

947. *The Oxidation of Aromatic Amines. Part V.* Oxidation by Perphosphoric Acids.*

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Aromatic amines are oxidised by permonophosphoric acid or a mixture of peracetic and phosphoric acid. Aniline is oxidised to *p*-aminophenol and *p*-aminophenyl dihydrogen phosphate, 2-naphthylamine to 2-amino-1-naphthol and 2-amino-1-naphthyl dihydrogen phosphate; but *NN*-dimethyl-2-naphthylamine gives its *N*-oxide, and anthranilic acid yields azoxybenzene-2 : 2'-dicarboxylic and 5-hydroxyanthranilic acid. The oxidation to phenolic derivatives does not proceed in neutral or alkaline solution, or in the absence of acetone or some other carbonyl derivatives.

AROMATIC amines are oxidised by mammals to aminophenols which are excreted as sulphuric esters or glucuronides. The possibility that the oxidations were oxidative phosphorylations, yielding aminophenyl phosphoric esters, has been examined¹ but no evidence for the presence of 2-amino-1-naphthyl dihydrogen phosphate could be found on biological oxidation of 2-naphthylamine. The oxidation of aromatic amines with perphosphoric acid has been studied (*a*) because it might be analogous to the biological oxidation, (*b*) as a method of preparation of the aminophenyl phosphates as reference compounds in connection with the biological oxidation of amines, and (*c*) for comparison with oxidation by persulphate.² Mammals excrete phenols as sulphuric esters and, surprisingly, not as phosphoric esters although much more phosphate than sulphate is excreted.

It was expected that phosphoric esters of aminophenols would be formed by oxidation with alkaline perdiphosphate because oxidation with alkaline neutral or acidified persulphate yields *o*-aminophenyl sulphates as the main products.² Neither potassium nor ammonium perdiphosphate oxidised 2-naphthylamine to phosphoric esters. The production of both 2-amino-1-naphthol and its phosphoric ester by oxidation by permonophosphoric acid in the presence of acetone was seen in preliminary experiments with the mixed acids formed by the reaction of pyrophosphoric acid with hydrogen peroxide.³ When the mixed acids were added to 2-naphthylamine in 50% aqueous acetone containing an excess of alkali, no aminonaphthol derivatives were formed at room temperature or at the boiling point. If the alkali was omitted, however, 2-amino-1-naphthol and 2-amino-1-naphthyl phosphate were produced, but only if acetone was present. As perdiphosphoric acid is stable in alkali but decomposed in acid solution, while permonophosphoric acid is stable in acid only,³ these results suggest that the oxidation to aminophenols requires permonophosphoric acid.

Permonophosphoric acid free from perdiphosphoric acid can be prepared by treating hydrogen peroxide with phosphoric oxide in acetonitrile.⁴ This material in acetone solution oxidised 2-naphthylamine to 2-amino-1-naphthol and to 2-amino-1-naphthyl dihydrogen phosphate. In aqueous acetone the yield of phosphate was greatly reduced, and in the absence of acetone or other ketones or in neutral solution no phosphate was formed. The yield was not significantly altered by changing the rate of addition of the per-acid or by varying the temperature of the reaction from -5° to the boiling point of the mixtures. Oxidation with an excess of permonophosphoric acid gave 2-carboxycinnamic acid. 2-Amino-1-naphthyl dihydrogen phosphate was also readily prepared by oxidation of 2-naphthylamine with peracetic acid in the presence of phosphoric acid and acetone. 2-Amino-1-naphthol, also produced in the oxidations, was not isolated but it was detected

* Parts I—IV, *J.*, 1953, 3623; 1954, 980; 1956, 1337; *Biochem. J.*, 1956, 62, 546.

¹ Boyland and Manson, *Biochem. J.*, 1955, 60, ii.

² Boyland, Manson, and Sims, *J.*, 1953, 3623.

³ Schmidlin and Massini, *Ber.*, 1910, 43, 91.

⁴ Toennies, *J. Amer. Chem. Soc.*, 1937, 59, 555.

by the green product formed on addition of ammonia, and was extracted by benzene as a purple solution.⁵ 2-Acetamidonaphthalene resisted oxidation by permonophosphoric acid or by a mixture of peracetic and phosphoric acid. *NN*-Dimethyl-2-naphthylamine with permonophosphoric acid in aqueous acetone gave the amine oxide; Auerbach and Wolfenstein⁶ found that hydrogen peroxide had no effect on *NN*-dimethylnaphthylamine.

Aniline and permonophosphoric acid gave *p*-aminophenol and *p*-aminophenyl dihydrogen phosphate in the presence of acetone, but not in acetonitrile or water alone. No *o*-aminophenol was detected. Aniline and peracetic acid in the presence of phosphoric acid gave *p*-aminophenyl dihydrogen phosphate (readily isolated as the monosodium salt) and some *p*-aminophenol (not isolated). For chromatographic identification, *p*-aminophenyl phosphate was prepared by catalytic reduction of disodium *p*-nitrophenyl phosphate.

Oxidation of anthranilic acid in aqueous acetone by permonophosphoric acid gave azoxybenzene-2 : 2'-dicarboxylic acid and a small amount of 5-hydroxyanthranilic acid, but no 3-hydroxyanthranilic acid. Oxidation of 1-naphthylamine, benzidine, or 2-amino-fluorene with permonophosphoric acid in acetone gave small amounts of phosphoric esters detected as slow-running amino-compounds on paper chromatograms. No 3 : 3'-di-hydroxybenzidine was detected among the products of the benzidine oxidation.

Different solvents for permonophosphoric acid oxidations were investigated, the formation of 2-amino-1-naphthol and 2-amino-1-naphthyl dihydrogen phosphate being studied. The results are tabulated. Some of the solvents were compared with acetone

Solvents in which no phenolic products were formed		Solvents in which 2-amino-1-naphthol and its phosphate were formed	
Water	Chloroform	Acetone	Acetylacetone
Acetonitrile	Pyridine	Aqueous acetone (50%)	Diacetyl
Pentyl alcohol (BS696)	Acetic acid	Ethyl methyl ketone	Et acetoacetate
Propan-2-ol	Ethyl acetate	Diethyl ketone	Pyruvic acid (10% aq.)
Ethanol	Diisobutyl ketone	Acetophenone	Formaldehyde (33% aq.) *
Ether	Salicylaldehyde	Benzophenone	Acetaldehyde (50% aq.) †
Dioxan		Acetylacetone	Benzaldehyde †

* Only 2-amino-1-naphthol formed. † Only the phosphate formed.

in the synthesis of the phosphoric ester on a preparative scale; ethyl methyl ketone gave a lower yield. If *N*-benzylidene-2-naphthylamine in aqueous suspension or in acetonitrile was treated with the per-acid, 2-amino-1-naphthyl phosphate was formed. From these results it appears that carbonyl derivatives facilitate the oxidation.

The formation of compounds between the permonophosphoric acid and acetone was investigated by comparing solutions in acetonitrile and in acetone on paper chromatograms. The acetone solution showed two spots which were not present in the acetonitrile solution: one (R_F 0.5) gave a positive reaction for phosphate ion and for oxidising activity: the other (R_F 0.85) consisted of an oxidising substance which gave no phosphate reaction. Neither of these spots was obtained if acetone was treated with hydrogen peroxide only. If an acetone solution of the per-acid was kept for two days at room temperature the per-acid disappeared, but the products giving the spots described above remained and the solution was still capable of oxidising 2-naphthylamine to 2-amino-1-naphthol and its phosphoric ester.

Horner and Schwenk⁷ proposed mechanisms for the reaction of benzoyl peroxide with aniline, methylaniline, and dimethylaniline: the postulated primary step is a transfer of one electron from the unshared pair of the nitrogen atom to one of the peroxidic oxygen atoms, resulting in fission of the -O-O- bond and formation of a radical and a negative ion. A similar mechanism may account for the formation of phenols and phosphoric

⁵ Liebermann and Jacobson, *Annalen*, 1882, **211**, 36.

⁶ Auerbach and Wolfenstein, *Ber.*, 1901, **34**, 2411.

⁷ Horner and Schwenk, *Angew. Chem.*, 1949, **61**, 411.

esters by permonophosphoric acid. The per-acid might be split by the transfer of an electron from the amino-nitrogen atom to give hydroxyl or phosphate radicals. The formation of *p*-aminophenol and 2-amino-1-naphthol and their phosphoric esters seems to occur only in the presence of a carbonyl compound. Robertson and Waters,⁸ and Criegee,⁹ have suggested that the oxidation of oxopolymethylenes to lactones by permonosulphuric acid (Baeyer and Villiger reaction¹⁰) might proceed by way of an addition compound between the carbonyl compound and the per-acid. It is also known that aldehydes and ketones react with hydrogen peroxide or hydroperoxides to give hydroxyalkyl peroxides. Doering and Dorfman¹¹ investigated the conversion of [¹⁸O]benzophenone into phenyl benzoate by perbenzoic acid and found the results to be consistent with an initial addition of the per-acid to the ketone. Similar addition compounds may play a part in the oxidation of amines by permonophosphoric acid in the presence of carbonyl compounds. The oxidation of *NN*-dimethyl-2-naphthylamine to an amine oxide, and of anthranilic acid to an azoxy-compound, are reactions typical of hydrogen peroxide or organic per-acids.

EXPERIMENTAL

Paper chromatography was carried out by ascending development on Whatman no. 1 paper, with butan-1-ol-acetic acid-water [(a) 2 : 1 : 1 or (b) 4 : 1 : 5 by vol.].

Preparation of Permonophosphoric Acid.—Toennies⁴ prepared the per-acid on a small scale. It was prepared safely in larger quantities provided the cooling and mixing were carefully controlled. Use of ether as a solvent on this scale (in place of acetonitrile), however, resulted in an explosion. Phosphoric oxide (14.2 g.) was suspended in acetonitrile (30 ml.) at -5° , and hydrogen peroxide (6.8 g. as 7.8 g. of 87% hydrogen peroxide; Laporte Ltd.) and water (0.8 g.) in acetonitrile (10 ml.) were added during 45 min. with stirring, so that the temperature did not rise above 10° . The mixture was kept cold for 1 hr. and then at room temperature overnight; it was stored in a refrigerator and assayed iodometrically before use as described by Toennies.⁴ The yield of per-acid was 10.5 g. (46%) and 3.3 g. of hydrogen peroxide remained unchanged. On storage at 5° the per-acid and hydrogen peroxide content fell. 1 ml. of solution, containing initially 0.34 g. of H_3PO_5 and 0.04 g. of hydrogen peroxide, contained 0.21 g. of per-acid and 0.02 g. of peroxide after 26 days. Another 1 ml., containing initially 0.25 g. of per-acid and 0.06 g. of peroxide, had after three months in the cold, 0.04 g. and 0.002 g. respectively.

Oxidation of 2-Naphthylamine by Permonophosphoric Acid.—(a) *In acetone.* To 2-naphthylamine (7 g.) in acetone (150 ml.) permonophosphoric acid (5 g., in acetonitrile) was added dropwise with stirring during 30 min. After a further 30 minutes' stirring, the solution was made alkaline with 2*N*-sodium hydroxide, and most of the acetone removed under reduced pressure. Water was added and the solution extracted with ether (5×100 ml.), acidified with concentrated hydrochloric acid, and extracted with butan-1-ol (5×100 ml.). The combined butanol extracts were made alkaline with aqueous ammonia (*d* 0.88), then evaporated to dryness under reduced pressure, and the residue was dissolved in dilute ammonia solution. The solution was treated with charcoal whilst hot, filtered, and acidified with concentrated hydrochloric acid, 2-amino-1-naphthyl dihydrogen phosphate (1.2 g.) separating. Recrystallisation by dissolution in alkali and precipitation with concentrated hydrochloric acid gave prisms, m. p. $247-249^{\circ}$ (Found: P, 12.7; N, 5.6. $C_{10}H_{10}O_4PN$ requires P, 13.0; N, 5.9%). Hydrolysis of the ester (0.5 g.) by 5*N*-sulphuric acid (5 ml.) at 100° for 30 min. yielded, on cooling, 2-amino-1-naphthyl hydrogen sulphate. The *N*-benzoylbenzoate formed needles (from ethanol), m. p. and mixed m. p. 180° (Found: N, 3.9. Calc. for $C_{24}H_{17}O_3N$: N, 3.8%). The phosphoric ester gave a brick-red colour after diazotisation and coupling with hexylresorcinol. It gave a positive reaction in Wade and Morgan's phosphate test,¹² but did not respond to Hanes and Isherwood's test,¹³ unlike 1-naphthyl dihydrogen phosphate. In solvent system (a) the ester had R_F 0.72.

⁸ Robertson and Waters, *J.*, 1948, 1574.

⁹ Criegee, *Annalen*, 1948, 560, 127.

¹⁰ Baeyer and Villiger, *Ber.*, 1899, 32, 3625; 1900, 33, 858.

¹¹ Doering and Dorfmann, *J. Amer. Chem. Soc.*, 1953, 75, 5595.

¹² Wade and Morgan, *Nature*, 1953, 171, 530.

¹³ Hanes and Isherwood, *ibid.*, 1949, 164, 1107.

When ethyl methyl ketone was used as a solvent in the oxidation, the yield of ester from 7 g. of amine was 0.4 g.

The ester reacted immediately as an amine with *p*-dimethylaminobenzaldehyde to give a yellow colour, and was only slowly hydrolysed by 5*N*-sulphuric acid at 100°.

(b) *In aqueous acetone.* 2-Naphthylamine (7 g.) was dissolved in acetone (100 ml.) and water (50 ml.), and per-acid (5 g.) was added during 15 min. The mixture was kept overnight and the phosphoric ester (0.1 g.) isolated as in (a). When the mixture was worked up 40 min. after the addition of the per-acid the yield was 0.15 g.; when the reaction was carried out at -5° and the mixture worked up after 40 min. it was 0.04 g.; after 1 hour's refluxing, it was 0.1 g.

(c) *Oxidation at pH 6.0.* The reaction was carried out as in (b) but the pH of the per-acid solution was adjusted to 6.0 by 2*N*-sodium hydroxide. Titration of an aliquot part indicated no loss of per-acid by this treatment. No phosphoric ester was isolated, although paper chromatography indicated that a trace was present.

(d) *Use of excess of per-acid in aqueous acetone.* 2-Naphthylamine (5 g.) in acetone (140 ml.) and water (70 ml.) was treated with per-acid (12 g.) and after 1 hr. the mixture extracted as in (a). The product (1.5 g.), isolated by the acidification of an aqueous solution of the residue from the butan-1-ol extract, had m. p. 190—192° after recrystallisation from aqueous ethanol. It was acidic, did not diazotise or couple with hexylresorcinol, and contained no nitrogen or phosphorus. It gave no depression of the m. p. with 2-carboxycinnamic acid (Found: C, 62.5; H, 4.4. Calc. for C₁₀H₈O₄: C, 62.5; H, 4.2%). As described by Titley¹⁴ the melt solidified on further heating and could then be remelted at a lower temperature (140—144°; Titley reports 151°). The diamide, prepared by treatment with thionyl chloride followed by reaction with ammonia, formed needles, m. p. and mixed m. p. 201—202° (Found: N, 14.9. Calc. for C₁₀H₁₀O₂N₂: N, 14.7%).

(e) *Oxidation in acetonitrile.* 2-Naphthylamine (7 g.) was treated in acetonitrile (60 ml.) with the per-acid (4 g.) during 30 min. Working up as before yielded only 2-carboxycinnamic acid (0.05 g.) from the butan-1-ol fraction. Chromatography of this and the original reaction mixture revealed no 2-amino-1-naphthyl dihydrogen phosphate.

Oxidation of 2-Naphthylamine by Peracetic Acid in the Presence of Phosphoric Acid.—2-Naphthylamine (7 g.) and phosphoric acid (9.8 g.) were dissolved in acetone (150 ml.). 40% Peracetic acid (10 ml.) was added with stirring during 30 min. Stirring was continued for a further 1.5 hr., then the mixture was made alkaline with 2*N*-sodium hydroxide, and most of the acetone removed under reduced pressure. After dilution with water, the solution was extracted several times with ether, and the aqueous layer acidified, to yield the phosphoric ester (3.5 g.), m. p. and mixed m. p. 242—244° (decomp.) (*N*-benzoylbenzoate, m. p. 180°).

Oxidation of NN-Dimethyl-2-naphthylamine.—The amine¹⁵ (5 g.) in acetone (100 ml.) and water (50 ml.) was treated with the per-acid (3.0 g.) during 20 min. and stirred for a further 1.5 hr. A crystalline precipitate (2.2 g.) was filtered off, and the filtrate neutralised and evaporated to small volume. The aqueous solution was extracted with ether (from which 0.9 g. of the amine was recovered) and, after acidification with concentrated hydrochloric acid, with butan-1-ol. The butanol extract was neutralised with ammonia and evaporated to dryness. From an aqueous solution of the residue, 0.5 g. of a substance, m. p. 160—163°, crystallised. Recrystallisation of the combined precipitates from 70% aqueous acetone gave plates, m. p. 167—169°. The product was acidic and contained phosphate ion, but was not precipitated on addition of alkali (the amine is not soluble in water). Analysis indicated that the compound was the *oxide phosphate* (Found: P, 10.8, 10.7; N, 4.9. C₁₂H₁₃ON, H₃PO₄ requires P, 10.9; N, 4.9%). The oxide (0.5 g.) was kept in concentrated hydrochloric acid with stannous chloride (0.5 g.) overnight at room temperature and then made alkaline and extracted with ether. Evaporation of the extract and crystallisation of the residue from aqueous ethanol yielded *NN*-dimethyl-2-naphthylamine, m. p. and mixed m. p. 44—45° (Found: C, 83.9; H, 8.1; N, 8.05. Calc. for C₁₂H₁₃N: C, 84.2; H, 7.7; N, 8.2%).

Oxidation of Aniline by Permonophosphoric Acid.—Permonophosphoric acid (10 g. in acetonitrile) was added during 30 min. with cooling and stirring to aniline (15 g.) in acetone (200 ml.). After a further 1.5 hr. the solution was neutralised with 2*N*-sodium hydroxide and evaporated to small volume under reduced pressure. After dilution with water and adjustment to pH 5.0, the solution was extracted with ether, then with butan-1-ol and again with this solvent at

¹⁴ Titley, *J.*, 1928, 2571.

¹⁵ Billman, Radike, and Munday, *J. Amer. Chem. Soc.*, 1942, **64**, 2977.

pH 2.0. The ether extracts contained *p*-aminophenol and evaporation of the butanol extracts and benzooylation of the residue in pyridine with benzoyl chloride yielded *p*-benzamidophenyl benzoate (10 mg.), m. p. and mixed m. p. 230—232°. Paper chromatography showed that the butanol extracts contained no *p*-aminophenyl phosphate. The ester was identified in the aqueous layer by comparison on paper chromatography with a known specimen [R_F 0.35 in solvent system (a)]. The spot gave a yellow colour after diazotisation and coupling with hexylresorcinol. Two other spots with the same colour reaction and with R_F respectively 0.56 and 0.16 were present but were not identified. *p*-Aminophenyl phosphate was not isolated.

Oxidation of Aniline by Peracetic Acid in the Presence of Phosphoric Acid.—40% Peracetic acid (38 ml.) was added during 45 min. with cooling to aniline (18.6 g.) and phosphoric acid (39.2 g.) in acetone (350 ml.). Water (50 ml.) was added and the mixture neutralised with 2*N*-sodium hydroxide and evaporated to small volume. More water (250 ml.) was added and the solution extracted with ether. Paper chromatography showed the extract to contain aniline and *p*-aminophenol. Extraction of the aqueous layer, adjusted to pH 5.0 by 2*N*-hydrochloric acid, with butan-1-ol removed more *p*-aminophenol. During this last extraction a solid (2.1 g.) crystallised from the aqueous layer, and was collected. The solution, acidified to pH 2.0, yielded no amino-compounds on extraction with butanol. It was neutralised and evaporated to dryness. The residue was extracted with hot methanol, and the extract evaporated to dryness. The residue was dissolved in water and the solution adjusted to pH 5.0 and cooled, to yield needles (1.1 g.). These, and the material obtained as above, were recrystallised from 10% ethanol to yield, in both cases, needles, m. p. 191—192° with no mutual depression of m. p. Paper chromatography in solvent system (a) showed both to have the same R_F (0.35) as the *p*-aminophenyl phosphate obtained as below. The ester was isolated as sodium *p*-aminophenyl hydrogen phosphate (Found: P, 14.3; N, 6.3; Na, 11.5. $C_6H_7O_4NPNa$ requires P, 14.7; N, 6.6; Na, 10.9%). Hydrolysis of the ester with 5*N*-hydrochloric acid at 100° for 30 min. and benzooylation of the product yielded *p*-benzamidophenyl benzoate, m. p. and mixed m. p. 230—232° (Found: N, 4.6. Calc. for $C_{20}H_{15}O_3N$: N, 4.4%). *p*-Aminophenyl phosphate gave colour tests like those of 2-amino-1-naphthyl phosphate.

Disodium p-Aminophenyl Phosphate formed by the Reduction of the Nitro-compound.—Disodium *p*-nitrophenyl phosphate (0.5 g.) in 50% aqueous ethanol (50 ml.) was reduced with hydrogen and Adams catalyst (0.1 g.) at room temperature and pressure. After filtration, the solution was evaporated to dryness and the residue crystallised from aqueous ethanol (approx. 50%), to yield disodium *p*-aminophenyl phosphate as needles (0.15 g., 30%) (Found: P, 13.1; N, 5.8. $C_6H_6O_4NPNa_2$ requires P, 13.3; N, 6.0%).

Oxidation of Anthranilic Acid.—Permonophosphoric acid (10 g., in acetonitrile) was added during 30 min. to anthranilic acid (14 g.) in acetone (50 ml.) and water (50 ml.). After 4 hours' stirring and storage overnight the solution was neutralised and evaporated to small volume. The solution was adjusted to pH 4.0 and continuously extracted with ether for 24 hr. Yellow prisms crystallised from the ether extract and, after recrystallisation from alcohol, had m. p. 245—246° (1.0 g.). Paper chromatography of the ether extracts in solvent system (b) showed the presence of anthranilic acid (R_F 0.95, yellow colour after diazotisation and coupling with hexylresorcinol) and 5-hydroxyanthranilic acid (R_F 0.6, red colour with above reagents). No 3-hydroxyanthranilic acid appeared to be present (the authentic compound had R_F 0.9 and formed a pale yellow colour with the above reagents). Acidification of the aqueous layer to pH 1.0, followed by extraction with ether, gave more (0.25 g.) of the compound, m. p. 245°, which was acidic, did not diazotise, couple with hexylresorcinol, or give a colour with diazotised sulphanilic acid. The compound gave no m. p. depression with azoxybenzene-2 : 2'-dicarboxylic acid¹⁶ (Found: C, 58.8; H, 3.5; N, 10.15. Calc. for $C_{14}H_{10}O_5N_2$: C, 58.7; H, 3.5; N, 9.8%). Examination of the aqueous fraction by paper chromatography revealed no diazotisable compounds.

Attempted Oxidation of 2-Naphthylamine with Alkaline Perdiphosphate.—2-Naphthylamine (0.5 g.) was treated with perdiphosphate (1 equiv.) and the mixture examined by paper chromatography in solvent system (a). No 2-amino-1-naphthyl phosphate was formed with either potassium or ammonium perdiphosphate under the following conditions: (1) neutral aqueous solution, at room temperature up to 10 days; (2) aqueous alkaline solutions at room temperature, or at 100° for 4 hr.; (3) alkaline 50% acetone for up to 10 days at room temperature. Reaction in the presence of added phosphoric acid gave no phosphoric esters unless acetone was

¹⁶ Heller, *Ber.*, 1908, **41**, 2690.

present. However, on a preparative scale (6.3 g. of amine) the use of this method at room temperature gave only a few mg. of phosphoric ester. Experiments with aniline gave similar results.

Paper Chromatography of Acetone and Acetonitrile Solutions of Permonophosphoric Acid.—Solutions (10%) of permonophosphoric acid in acetonitrile or acetone were kept for 2 hr. at room temperature and samples of each applied to chromatography paper. The spots were neutralised with ammonia vapour, and the chromatograms developed in solvent system (a) for 16 hr. Phosphates were detected by Hanes and Isherwood's method¹³ (ascorbic acid as the reducing agent¹⁷). Oxidising substances were detected by a 5% aqueous potassium iodide spray. Permonophosphoric acid had R_F 0.25 and phosphoric acid R_F 0.35. If the acetone solution was kept for 48 hr. at room temperature only the oxidising spots at R_F 0.5 and 0.85 and phosphoric acid were detectable.

The effects of solvents on the oxidation of 2-naphthylamine were studied by dissolving the amine (0.5 g.) in the solvent (15 ml.), and adding 0.3 g. of permonophosphoric acid. The mixtures were examined by paper chromatography.

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¹⁷ Rouser and Neuman, *Fed. Proc.*, 1952, **11**, 278.
