Table III

Smoothed Values of Isobaric Heat Capacities of Organic Liquids at Bubble Point

Temp. °C.	Aniline	Ethylenediamine	Furfuryl alcohol	Isopropylamine	Methyl alcohol	Nitromethane
20			0.482[a]			
30		0.704[a]	.491	0.653[a]		0.422[a]
40	0.503[a]	.710	.501	.663	0.620[a]	.426
50	.507	.716	.510	.673	.643	.429
60	.511	.723	.519	.683	.667	.432
70	.515	.730[a]	.529[a]	.693	.692	.436
80	.520			.703[a]	.715	.440
90	.524				.739[a]	.444
100	.528					.448[a]
120	.536					
140	.544					
160	.552					
180	.561					

[a] These values are extrapolated.

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Some *p*-Nitrophenyl Derivatives of *o*-Phosphoric and *o*-thiophosphoric Acid

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Several new compounds related to parathion (O,O′-diethyl O″-*p*-nitrophenyl thiophosphate) have been prepared.

O-Ethyl O′,O″- Bis-(*p*-nitrophenyl) Thiophosphate (I).—To 0.25 mole of thiophosphoryl chloride in 150 ml. of acetone was added in portions 0.5 mole of freshly dried powdered sodium *p*-nitrophenoxide, while stirring and cooling. The reaction proceeds rapidly even at 0°. After completion, 0.25 mole of sodium ethoxide in ethanol was added with cooling, and the mixture was poured into a large quantity of water. The precipitate was collected, washed, boiled with 500 ml. of ethanol and filtered hot. From the filtrate on cooling compound I separated and was recrystallized from ethanol, yield 25 g., m. p. 125–126°, colorless needles, soluble in acetone. *Anal.* Calcd. for $C_{14}H_{13}N_2O_7PS$: C, 43.73; H, 3.39; N, 7.29; S, 8.34; P, 8.06. Found: C, 44.36; H, 3.53; N, 7.04; S, 8.66; P, 8.26.[1]

O,O′,O″-Tris-(*p*-nitrophenyl) Thiophosphate (II).—The theoretical amount of sodium *p*-nitrophenoxide was added to thiophosphoryl chloride as described under I. The product is insoluble in boiling ethanol and can be obtained pure by recrystallization from acetone, yield 83%; very light yellow crystals, m. p. 174°. *Anal.* Calcd. for $C_{18}H_{12}N_3O_9PS$: C, 45.28; H, 2.52; N, 8.80; S, 6.71; P, 6.50. Found: C, 45.36; H, 2.44; N, 8.94; S, 6.88; P, 6.63.

The ethanol-insoluble portion of the preceding preparation is also tris-(*p*-nitrophenyl) thiophosphate. About 35 g. was obtained in this way, giving a total yield of I and II, based on sodium *p*-nitrophenoxide, of about 75%.

O-Methyl O′,O″-bis-(*p*-nitrophenyl) thiophosphate (III) was prepared using the same procedure as described for the ethyl homolog, but using sodium methoxide in methanol instead of sodium ethoxide. It melts at 96° and its properties are analogous to those of I; yield about 25% with 50% of compound II as a by-product. *Anal.* Calcd. for $C_{13}H_{11}N_2O_7PS$: C, 42.16; H, 2.98; N, 7.57; P, 8.38. Found: C, 42.28; H, 2.99; N, 7.71; P, 8.30.

Methyl Bis-(*p*-nitrophenyl) Phosphate (IV).—To 0.25 mole of phosphorus oxychloride and 100 ml. of dioxane was added 0.5 mole of sodium *p*-nitrophenoxide in portions while stirring and cooling. The temperature should be kept below 35°. After completion of this reaction 0.25 mole of sodium methoxide in methanol was added slowly. The mixture was stirred for about 30 minutes, poured into a large quantity of water and the residue collected. About 20 g. of IV, m. p. 141–142.5°, was obtained from this residue by treatment with boiling ethanol (see I). *Anal.* Calcd. for $C_{13}H_{11}N_2O_8P$: C, 44.07; H, 3.11; N, 7.91. Found: C, 43.96; H, 2.93; N, 7.87.

Ethyl bis-(*p*-nitrophenyl) phosphate (V) was prepared as described under IV, but using sodium ethoxide in ethanol instead of sodium methoxide. An analogous yield was obtained, m. p. 132–136°. *Anal.* Calcd. for $C_{14}H_{13}N_2O_8P$: C, 45.65; H, 3.54; N, 7.61; P, 8.41. Found: C, 45.51; H, 3.52; N, 7.68; P, 8.33.

Tris-(*p*-nitrophenyl) phosphate (VI) was prepared by adding 0.167 mole of phosphorus oxychloride in 100 ml. dioxane slowly to 0.5 mole of powdered dry sodium *p*-nitrophenoxide in 200 ml. of dioxane while stirring and cooling with ice-water. After addition the mixture was heated to 100°, filtered hot, and the precipitated sodium chloride washed with hot dioxane. From the combined filtrate compound VI separated on cooling; yield 50–60%, m. p. 156°, soluble in acetone. *Anal.* Calcd. for $C_{18}H_{12}N_3O_{10}P$: C, 46.85; H, 2.60; N, 9.10. Found: C, 46.66; H, 2.45; N, 9.22.

The portion of the residue insoluble in boiling ethanol in the preparation of compound IV or V is also tris-(*p*-nitrophenyl) phosphate. The total yield of bis- and tris-compound on the quantity of sodium nitrophenoxide used is about 50%.

We have also prepared by Schrader's method[2] the dimethyl analog of parathion, O,O′-dimethyl O″-*p*-nitrophenyl thiophosphate. It separates as white needles, m. p. 36.5°, from alcoholic solution. *Anal.* Calcd. for $C_8H_{10}NO_5PS$: C, 36.50; H, 3.81; S, 12.18; P, 11.80. Found: C, 36.54; H, 3.86; S, 12.07; P, 11.90.

Reduction of compound I and coupling with N-naphthylethylenediamine according to the method of Averell and Norris[3] for the determination of parathion also gives the same magenta color. However the presence of I in parathion can be detected by measuring the rate of hydrolysis.[4]

These compounds (I to VI) do not have significant activity as contact-insecticides (test insect, *calandra granaria*).

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[1] Micro-analyses were carried out by Messrs. P. J. Hubers and H. Pieters.

[2] G. A. Schrader, B I O S Final Report 1808, Synthetic Insecticides.

[3] P. R. Averell and M. V. Norris, *Anal. Chem.*, **20**, 753 (1948).

[4] J. A. A. Ketelaar, *Rec. trav. chim.*, **69**, 649 (1950).

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Further Applications of the Schmidt Reaction

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The reaction of olefinic compounds with hydrazoic acid probably involves a carbonium ion intermediate analogous to the oxocarbonium ion and the oxycarbonium ion postulated in the reaction of acids or carbonyl compounds with hydrazoic acid.[1] Although the Schmidt reaction has been widely used on acids and carbonyl compounds, it has been infrequently applied to olefins.[2] The reaction has now been applied to various substituted

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[1] (a) Newman and Gildenhorn, This Journal, **70**, 317 (1948); (b) P. A. S. Smith, *ibid.*, **70**, 318 (1948).

[2] (a) German Patent 583,565 (*Frdl.*, **20**, 947 (1935); (b) C. Schuerch and E. H. Huntress, This Journal, **71**, 2233, 2238 (1949); (c) W. E. McEwen, M. Gilliland and B. I. Sparr, *ibid.*, **72**, 3212 (1950).