

TABLE III
SMOOTHED VALUES OF ISOBARIC HEAT CAPACITIES OF
ORGANIC LIQUIDS AT BUBBLE POINT

Temp. °C.	Aniline	Ethyl- enedi- amine	Fur- furyl alcohol	Iso- propyl- amine	Methyl alcohol	Nitro- methane
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

By J. A. A. KETELAAR AND H. R. GERSMANN

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 C₁₄H₁₃N₂O₇PS: 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 C₁₅H₁₂N₃O₈PS: 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 C₁₃H₁₁N₂O₇PS: 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 por-

tions 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 C₁₃H₁₁N₂O₆P: 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 C₁₄H₁₃N₂O₆P: 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 C₁₅H₁₂N₃O₁₀P: 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 method² 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 C₈H₁₀NO₅PS: 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 Norris³ 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*).

(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 oxocarbenium 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

(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 (*Frtd.*, **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).

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

ethylenes to yield ketones and amines as shown in Table I. Nitrogen was also obtained in each instance.

Some olefins, such as styrene and indene, polymerize so rapidly in concentrated sulfuric acid, which was used as the reaction medium that they do not react with hydrazoic acid; others, such as stilbene and tetraphenylethylene are insoluble in concentrated sulfuric acid and for this reason do not react under our experimental conditions.

TABLE I

ACTION OF HYDRAZOIC ACID IN SULFURIC ACID SOLUTION

Reactant	Products and yields, %
1,1-Diphenylethylene	Aniline 40, acetophenone 30
Diphenylmethylcarbinol	Aniline 65, acetophenone 40
1,1-Diphenyl-1-butene	Aniline 57, butyrophenone 64
1-Anisyl-1-phenylethylene	<i>p</i> -Anisidine, acetophenone, aniline, <i>p</i> -methoxyacetophenone
Triphenylethylene	Aniline 30, phenylbenzylketone 25

The behavior of 1,1-diphenylethylene was typical of the compounds studied. It reacted smoothly at room temperature with the formation of 1 mole of nitrogen per mole of azide. Aniline and acetophenone were obtained from the reaction mixture. The plausible sequence of reactions suggested recently by McEwen, *et al.*,²⁰ and which were arrived at independently by us accounts for the products obtained and illustrates the similarity of the reaction of carbonium ions with the reactivity of oxy- and oxocarbenium ions. The fact that the same products are obtained whether the starting material is diphenylmethylcarbinol or diphenylethylene indicates that each yields the same reactive intermediate, the diphenylmethylcarbonium ion. With unsymmetrical ethylenes such as anisylphenylethylene, two reactions are possible. The first involves the migration of the anisyl group to yield anisidine and acetophenone and the second involves the migration of the phenyl to yield aniline and *p*-methoxyacetophenone. We have found that the former reaction predominates since the ketone fraction of the products contains $75 \pm 5\%$ acetophenone and $25 \pm 5\%$ of the methoxy derivative. This is the same dependence of migrating aptitude upon electronic character as is shown in other rearrangements such as the pinacol rearrangement³ which involves the migration of a group with its binding electrons.

Experimental

Two grams of each substance was added slowly with stirring to a 10% molar excess of sodium azide in concentrated sulfuric acid at room temperature. When gas evolution ceased the reaction mixture was poured into ice-water and extracted with ether. From the ether extract the ketone was isolated and identified as the semicarbazone by its melting point and mixed melting point with an authentic sample. It was further identified by a comparison of the infrared curve with that of an authentic

sample. The aqueous portion after ether extraction was made alkaline and extracted with ether. From this extract the aniline was obtained and precipitated as the hydrochloride. Because sulfonation took place when 1-anisyl-1-phenylethylene was dissolved in concentrated sulfuric acid, its reaction with hydrazoic acid was run in 75% sulfuric. The ketone fraction, obtained in 80% yield, in this instance was not converted to the semicarbazone. An infrared curve of this material was the same as the curve of a synthetic mixture of 75% acetophenone and 25% *p*-methoxyacetophenone. After removal of the ether from the second extract of this experiment the residue was recrystallized from water to yield *p*-anisidine. The filtrate from the crystallization was extracted with ether and yielded aniline hydrochloride. Triphenylethylene is difficultly soluble in concentrated sulfuric acid and for this reason was run at 40°.

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Methyl Ester of Dehydroperillic Acid, an Odoriferous Constituent of Western Red Cedar (*Thuja plicata*)

By E. F. KURTH

Anderson and Sherrard¹ isolated an acid, $C_{10}H_{12}O_2$, termed dehydroperillic acid and Erdtman and Gripenberg² found three additional isomerides, α -, β - and γ -thujaplicin, in the heartwood of *Thuja plicata* D. Don. During the past two years the author examined some highly fragrant crystals that were found in western red cedar sawlogs at Garibaldi, Oregon. The operator of a sawmill at this place reported observing the crystals occasionally in western red cedar logs.

The crystals were clear, water-white parallelepipeds, which melted at 34.5 to 35°. One large crystal had the dimensions 9 × 18 × 20 mm. Anderson and Sherrard prepared the methyl ester of their acid and found it had a pleasant odor and m. p. 34.5 to 35°. Erdtman and Gripenberg found α -thujaplicin, m. p. 34°, in Swedish grown *Thuja plicata* but not in American grown wood. An investigation of the crystals found in the American western red cedar sawlogs disclosed that they were the methyl ester of dehydroperillic acid. This compound is readily saponified with dilute alkalis to dehydroperillic acid. Inasmuch as the former workers used alkalis in their isolation of dehydroperillic acid and the thujaplicins, the methyl ester of dehydroperillic acid was not recognized as probably the chief odoriferous constituent of *Thuja plicata*.

Experimental

The crystals were readily soluble in ethyl ether, acetone, ethanol, chloroform and light petroleum. They were insoluble in cold sodium hydrogen carbonate solution. Tests with ferric chloride and copper acetate reagents² indicated the complete absence of thujaplicins. Refluxing with dilute sodium hydroxide solution followed by acidification with dilute sulfuric acid gave white crystals m. p. 88°, which is the same as that reported for dehydroperillic

(1) Anderson and Sherrard, *THIS JOURNAL*, **55**, 3813 (1933).

(2) Erdtman and Gripenberg, *Nature*, **161**, 719 (1948); *Acta Chem. Scand.*, **2**, 625 (1948).

(3) Bachmann and Moser, *THIS JOURNAL*, **54**, 1124 (1932); **56**, 2081 (1934); Pollak and Curtin, *ibid.*, **72**, 961 (1950).