product was saponified by refluxing it (5.5 g.) with a solution of potassium hydroxide (3.0 g.) in ethanol (50 ml.) for two hours. The potassium phthalate was filtered from the cooled mixture, and the filtrate was made exactly neutral by addition of dilute hydrochloric acid. Evaporation to dryness *in vacuo* yielded a residue which was taken up in ethyl acetate and was filtered to remove inorganic salt. From the filtrate there resulted on standing 2.5 g. of product which, when crystallized from the same solvent, melted at 125–126°.

The Periodate Oxidation of the 9,10-Dihydroxystearic Acids in Aqueous Suspension.—All of the oxidations by periodate were performed at 24° using aqueous 0.05 *M* periodate (buffered, *p*H 4.2) prepared from trisodium paraperiodate and acetic acid.[19] The periodate oxidations of both forms of 9,10-dihydroxystearic acid were carried out in aqueous suspension in the presence of a known quantity of sodium β-alkylaminopropionate in which the alkyl moiety was derived from soybean oil fatty acids. The titrations of the aliquot portions of the reaction mixtures were carried out according to the method of Fleury and Lange[20] as modified by Grangaard, Gladding and Purves.[21] Corrections were made for blanks. The results of the periodate oxidation in aqueous suspension are given in Table I.

The Periodate Oxidation of the 9,10-Dihydroxystearic Acids and the 1,9,10-Trihydroxyoctadecanes in Ethanol–Water.—Since ethanol proved to be a suitable solvent for all of the glycols under investigation, the oxidations by periodate in homogeneous medium were carried out at 24° in the following manner: The compounds (0.0200 g.) were dissolved in absolute ethanol (15 ml.); a solution of periodate (0.05 *M*, 5 ml.) was added and the oxidations were permitted to continue for the periods of time indicated in Table II. The titrations were performed as previously described and corrections were made for blanks. Perfectly clear reaction mixtures resulted in all oxidations of this type. The results obtained are given in Table II.

Identification of Pelargonic Aldehyde among the Scission Products of 1,9,10-Trihydroxyoctadecane.—1,9,10-Trihydroxyoctadecane (5.0 g., m. p. 75–76°) was dissolved in absolute ethanol (100 ml.), and 0.5 *M* periodate (50 ml.) was added. After one hour at room temperature the reaction mixture was poured into water and was extracted with ether. From the ether solution there resulted an oil (4.8 g.) which was converted, during refrigeration, to a pasty solid. This crude product was dissolved in warm Skellysolve B. Cooling yielded a small amount of solid which was probably unreacted glycol. From the filtrate there was obtained an oil which was treated with 2,4-dinitrophenylhydrazine in the conventional manner. The crude dinitrophenylhydrazone first obtained melted at 91–96°. After three recrystallizations from ethanol the product melted at 104–5° (uncor., lit. 100°).[22]

Anal. Calcd. for $C_{15}H_{22}O_4N_4$: C, 55.9; H, 6.8; N, 17.4. Found: C, 55.8; H, 6.9; N, 17.7.

Conductivity of the Borate Complexes of the 9,10-Dihydroxystearic Acids.—The conductivity measurements were carried out in a one normal solution of boric acid in absolute ethanol with the aid of an alternating current, 1000 cycle, conductivity Wheatstone bridge. The results are contained in Table III.

Summary

The results of periodate oxidation have been used to show that the hydroxyl groups are more proximal in the low-melting forms of the 9,10-dihydroxystearic acids and the 1,9,10-trihydroxyoctadecanes than in the high-melting forms.

The low-melting form of 9,10-dihydroxystearic acid has been shown to form a cyclic, acidic complex with boric acid, whereas the high-melting form does not.

MINNEAPOLIS, MINNESOTA RECEIVED AUGUST 28, 1947

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[19] (a) D. H. Grangaard, J. H. Michell and C. B. Purves, THIS JOURNAL, **61**, 1290 (1939); (b) O. A. Moe, S. E. Miller and M. H. Iwen, *ibid.*, **69**, 2621 (1947).

[20] P. Fleury and J. Lange, *J. pharm. chim.*, [8] **17**, 107, 196 (1933).

[21] D. H. Grangaard, E. K. Gladding and C. B. Purves, *Paper Trade J.*, **115**, no. 7, 41 (1942).

[22] H. H. Strain, THIS JOURNAL, **57**, 758 (1935).

[CONTRIBUTION FROM THE MORLEY CHEMICAL LABORATORY OF WESTERN RESERVE UNIVERSITY]

The Reaction of Amines with Phosphorus Pentasulfide; Thiophosphoric Amides

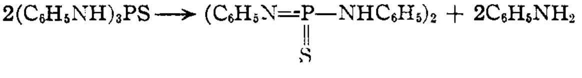
BY ALLEN C. BUCK,[1a] JOHN D. BARTLESON[1b] AND HERMAN P. LANKELMA

Previous investigations of products obtained by the action of amines on phosphorus pentasulfide have been limited to a single reaction. Knop[1c] observed that six moles of aniline and one mole of phosphorus pentasulfide heated at a temperature not exceeding 150° evolved hydrogen sulfide and gave a pungent smelling product in the form of monoclinic crystals which melted at 153°. Rudert[2] prepared the same product from aniline and thiophosphoryl chloride and showed it to be thiophosphoric trianilide, $(C_6H_5NH)_3PS$.

Knop's results were repeated in this Laboratory. A 50% yield of thiophosphoric trianilide melting at 153–154° was obtained. This product did not depress the melting point of thiophosphoric trianilide prepared from aniline and thiophosphoryl chloride. Although Knop regarded temperatures in excess of 150° to be detrimental, we obtained the maximum yield at a reaction temperature of 180°.

The anilide was not hydrolyzed upon refluxing with dilute acid or with aqueous or alcoholic potassium hydroxide, but was by heating with concentrated phosphoric acid at 130°, for two hours, and with glacial acetic acid for twenty hours.

When thiophosphoric trianilide was heated at 225° *in vacuo*, it lost aniline and formed dimeric thiophosphoric anil anilide:



$$2(C_6H_5NH)_3PS \longrightarrow (C_6H_5N{=}\underset{\underset{S}{\|}}{P}{-}NHC_6H_5)_2 + 2C_6H_5NH_2$$

Upon refluxing the anil anilide in aniline the reaction was reversed. This reaction will be discussed in a future paper.

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[1b] Standard Oil Co., Cleveland, Ohio.

[1c] Knop, *Ber.*, **20**, 3352 (1887).

[2] Rudert, *ibid.*, **26**, 565 (1893).

The addition of four moles of aniline to one mole of phosphorus pentasulfide at 30° gave a copious evolution of hydrogen sulfide and rapidly formed thiophosphoric dianilide, $(C_6H_5NH)_2PSSH$. Thiophosphoric dianilide formed salts with silver, lead and mercury ions. These salts were insoluble in water and in organic solvents and could not be purified. The dianilide, unlike the trianilide, was immediately hydrolyzed by refluxing in water, dilute acids or bases.

Thiophosphoric dianilide was converted to thiophosphoric trianilide by refluxing in aniline. This reaction indicates that the formation of thiophosphoric trianilide from six moles of aniline and one mole of phosphorus pentasulfide involves the rapid formation of thiophosphoric dianilide followed by the slower formation of the trianilide at the higher reaction temperatures.

The reaction of two moles of aniline and one mole of phosphorus pentasulfide did not give a monoanilide, $C_6H_5NHPS(SH)_2$. Instead the dianilide and unreacted phosphorus pentasulfide were obtained.

The reaction of phosphorus pentasulfide was studied with a number of additional amines both aromatic and aliphatic.

With *p*-chloroaniline excellent yields of thiophosphoric tri-*p*-chloroanilide were obtained. With *o*-chloroaniline, however, no triamide could be obtained either from phosphorus pentasulfide or thiophosphoryl chloride. Excellent yields of the diamide were obtained using a 4:1 molar ratio of *o*-chloroaniline to phosphorus pentasulfide. The failure of the trianilide to form here may be ascribed to the much weaker basic character of the *o*-chloroaniline.

With 2-naphthylamine, the product obtained was phosphoric tri-2-naphthalide instead of thiophosphoric tri-2-naphthalide. It is probable that thiophosphoric tri-2-naphthalide was first formed but was hydrolyzed to the phosphoric 2-naphthalide in the purification process which included steam distillation. Rudert[2] also obtained phosphoric tri-2-naphthalide upon recrystallizing the reaction product of 2-naphthylamine and thiophosphoryl chloride from acetic acid.

With a high boiling aliphatic amine, benzylamine, 43% yields of tribenzyl thiophosphoric amide were obtained. Low boiling aliphatic amines, such as *n*-propyl amine, would not permit sufficiently high reaction temperatures at atmospheric pressure. However, in a sealed tube, low yields of tri-*n*-propyl thiophosphoric amide were obtained.

With a secondary amine, oily products which could not be purified were usually obtained. However, two crystalline secondary amine thiophosphoric triamides were obtained. Tetrahydroquinoline gave low yields of a crystalline triamide and piperidine gave a crystalline triamide by reaction with thiophosphoryl chloride according to the method of Michaelis.[3]

The secondary amine thiophosphoric triamides, exhibited stability to prolonged reflux in dilute acids, bases, and in glacial acetic acid.

Experimental

Materials.—The phosphorus pentasulfide was a commercial grade purified by extraction with carbon bisulfide using a Soxhlet extractor. The purified product melted at 273–277°. *Anal.* Calcd. for P_2S_5: P, 27.90; S, 72.09. Found: P, 27.64; S, 69.6. The amines were purified by distillation and where necessary, previously dried over potassium hydroxide. Tetrahydroquinoline was prepared from quinoline by the method of Hoffman and Koenigs[4] and purified by the method of Rupe, *et al.*[5]

Preparation of Thiophosphoric Triamides from Amine and Phosphorus Pentasulfide.—A mixture of phosphorus pentasulfide and amine, in a molar ratio of 1:6 with a small excess of amine, was heated in a three-neck round-bottom flask equipped with a stirrer and reflux condenser. The reaction was usually highly exothermic. After the initial reaction had subsided, the mixture was heated from two to four hours at a temperature of 180° to complete the reaction. (In the case of the volatile *n*-propylamine, the mixture was heated in a sealed tube.) The excess amine was removed by steam distillation or by treatment with dilute hydrochloric acid and the residual amide was purified by crystallization from alcohol. The yields and melting points of the products were:

Amide	Yield, %	M. p., °C.
Triphenyl	50	153–154
Tri-*p*-chlorophenyl	97	225–226
Tribenzyl	43	125–126
Tripropyl	10	73–74
Tri-tetrahydroquinolyl	15	190–192

Tri-*p*-chlorophenylthiophosphoricamide. *Anal.* Calcd. for $C_{18}H_{15}Cl_3N_3$ PS: N, 9.49; P, 7.01; S, 7.2. Found: N, 9.24; P, 7.42; S 7.35.

Preparation of Thiophosphoric Diamides from Amine and Phosphorus Pentasulfide.—The amine was added dropwise to a mixture of phosphorus pentasulfide in 5 to 10 parts of toluene, with stirring. A small excess over 4 moles of amine to 1 mole of phosphorus pentasulfide was employed. The temperature was kept at 30° for two hours. The diamide separated as a white solid. It could be purified by dissolving in ice cold sodium hydroxide solution and extracting with ether to remove the amine. The diamide was then precipitated with dilute ice cold hydrochloric acid, washed with ether and carbon disulfide and dried.

Diphenylthiophosphoricamide, yield 47%, m. p. 161°–163°. *Anal.* Calcd. for $C_{12}H_{13}N_2PS_2$: N, 10.00; P, 11.07; S, 22.85. Found: N, 10.50; P, 10.90; S, 22.61. Di-*o*-chlorophenylthiophosphoric amide, yield 95%, m. p. 183–190°. It could not be recrystallized without decomposition.

Hydrolysis and Aminolysis of Thiophosphoric Diamides.—Thiophosphoric dianilide and *o*-chloroanilide, unlike the triamides were very sensitive to hydrolyses. Upon exposure to air, hydrolysis occurred slowly; rapid hydrolysis occurred upon boiling with water or treatment with aqueous acid or alkali.

The aminolysis of thiophosphoric dianilide was carried out with aniline, and of thiophosphoric di-*o*-chloroanilide with benzylamine. A mixture of 5.0 g. of thiophosphoric dianilide and 10 g. of aniline was heated at 180° for four hours. Three grams of thiophosphoric trianilide, melting point 150–153°, was obtained. It was identified by a mixed melting point.

Fifty grams of thiophosphoric di-*o*-chloroaniline was dissolved in 10.7 g. of benzylamine with cooling. The mixture was then heated to 180° for three hours. The crude product was washed with dilute hydrochloric acid to remove excess benzylamine and the residue recrystallized

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(3) Michaelis, *Ann.*, **326**, 129-258 (1903).

(4) Hoffman and Koenigs, *Ber.*, **16**, 728 (1883).

(5) Rupe, Seiberth and Kussmaul, *Helv. Chim. Acta*, **3**, 75 (1920)

from alcohol. One and six-tenths grams of tribenzyl thiophosphoric amide, melting point 121–123°, was obtained. It was identified by a mixed melting point.

Thermal Decomposition of Thiophosphoric Triamides to Dimeric Thiophosphoric Acid Imide Amides.—Thiophosphoric trianilide and thiophosphoric tribenzylamide were converted to the imide amide. Twenty-three grams of thiophosphoric trianilide was heated at 215–225° for two hours under a vacuum of 30 mm. mercury. Six grams of aniline distilled over. The residual solid was recrystallized from alcohol and gave 10 g. of thiophosphoric anil anilide, m. p. 233–235°. This product did not depress the melting point of a sample of the material prepared by the method of Michaelis and Karstens.[6] The anil anilide was readily converted back to the triamide by heating with an excess of aniline at the boiling point for four hours.

Tribenzylthiophosphoric amide was converted to the imide amide by the same method, yield 70%, m. p. 197–199°. *Anal.* Calcd. for $C_{28}H_{30}N_4P_2S_2$: N, 10.22; P, 11.31; S, 11.68; mol. wt., 548 Found: N, 10.34; P, 11.01; S, 11.68; mol. wt., 560.

The Reaction of 2-Naphthylamine and Phosphorus Pentasulfide.—A mixture of 9.2 g. of phosphorus pentasulfide, 45 g. of 2-naphthylamine and 70 g. of diethylbenzene was heated for two hours at 185° with stirring. The diethylbenzene was removed by steam distillation and the excess amine by extraction with cold alcohol. The residue was recrystallized from alcohol and gave 7 g. of phosphoric tri-2-naphthalide, m. p. 168–170°. A mixed melting point with a sample of the material prepared from 2-naphthylamine and phosphorus oxychloride by the method of Rudert[2] gave no depression.

Summary

The reaction of six moles of a primary aliphatic or aromatic amine with one mole of phosphorus pentasulfide at 130–180° gave crystalline thiophosphoric triamides. Secondary amines usually gave oily products, piperidine and tetrahydroquinoline being exceptions.

The reaction of four moles of aniline with one mole of phosphorus pentasulfide at room temperature gave thiophosphoric dianilide. This dianilide appears to be an intermediate in the formation of the trianilide. The thiophosphoric triamides are very stable toward hydrolysis; the phosphorus sulfur linkage of thiophosphoric tri-2-naphthalide is an exception. The triamides of primary amines are hydrolyzed on prolonged heating with 85% phosphoric acid or glacial acetic acid.

Thiophosphoric diamides are very sensitive to hydrolysis.

The primary amine triamides upon heating to 225°, *in vacuo*, lose amine to form a dimeric imide amide. This reaction is easily reversible.

The preparation of thiophosphoric monoanilide from aniline and phosphorus pentasulfide was unsuccessful.

CLEVELAND, OHIO RECEIVED SEPTEMBER 8, 1947

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[6] Michaelis and Karstens, *Ber.*, **28**, 1237, 1895.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

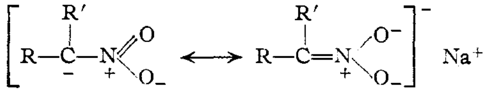
The Basis for the Reported Optical Activity of the Salts of Aliphatic Nitro Compounds: 2-Nitrobutane[1]

BY NATHAN KORNBLUM, JOHN T. PATTON[2] AND JOSEPH B. NORDMANN

The experimental basis for the report that 2-nitrobutane gives an active sodium salt[3] has been reëxamined in view of the recent finding that the optical activity attributed to the salts of 2-nitrooctane is really due to the presence of 2-octyl nitrate.[4] It has now been found that the 2-nitrobutane previously employed was contaminated with 2-butyl nitrate and that the activity ascribed to the sodium salt of 2-nitrobutane is due to this impurity.

Dextrorotatory-2-nitrobutane prepared according to the earlier workers[3] is only partially soluble in aqueous sodium hydroxide. The resulting aqueous alkaline solution, which contains the sodium salt of 2-nitrobutane, is devoid of activity whereas the insoluble portion is still *dextro*rotatory. Examination of the alkali insoluble material reveals that it is *d*-2-butyl nitrate $[\alpha]^{24}\text{D}$ +7.0°.

The "*d*-2-nitrobutane" was freed of *d*-2-butyl nitrate, and any other contaminants, by treatment with cold 96% sulfuric acid. Thus purified, *d*-2-nitrobutane has $[\alpha]^{20}\text{D}$ +7.2°, gives a negative test for nitrate esters, and is completely soluble in aqueous sodium hydroxide; the resulting solution is inactive. When sodium methoxide is used as the base the sodium salt is again devoid of activity and the 2-bromo-2-nitrobutane produced by brominating this salt is also inactive. These results, as well as the various other properties of the salts of aliphatic nitro compounds, lead to the conclusion that they possess the hybrid structure I.[5]



$$\left[R-\overset{R'}{\underset{-}{C}}-\overset{+}{N}\begin{matrix}\nearrow O\\ \searrow O^-\end{matrix} \longleftrightarrow R-\overset{R'}{C}=\overset{+}{N}\begin{matrix}\nearrow O^-\\ \searrow O^-\end{matrix}\right]^- Na^+$$

I

In addition to establishing I as the structure of the salts of aliphatic nitro compounds the present investigation corroborates the recent observation[4] that, contrary to the accepted view, the reaction of an alkyl halide with silver nitrite (The Victor

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[1] Presented at the Atlantic City meeting of the American Chemical Society, April, 1947.

[2] Allied Chemical and Dye Fellow 1945–1947.

[3] Kuhn and Albrecht, *Ber.*, **60**, 1297 (1927).

[4] Kornblum, Lichtin, Patton and Iffland, THIS JOURNAL, **69**, 307 (1947).

[5] L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 67.