water or ethanol, which would remove aniline hydrochloride if it were present. Aniline is apparently too weak a base $(pK_a = 4.58)^{14}$ to cause the displacement of formaldehyde and HCl which is characteristic of secondary (eq 1)⁵ and tertiary^{15,16} amines.

 $4R_2NH + 1 \longrightarrow (R_2NCH_2)_2P + CH_2O + R_2NH \cdot HCl \quad (1)$

When stirred with a slight excess of triethylamine in acetone for 1 hr at room temperature, 2 gives triethylamine hydrochloride (correct ir,¹⁷ melting point, 84.0%), aniline (correct ir, nD, 62.5%), and a white, crystalline solid (76.0%) identified as 5-anilinomethyl-1,3-diphenyl-1,3,5-diazaphosphorinane (3a, Scheme I). The ir spectrum of 3a shows a weak but sharp N-H band at 3340 cm⁻¹. The ¹H nmr spectrum shows overlapping multiplets in the 3.2-4.0-ppm region (PCH₂, NH), an ABX sextet (NCH₂N) in the 4.0-5.2ppm region, and a multiplet (C_6H_5) in the 6.3-7.4ppm region, in the ratio 7.0:2.0:15. The ABX pattern, which appears as a sextet owing to coupling of the upfield proton to phosphorus (X = ${}^{31}P$), is assigned to the NCH₂N protons because its position (mean chemical shift, $\delta = 4.65$ ppm) is close to the 4.77 ppm reported for hexahydro-1,3,5-triphenyl-s-triazine,¹⁸ and the separation ($\Delta \mu = 49.9$ Hz) between the chemical shifts of the two protons is close to the 52.8 and 53.8 Hz reported^{19,20} for hexahydro-1,3,5-trimethyl-s-triazine at low temperatures.²¹⁻²⁶

The mass spectrum of 3a exhibits the fragmentation pattern characteristic of methyleneaniline derivatives,^{27,28} with m/e 93 (PhNH₂·+), 104 (PhN=CH+) and 105 (PhN= CH_2^+) as the most abundant ions.

This product is evidently formed by the displacement of aniline and HCl from 2, perhaps via the intramolecular mechanism shown in Scheme II.²⁹⁻³¹

(14) A. Albert and E. P. Serjeant, "Ionization Constants of Acids and Bases," Wiley, New York, N. Y., 1962, p 144.
(15) K. A. Petrov, V. A. Parshina, and M. B. Luzanova, Zh. Obshch.

Khim., 32, 553 (1962); Chem. Abstr., 58, 5714 (1963)

(16) S. E. Ellzey, Jr., W. J. Connick, Jr., and G. J. Boudreaux, Can. J. Chem., 49, 3581 (1971).

(17) Sadtler Infrared Prism Spectra, No. 6605, Sadtler Research Labora-

(17) Sadder Hinated Firsh Spectra, No. 6003, Sadder Research Laboratories, Philadelphia, Pa., 1959.
 (18) L. Stefaniak, T. Urbanski, M. Witanowski, and H. Januszewski, *Rocz. Chem.*, 43, 1687 (1969); *Chem. Abstr.*, 72, 21072 (1970).
 (19) R. F. Farmer and J. Harmer, *Chem. Commun.*, 866 (1966).

(20) H. S. Gutowsky and P. A. Temussi, J. Amer. Chem. Soc., 89, 4358 (1967)

(21) The nmr spectrum is consistent with a model in which there is rapid inversion of the diazaphosphorinane ring and of the nitrogen atoms, but not of the phosphorus atom. This allows two stable chair conformations for the diazaphosphorinane ring, depending on whether the phosphorus lone pair (or, in the case of **3b** or **3c**, the oxygen or sulfur atom) is equatorial or axial. If the preferred conformation is equatorial, as in other phosphorinane ring systems, $^{22-26}$ the trans NCH₂N proton (H_A) is in a favorable zig-zag geometry for long-range splitting by phosphorus. Neither conformation for the cis proton (H_B) has this feature. On this basis, H_A is tentatively assigned the upfield chemical shift, $\delta 4.23$ ($^{4}J_{\rm PH}_{\rm A} = 3.0$ Hz), and H_B the downfield chemical shift, δ 5.06 (⁴J_{PHB} = 0 Hz). The preferred conformation is illustrated in Scheme I

(22) L. D. Hall and R. B. Malcolm, Chem. Ind. (London), 92 (1968)

(23) H. J. Geise, Recl. Trav. Chim. Pays-Bas, 86, 362 (1967).
(24) K. D. Bartle, R. S. Edmundson, and D. W. Jones, Tetrahedron, 23,

1701 (1967)

(25) D. Gagnaire, J. B. Robert, and J. Verrier, Bull. Soc. Chim. Fr., 2392 (1968).

- (26) J. B. Lambert and W. L. Oliver, Jr., Tetrahedron, 27, 4245 (1971)
- (27) E. Schumacher and R. Taubenest, *Helv. Chim. Acta*, 49, 1439 (1966).
 (28) R. Colton and Q. N. Porter, *Aust. J. Chem.*, 21, 2215 (1968).

(29) The direct displacement of an anilinomethyl group as PhN==CH2

would probably result instead in the formation of the cyclic trimer, hexa-hydro-1,3,5-triphenyl-s-triazine.^{30,31}

(30) C. Eberhardt and A. Welter, Ber., 27, 1804 (1894).

(31) H. Krässig and H. Ringsdorf, Makromol. Chem., 22, 163 (1957).



The same product (3a) is obtained in 77.0% yield when 1 is neutralized with sodium ethoxide in ethanol prior to reaction with aniline (Scheme I).

Oxidation of 3a with hydrogen peroxide in acetone gives the phosphine oxide 3b in 93.1% yield. The corresponding phosphine sulfide 3c is obtained from 3a and sulfur in benzene in 60.4% yield, together with 7.9% unidentified by-product.

An entirely different series of products is obtained from formaldehyde-free tris(hydroxymethyl)phosphine (4). Reaction of 4 with aniline in benzene, carried out at reflux with azeotropic removal of the water,³² gives tris(anilinomethyl)phosphine (5a) as a white, crystalline solid in 81.3% yield (Scheme I). 5a shows a much stronger N-H band in the ir than 3a, and its nmr spectrum shows none of the fine structure associated with **3a**. There is a sharp doublet at δ 3.52 (PCH₂), a singlet at 3.64 (NH), and a multiplet (C_6H_5) in the 6.6– 7.2-ppm region, in the ratio 6.1:2.9:15.

Oxidation of 5a with hydrogen peroxide in acetone gives the phosphine oxide 5b in 82.9% yield. The corresponding phosphine sulfide 5c is obtained from 5a and sulfur in benzene in 94.2% yield. The physical properties and spectra of these derivatives are clearly different from those of **3b** and **3c**.

5a can also be prepared from 2 in 61.9% yield by reaction with ammonia instead of triethylamine (Scheme I). The ammonia presumably functions by tying up the excess formaldehyde as hexamethylenetetramine,³³ though none was found in this experiment.

Still another method is the displacement of dimethylamine from tris(dimethylaminomethyl)phosphine (6) by aniline, which takes place smoothly at $160-170^{\circ}$ giving 5a in 45.4% yield (eq 2).

$$(Me_2NCH_2)_3P + 3PhNH_2 \longrightarrow 5a + 3Me_2NH$$
(2)
6

This type of displacement has not been reported previously, though compounds like 6 are known to react with active hydrogen compounds such as acetoacetic ester or phenol or dialkyl phosphites with the displacement of 1 equiv of secondary amine.⁵

Efforts to prepare N-methylol or N-methylene (e.g.,**3a**) derivatives of **5a** by reaction with aqueous formalin or with paraformaldehyde in ethanol were unsuccessful, owing to the tendency of 5a to disproportionate to substances richer and poorer in N-H. This tendency

⁽³²⁾ Under these conditions, the reaction of 1 with aniline gives a yellow powder, dec pt 250°, which appears to be the product of displacement of three of the four hydroxyl groups. Anal. Calcd for C₂₂H₃₇ClN₈OP: C, 63.53; H, 6.54; Cl, 8.53; N, 10.11; P, 7.45. Found: C, 62.97; H, 6.41; Cl, The product is insoluble in water and in all or 8.75; N, 9.91; P, 7.40. ganic solvents except DMSO and appears to be unaffected by triethylamine or sodium hydroxide.

⁽³³⁾ J. F. Walker, "Formaldehyde," 3rd ed, Reinhold Publ. Corp., New York, N. Y., 1964, p 234.

was manifested to some extent in all of the aniline derivatives described in this paper. The phosphonium chloride 2, for example, appears to be easily recrystallized from methanol or ethanol, but the product which separates on cooling is a high-melting white, crystalline solid, mp 170–171°, having the composition $C_{16}H_{18}N_2P_2$ (41.0%). None of the 2 is recovered. This same substance is obtained from **5a** simply on stirring in ethanol at room temperature overnight (2.1%). The nature of this disproportionation, which seems to be related to the known disproportionation of N,N'diphenylmethanediamine to aniline and hexahydro-1,3,5-triphenyl-s-triazine,³⁰ is currently under investigation.

Experimental Section³⁴

Starting Materials.—Tetrakis(hydroxymethyl)phosphonium chloride³⁵ (1) was recrystallized from 2-propanol: mp 149–149.5°. Tris(hydroxymethyl)phosphine³⁶ (4), dried by azeo-tropic distillation with benzene,³⁷ analyzed^{38,39} 73.92% 4 and 0.08% CH₂O, the remainder being tris(hydroxymethyl)phosphine oxide. Tris(dimethylaminomethyl)phosphine (6), bp 65–67° (0.4 mm), was prepared by the reaction of 1 with dimethyl-amine.⁴⁰ Aniline was distilled from a pinch of zinc dust before use.

Tetrakis(anilinomethyl)phosphonium Chloride (2).—Aniline (7.70 g, 83.0 mmol) was added to a solution of 1 (3.83 g, 20.0 mmol) in 75 ml of ethanol. There was a mild exotherm, followed immediately by the separation of solids. The mixture was stirred for 2 hr and filtered, giving 9.15 g (93.0%) of 2 as a white crystalline solid: mp 129–130°; ir (Nujol) 689 (s, C₆H₅), 695 (m, sh), 745 (vs, C₆H₅), 755 (vs, C₆H₅), 786 (w), 795 (w), 875 (w), 885 (w), 908 (m), 922 (m), 1020 (w), 1060 (w), 1090 (w), 1150 (w), 1180 (m), 1205 (m), 1245 (s, CN_{arom}), 1280 (m), 1310 (m, CN_{arom}), 1410 (w), 1500 (vs, C=C_{arom}), 1510 (s, sh), 1608 (vs, C=C_{arom}), 3290 (vs, NH) cm⁻¹; ¹H nmr (DMSO-d₆) δ 3.3–5.0 (m, 8 H, CH₂, strong peak at 4.47), 6.3–7.3 (m, 24 H, C₆H₅ and NH).

Anal. Calcd for C₂₈H₃₂ClN₄P: C, 68.49; H, 6.57; N, 11.41; P, 6.31. Found: C, 68.18; H, 6.88; N, 11.33; P, 6.33.

No further solids separated from the filtrate in the next 5 hr. The filtrate and washings, stripped under vacuum, left 1.15 g of yellow oil, n^{20} D 1.5923, which contained 2 and the excess aniline (ir).

2 yellows rapidly on exposure to light. It is insoluble in water and in organic solvents, with the exception of dimethyl sulfoxide (DMSO) and dimethylformamide. It dissolves readily in hot chloroform or acetone, giving yellow solutions which deposit gums on work-up, and in hot methanol or ethanol, giving disproportionation products. Even in DMSO there is evidence of partial decomposition (¹H nmr).

A similar reaction with acetone as the solvent gave a 66.0% yield of 2, mp 120-121°, together with deep yellow liquid by-products.

5-Anilinomethyl-1,3-diphenyl-1,3,5-diazaphosphorinane (3a). A. From 2.—Triethylamine (6.05 g, 60.0 mmol) was added to a well-stirred slurry of 2 (18.85 g, 38.4 mmol) in 250 ml of acetone. There was no exotherm, but the appearance of the solid gradually changed to that of a much less voluminous, granular solid. After 1 hr, the solid was collected on a filter, washed with acetone, and dried, giving 4.45 g (84.0%) of triethylamine hydrochloride, mp 251-253° (correct ir¹⁷). No more separated on standing, nor upon the addition of more triethylamine. The filtrate was stripped of solvent under vacuum, and the residue, a yellow oil, was shaken vigorously with ethanol (250 ml), whereupon it crystallized. After 2 hr, the solid was collected on a filter, washed with ethanol, and dried, giving 10.50 g (76.0%) of **3a** as a white, granular solid, mp 96-97°. This product was identical (melting point, ir, nmr) to the **3a** from neutralized 1, described below. The filtrate and washings from the **3a** yielded 7.40 g of yellow oil, from which 2.25 g (62.5%) of aniline (ir, n_D) was recovered by extracting with ether, drying over potassium hydroxide, and distilling.

B. From Neutralized 1.-1 (4.75 g, 25.0 mmol) was added to a solution of sodium (0.60 g, 25.0 mmol) in ethanol (25 ml), stirred for 1 hr under nitrogen, and filtered to remove sodium chloride (1.55 g, 26.5 mmol). The filtrate was treated with aniline (9.30 g, 100.0 mmol) and stirred at room temperature overnight. A mild exotherm (from 24 to 32°) occurred, followed by the separation of an oil which solidified after 2.5 hr. After 20 hr, the solid was collected on a filter, washed with ethanol, and dried, giving 6.95 g (77.0%) of **3a** as a white, crystalline solid, mp 96-97°. Two crystallizations from cyclohexane gave an analytical sample: mp 96–97°; ir (Nujol) 687 (s, C₆H₅), 706 (m), 743 (vs, C₆H₅), 748 (s, sh), 774 (m), 850 (m), 860 (m), 897 (m), 910 (m), 925 (m), 995 (m), 1025 (w), 1060 (m), 1095 (m), 1145 (w), 1170 (m), 1180 (s), 1195 (s), 1210 (s), 1230 (s), 1255 (w), 1310 (s, CN_{arom}), 1415 (m), 1490 (vs, $C=C_{srom}$), 1600 (vs, $C=C_{arom}$), 3340 (s, NH) cm⁻¹; ¹H nmr (CDCl₃) δ 3.2-4.0 (m, 7 H, PCH_2 and NH), $H_{\rm A}$ at 4.23 and $H_{\rm B}$ at 5.06 (ABX sextet, 2 H, NCH_2N , ${}^1\!J_{\text{HH}} = 13.0$, ${}^4\!J_{\text{PH}_A} = 3.0$, ${}^4\!J_{\text{PH}_B} = 0 \text{ Hz}$), 6.3–7.4 (m, 15 H, C₆H₅) (the ¹H spectrum was not visibly altered by D₂O, but the integration showed one less proton in the 3.2-4.0-ppm region⁴¹); mass spectrum m/e (% relative abundance, ion fragment), 121 (4), 106 (7, PhNH=CH₂+), 105 (71, PhN=CH₂·+), 104 (53, PhN=CH⁺), 94 (27), 93 (100, PhNH₂·+), 92 (33, PhNH⁺), 91 (2, PhN⁺), 94 (51), 78 (7), 77 (27, Ph⁺), 69 (9), 66 (18, C₅H₆⁺), 65 (11, CH⁺), 56 (27), 55 (0), 70.5 (2, PhN), CH², 25 (4)65 (11, $C_5H_5^+$), 56 (27), 55 (9), 52.5 (2, PhN=CH₂²⁺), 51 (4, $C_4H_3^+$), 41 (11).

Anal. Caled for $C_{22}H_{24}N_3P$: C, 73.11; H, 6.69; N, 11.63; P, 8.57; mol wt, 361. Found: C, 73.36; H, 6.73; N, 11.48; P, 8.34; mol wt (osmometric, in CHCl₃), 359.

3a is soluble in chloroform, acetone, and benzene and insoluble in water and ether. It can be recrystallized from cyclohexane (10 ml/g) or ethanol, but tends to oil out from either solvent unless seeded or scratched during cooling. Prolonged heating in ethanol, however, results in a hard, transparent gum from which no **3a** can be recovered. **3a** gives a positive test with iodine,⁴² but dissolves in carbon disulfide without giving the red color characteristic of tertiary phosphines.⁴³

5-Anilinomethyl-1,3-diphenyl-5-oxo-1,3,5-diazaphosphorinane (**3b**).—**3a** (1.805 g, 5.0 mmol) in acetone (15 ml) was oxidized with 30% hydrogen peroxide, giving 1.755 g (93.1%) of **3b** as a white, crystalline solid, mp 165–168°. One recrystallization from benzene gave an analytical sample: mp 170–171°; ir (Nujol) 690 (m, C₆H₅), 752 (s, C₆H₅), 762 (s, C₆H₃), 782 (w), 822 (w), 897 (s), 932 (w), 990 (w), 1030 (w), 1055 (w), 1090 (w), 1120 (m), 1160 (vs, P=O), 1180 (w), 1200 (w), 1235 (s), 1260 (m), 1320 (s, CN_{arom}), 1410 (w), 1495 (vs, C=C_{arom}), 1530 (w), 1600 (s, C=C_{atom}), 3310 (m, NH) cm⁻¹; ¹H nmr (CDCl₃) δ 3.3–4.5 (m, 7 H, PCH₂ and NH), H_A at 4.21 and H_B at 5.04

⁽³⁴⁾ Melting points are corrected. Analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn. Ir spectra were taken on a Perkin-Elmer Model 137B instrument with NaCl optics. ¹H nmr spectra were taken on a Varian A-60 spectrometer, using TMS as an internal standard, and ³¹P nmr spectra were taken on a Varian HA-60-IL instrument at 24.3 Mc, using 85% H₃PO₄ as an external standard.

⁽³⁵⁾ Hooker Chemical Corp., Niagara Falls, N. Y. Name of firms or their products in this paper does not imply their endorsement by the Department of Agriculture.

⁽³⁶⁾ M. Reuter and L. Orthner (to Farbwerke Hoechst A.-G.), U. S. Patent 3,030,421 (1962).

 ⁽³⁷⁾ R. K. Valetdinov, E. V. Kuznetsov, R. R. Belova, R. K. Mukhaeva,
 T. I. Malykhina, and M. Kh. Khasanov, Zh. Obshch. Khim., 37, 2269 (1967);
 Chem. Abstr., 68, 87350 (1968).

 ⁽³⁸⁾ E. I. Grinshtein, A. B. Bruker, and L. Z. Soborovskii, Zh. Obshch. Khim., 36, 302 (1966); Chem. Abstr., 64, 17629 (1966).

⁽³⁹⁾ A. W. Frank and G. L. Drake, Jr., J. Org. Chem., 36, 549 (1971).
(40) H. Coates and P. A. T. Hoye [To Albright & Wilson (Mfg.) Ltd.], German Patent 1,077,214 (1960).

⁽⁴¹⁾ The NCH₂N assignment was further supported by the 100-Mc spectrum of **3a**, which also showed an ABX pattern: δ (CDCl₃), H_A at 4.15, H_B at 4.98 ppm (${}^{1}J_{HH} = 13.0, {}^{4}J_{PH_A} = 3.0, {}^{4}J_{PH_B} = 0$ Hz). The chemical shifts were slightly lower, but the separation (0.83 ppm) was identical.

⁽⁴²⁾ Iodine test: dissolve sample in a little benzene, ethanol, or chloroform, add 2% iodine in benzene by means of a medicine dropper, and note if the yellow iodine color is discharged. This is a useful test for trivalent phosphorus in organic phosphorus compounds. The test was positive with **4** and **6**, negative with **3b**, **3c**, **5b**, and **5c**, and a slow discharge of the iodine color was observed with **1** and **2**.

color was observed with 1 and 2. (43) G. M. Kosolapoff, "Organophosphorus Compounds," Wiley, New York, N. Y., 1950, pp 25, 26.

(ABX sextet, 2 H, NCH₂N, ${}^{1}J_{HH} = 13.0$, ${}^{4}J_{PH_{\Lambda}} = 4.0$, ${}^{4}J_{PH_{B}} = 0$ Hz), 6.2-7.4 (m, 15 H, C₆H₅).

Anal. Calcd for C₂₉H₂₄N₃OP: C, 70.01; H, 6.41; N, 11.14; P, 8.21. Found: C, 69.92; H, 6.51; N, 10.87; P, 8.10.

3b is soluble in chloroform and insoluble in acetone, water, and other solvents. It can be recrystallized from benzene (40 ml/g) or ethanol (80 ml/g).

5-Anilinomethyl-1,3-diphenyl-5-thiono-1,3,5-diazaphosphorinane (3c).—3a (1.805 g, 5.00 mmol) was stirred overnight at room temperature with 0.160 g (5.00 mmol) of sulfur in benzene (30 ml), giving an acetone-soluble product, 1.186 g (60.4%), mp 127–128°, and an acetone-insoluble product, 0.156 g (7.9%), mp 159–160°. The acetone-soluble product, 3c, a white crystalline solid, was recrystallized from ethanol and dried *in vacuo* at 80°: mp 127–128°; ir (Nujol) 690 (s, C₆H₅), 702 (m), 716 (w), 754 (s, C₆H₅), 772 (m, sh), 806 (w), 818 (w), 834 (w), 855 (w), 904 (m), 931 (w), 978 (w), 998 (w), 1030 (w), 1055 (w), 1075 (w), 1095 (w), 1110 (w, sh), 1190 (m, sh), 1200 (s), 1235 (m), 1315 (m), 1410 (m), 1490 (vs, C=c_{arom}), 1600 (vs, C=c_{arom}), 3370 (w, NH) cm⁻¹; ¹H nmr (CDCl₅) δ 3.3–4.5 (m, 8 H, PCH₂, NH, and H₄ of NCH₂N), H_B at 5.09 (d, 1 H, H_B of NCH₂N, ¹J_{HH} = 13.0, ⁴J_{PH_B} = 0 Hz), 6.2–7.4 (m, 15 H, C₆H₅). The upfield portion (H_A) of the ABX pattern was not discernible.

Anal. Calcd for $C_{22}H_{24}N_3PS$: C, 67.15; H, 6.15; N, 10.68; P, 7.87, S, 8.15. Found: C, 67.35; H, 6.15; N, 10.60; P, 7.63; S, 7.93.

3c is soluble in acetone, chloroform, and benzene and insoluble in water and cyclohexane. It can be recrystallized from ethanol (60 ml/g) or carbon tetrachloride (20 ml/g).

The acetone-insoluble product was an unidentified white crystalline solid: ir (Nujol) 686 (s, C_6H_5), 740 (s, sh), 750 (vs, C_6H_5), 813 (m), 862 (m), 891 (m), 930 (w), 978 (w), 992 (w), 1030 (w), 1115 (w), 1200 (s), 1210 (s), 1230 (vs, CN_{arom}), 1320 (w), 1410 (m), 1490 (vs, $C=C_{arom}$), 1600 (vs, $C=C_{arom}$), 3400 (w, NH) cm⁻¹.

(w, NH) cm⁻¹. The same two products were obtained when the reaction was carried out at reflux (30 min) instead of room temperature.

Tris(anilinomethyl)phosphine (5a). A. From 4.—A mixture of 4 (3.10 g of 73.92% titer, 18.5 mmol), aniline (9.30 g, 100 mmol), and benzene (25 ml) was heated in a nitrogen atmosphere under reflux in an apparatus equipped with a Dean-Stark trap for azeotropic removal of the water. In 2 hr, a total of 1.00 ml (theory 1.00 g) of water was collected in the trap. The solution was allowed to cool, decanted from the unreacted oil [0.55 g, n^{20} D 1.5550, identified by ir as tris(hydroxymethyl)phosphine oxide], and stripped of solvent under vacuum. The residue, a white, crystalline mass containing 5a and the excess aniline, was triturated under ether with a mortar and pestle, filtered, and washed with ether, giving 5.30 g (73.7%) of 5a as white flakes, mp 82-83°. Another 0.55 g (7.6%) of 5a, and 4.25 g (theory 4.14 g) of aniline (ir, nD) was recovered from the ether Two recrystallizations from benzene (6 ml/g), followed filtrate. by thorough drying *in vacuo* at room temperature, gave an analytical sample: mp 85-86°; ir (Nujol) 676 (m, C_6H_6 solvate), 692 (m, C_6H_5), 747 (vs, C_6H_5), 863 (w), 890 (w), 981 (w), 1055 (w), 1080 (w), 1140 (w), 1165 (w), 1195 (w), 1230 (s, CN_{arom}), 1310 (s, CN_{arom}), 1450 (vs), 1500 (vs, $C=C_{arom}$), 1590 (vs, C=C_{arom}), 3440 (s, NH) cm⁻¹; ¹H nmr (CDCl₃) δ 3.52 (d, CH₂, J = 5.0 Hz), 3.64 (s, NH), 6.6–7.2 (m, 15 H, C₆H₅), and 7.37 (s, 3 H, C₆H₆ solvate); ³¹P nmr δ +32.5 ppm. The NH peak vanished when D_2O was added, changing the C_8H_5 : (CH₂ + NH) ratio from 15:9.0 to 15:6.1.

Anal. Calcd for $C_{21}H_{24}N_3P \cdot 0.5C_6H_6$: C, 74.20; H, 7.01; N, 10.82; P, 7.97. Found: C, 73.81; H, 7.17; N, 10.73; P, 7.79.

The presence of solvate benzene was evident in both the ir (676 cm⁻¹) and ¹H nmr (7.37 ppm). The compound retains solvent tenaciously. A sample of 5a dried in a drying pistol over boiling benzene (80°), however, lost 37.2% of its weight and was no longer crystalline.

5a is insoluble in water or ether, but dissolves instantly in acetone or chloroform. It gives a positive test with iodine,⁴² but dissolves in carbon disulfide without giving the red color characteristic of tertiary phosphines.⁴³

characteristic of tertiary phosphines.⁴³ 5a was also obtained when 4 was stirred with aniline in ethanol at room temperature overnight. The product was an off-white, crystalline solid (70.5%), mp 61-63°, ir identical with ir of the product described above except for the C₆H₆ band at 676 cm⁻¹. Prolonged stirring should be avoided, however, as the product disproportionates in ethanol, even at room temperature. **B.** From 6.—6 (10.25 g, 0.05 mol) was added by means of a syringe to 18.60 g (0.20 mol) of aniline under nitrogen in a small distillation assembly and heated rapidly to $160-170^{\circ}$. Gas evolution was strong, but steady, and subsided within 30 min. The solution was kept at this temperature for 1 hr, allowed to cool to $130-140^{\circ}$, and stripped under water-pump vacuum to remove the excess aniline (4.15 g, n^{24} D 1.5803, correct ir, 89.5%). The still contents (17.60 g) solidified on cooling to a waxy, malodorous solid, ir similar to 5a, but without the C₆H₆ band (676 cm⁻¹). One recrystallization from benzene gave 8.80 g (45.4%) of 5a, mp 85-86°, identical with the product prepared from 4.

A preliminary experiment in ethanol solution (3 hr at reflux) produced no dimethylamine until most of the ethanol was distilled off.

C. From 2.—Ammonia was bubbled into a slurry of 2 (4.90 g, 10.0 mmol) in acetone (50 ml) for 5 min at room temperature, during which time the 2 dissolved and was replaced by a finely divided white precipitate. After 30 min, the mixture was filtered, giving 0.50 g (93.5%) of ammonium chloride (ir, NaOH test, Beilstein test) and a pale yellow oil (5.60 g, n^{26} D.6117) which contained no chlorine (Beilstein test). The oil, on work-up, yielded 2.40 g (61.9%) of 5a, isolated as the C₆H₆ hemisol-vate, mp 87-88°, and 0.90 g (96.8%) of aniline (ir, nD). A careful check of each of the fractions failed to reveal the presence of any hexamethylenetetramine.

Tris(anilinomethyl)phosphine Oxide (5b).—5a (1.747 g, 4.50 mmol) in acetone (20 ml) was oxidized with 30% hydrogen peroxide as described for 3a, giving 1.416 g (82.9%) of 5b, mp 119–122° after recrystallization from ethanol-water. Two recrystallizations from carbon tetrachloride gave an analytical sample, mp 122–123°, after drying *in vacuo* over refluxing benzene: ir (Nujol) 786 (s, C₆H₃), 793 (m), 745 (vs, C₆H₃), 753 (s), 780 (m), 870 (w), 885 (w), 900 (m), 990 (w), 1030 (w), 1070 (w), 1090 (m), 1110 (w), 1135 (vs, P=O), 1150 (m, sh), 1180 (m), 1220 (w), 1235 (w), 1260 (m, CN_{arom}), 1290 (m), 1315 (m), 1410 (ws, NH) cm⁻¹; ¹H nmr (CDCl₃) δ 3.66 (d, 6 H, CH₂, J = 7.0 Hz), 4.23 (s, 3 H, NH), 6.6–7.3 (m, 15 H, C₆H₃). The NH peak vanished when D₂O was added.

Anal. Calcd for $C_{21}H_{24}N_3OP \cdot H_2O$: C, 65.78; H, 6.84; N, 10.96; P, 8.08. Found: C, 65.50; H, 6.36; N, 10.70; P, 8.18.

5b is soluble in acetone, chloroform, and ethanol and insoluble in water and ether. It can be recrystallized from carbon tetrachloride (30 ml/g), but must then be dried *in vacuo* over refluxing benzene (80°) or butanol (118°) to remove the solvent (CCl band at 787 cm⁻¹ in the ir). Drying over acetone (56°) is insufficient.

Tris(anilinomethyl)phosphine Sulfide (5c).—5a (1.747 g, 4.50 mmol) and sulfur (0.160 g, 5.00 mmol) in benzene (20 ml) yielded 1.615 g (94.2%) of 5c, mp 105–106°. A portion of this compound was recrystallized from acetone-water and dried *in vacuo* over refluxing acetone: mp 105–106°; ir (Nujol) 792 (s, C₆H₅), 725 (w), 747 (vs, C₆H₅), 758 (s, sh), 768 (w), 787 (m), 806 (w), 827 (w), 877 (m), 896 (w), 917 (w), 956 (w), 995 (w), 1020 (w), 1065 (w), 1110 (w), 1155 (w), 1180 (m), 1210 (w), 1240 (m), 1250 (s), 1290 (m), 1315 (s), 1420 (w), 1440 (s), 1505 (vs, C=C_{arom}), 1610 (vs, C=C_{arom}), 3400 (s, NH) cm⁻¹; ¹H nmr (CDCl₅) δ 3.66 (d, 6 H, CH₂, J = 5.0 Hz), 4.14 (s, 3 H, NH), 6.5–7.3 (m, 15 H, C₆H₅). The NH peak vanished when D₂O was added.

Anal. Calcd for $C_{21}H_{24}N_3PS$: C, 66.12; H, 6.34; N, 11.02; P, 8.12. Found: C, 65.46; H, 6.27; N, 10.86; P, 7.93.

5c is soluble in acetone, chloroform, and acetonitrile and insoluble in water and ether.

Registry	No	-1, 124-64-1;	2,	34885-67-1;	3a,
34885-68-2;	3b ,	34885-69-3;	3c,	34885-70-6;	5a,
34885-71-7;	5b,	34885-72-8;	5c,	34885-73-9;	6,
24577-28-4.					

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