Experimental

***p,p'*-Ditrityldiphenylamine.**—The following substances were refluxed for eight hours: 0.02 mole (5.58 g.) of trityl chloride, 0.01 mole (1.69 g.) of diphenylamine and 5 ml. of chlorobenzene. During the refluxing hydrochloric acid was evolved. The chlorobenzene was mostly evaporated and then the remaining semisolid mass was extracted with 5 ml. of *o*-dichlorobenzene at about 150°. After washing with hot chlorobenzene a fine white powder remained; yield 3.8 g. (58%), m. p. 343-348°. The compound was crystallized from *o*-dichlorobenzene and then melted at 350-351°.

Anal. Calcd. for $C_{50}H_{39}N$: C, 91.84; H, 6.02; N, 2.14. Found: C, 91.37, 91.58; H, 6.10, 6.23; N, 2.24.

The extract from this compound was evaporated to provide a 0.77 g. yield (19%) of *p*-trityldiphenylamine which melted at 245-248°.

The reaction of equimolecular amounts of the starting materials in boiling benzene does not go to completion in the absence of added catalyst during four hours. Under these conditions *p*-trityldiphenylamine is the main product. When a higher boiling solvent such as toluene, xylene or chlorobenzene is used, however, the trityl chloride is consumed and then the ditrityl derivative is the main product. The reaction of amine and chloride in 5:1 molar ratio in boiling chlorobenzene formed the monotrityl derivative in 85% yield. Ditrityldiphenylamine resulted in good yield by the reaction of trityl chloride with *p*-trityldiphenylamine.

p,p'-Ditrityldiphenylamine (0.200 g.) and 0.05 g. of zinc chloride was refluxed for one hour with 5 ml. of phenol and the hot mixture poured into water. The solid, which precipitated immediately, was recrystallized from benzene. It then weighed 0.27 g. and melted at 222-267°. This solid was recrystallized from benzene to give 0.155 g. of *p*-tritylphenol, m. p. 280-282° alone or mixed with an authentic specimen. The mother liquor was evaporated to dryness and extracted with hexane to remove diphenylamine which was identified by the preparation of the tetrabromo derivative, m. p. 183° alone or at 183-185° mixed with an authentic specimen. The hexane extracted residue was then crystallized from benzene to give an additional yield of 0.025 g. of *p*-tritylphenol, m. p. 280-282°. The total yield of this product thus was 0.18 g. (87%).

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Trimeric Phosphonitrilic Dibutyl and Dimethyl Ester

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In a previous paper,[1] the preparation of *polymeric* phosphonitrilic esters from polymeric phosphonitrilic chloride $(NPCl_2)_x$, has been described; it has been shown that upon treatment with alcohols, part of the halogen is replaced by alkoxyl groups, part of the PCl_2 radicals transformed into P=O.

It appeared interesting for the sake of comparison to study the alcoholysis of the lower-molecular soluble phosphonitrilic chlorides, such as the trimer. Wisseman,[2] who used alcohols with or without pyridine as condensing agent at elevated temperature, and Lipkin,[3] who employed metal alkoxides in alcoholic solution, did not obtain any well-defined products; it was shown that both hydrogen chloride and alkyl chloride were liberated in the course of the reaction.

Our own experiments have shown that it is possible to isolate by both methods the trimeric phosphonitrilic esters as colorless liquids. However, they are fairly sensitive and prone to polymerization and decomposition even under the conditions of vacuum distillation. The trimeric *phosphonitrilic dibutyl* and *dimethyl esters* $(NP(OR)_2)_3$ have been obtained in pure state, containing practically no halogen (at worst, traces). The *diallyl* ester polymerized easily to a highly viscous oil.

Phosphonitrilic Dibutyl Ester.—To a solution of 6.2 g. of trimeric phosphonitrilic chloride[4] in 26 cc. of pyridine, 31 cc. of butyl alcohol were added at 0°, with vigorous stirring. The mixture was kept at room temperature for twenty-four hours, diluted with 25 cc. of petroleum ether, treated successively with dilute hydrochloric acid, sodium bicarbonate solution and water and dried over anhydrous sodium sulfate. Distillation gave 58 g. (56%) of the desired ester; b. p. 170-171° (0.03 mm.); the remainder was a non-distillable resin, $n^{28.6}{}_D$ 1.4473; $d^{28.6}{}_4$ 1.0342. (*Anal.* Calcd. for $(C_8H_{18}O_2NP)_3$; C, 50.2; H, 9.4; N, 7.3. Found: C, 50.1; H, 9.4; N, 7.5.)

Phosphonitrilic Dimethyl Ester.—A solution of 11.6 g. of trimeric phosphonitrilic chloride in 58 cc. of benzene was added to an ice-cold solution of 4.6 g. of sodium in 50 cc. of methyl alcohol. The mixture was kept at 0° for twenty-four hours and then washed with acid, bicarbonate and water as above. The ester boiled at 127-218° under 0.1 mm. pressure. (*Anal.* Calcd. for $(C_2H_6O_2NP)_3$: C, 22.4; H, 5.6; N, 13.1. Found: C, 22.0; H, 5.2; N, 12.9.) Even under these conditions, however, the greater part of the product was converted to a water-soluble, benzene-insoluble resin with lower carbon content. (Found in different batches: C, 18.0, 16.3; H, 5.2, 5.3.) It is likely that the decomposition reaction, indicated by the analytical figures, is accompanied by condensation processes.

The observed molecular refraction of the dibutyl ester is 148.17. With the atomic equivalents 1.643 for oxygen (ether-oxygen), 4.39 for phosphorus (as in the trialkyl phosphates[5]) and 4.10 for nitrogen (as in C—N=C compounds),[6] one arrives at a theoretical value of 152.76.

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[1] Goldschmidt and Dishon, *J. Polymer Science*, **3**, 481 (1948).

[2] Wissemann, quoted by Audrieth, Steinmann and Toy, *Chem. Rev.*, **32**, 129 (1943).

[3] Lipkin, U. S. Patent 2,192,921; (*C. A.*, **34**, 4836 (1940)).

[4] Schenck and Roemer, *Ber.*, **57**, 1343 (1924).

[5] Jones, Davies and Dyke, *J. Phys. Chem.*, **37**, 583 (1933).

[6] Auwers and Ottens, *Ber.*, **57**, 446 (1924).

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Synthesis of Methyl Phthalaldehydate and Phthalaldehydic Acid by the Rosenmund Reduction[1]

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Phthalaldehydic acid is available from phthalic anhydride by various methods in an over-all yield of about 55%.[2] Its normal methyl ester, however, has been obtained only by treatment of the silver salt with methyl iodide[3] since other methods of esterification yield the pseudo-ester.[3]

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[1] From the thesis for the B.S. degree of A. Burgstahler, University of Notre Dame.

[2] Shriner and Wolf, "Organic Syntheses," Vol. XXIII, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 74.

[3] Auwers and Heinze, *Ber.*, **52**, 595 (1919).

The Rosenmund reduction[4] of the chloride of methyl hydrogen phthalate has not previously been described; in fact, there is a statement in the literature[5] to the effect that the acid chloride on warming decomposes into phthalic anhydride and methyl chloride. We have found that this decomposition can be prevented almost entirely by limiting the time of the reaction of thionyl chloride with methyl hydrogen phthalate. Under controlled conditions methyl phthalaldehydate is readily obtained from the phthalate ester in a reproducible yield of about 80%. It can be converted into phthalaldehydic acid in 90% yield by acid hydrolysis; the over-all yield of this acid from phthalic anhydride is 60%.

Experimental[6]

Preparation of Methyl Hydrogen Phthalate.—Phthalic anhydride (74 g., 0.5 mole) and absolute methanol (50 ml.) were refluxed for two hours. The excess methanol was distilled and 25 ml. of dry benzene was added. Distillation was continued for ten minutes to ensure removal of unreacted methanol, whose presence impeded crystallization of the product. The residue was filtered hot through a cotton plug into a one-liter flask and diluted to about 300 ml. with benzene. Ligroin (b. p. 30-60°) was added to the solution until the volume approximated 600 ml., at which point crystallization commenced. After standing overnight in the refrigerator, the product was collected, washed twice with 50-ml. portions of ligroin and dried in air, giving 75 g. (83%) of pure methyl hydrogen phthalate, m. p. 82-82.5° (lit.[7] 82.4-82.7°).

Conversion of Methyl Hydrogen Phthalate to the Acid Chloride.—A mixture of 18 g. (0.1 mole) of methyl hydrogen phthalate and 50 ml. of thionyl chloride (Eastman Kodak Co. White Label grade) was refluxed exactly one hour on the water-bath. (Excessive prolongation of this heating period led to the production of considerable quantities of phthalic anhydride in the reduction product.[5] Reduction of the reflux time likewise diminished the final yield of aldehyde considerably.) The excess thionyl chloride was removed under reduced pressure. Dry benzene (three 25-ml. portions) was then added and distilled off the acid chloride *in vacuo* three times to complete the removal of unreacted thionyl chloride. The acid chloride thus prepared was used immediately in the following step.

Methyl Phthalaldehydate.—The Rosenmund procedure followed was essentially that described in "Organic Reactions."[4] Xylene (*ca.* 60 ml. for a 0.1-mole run) was employed as the solvent for the reduction. The quinoline-S poison[4] was used to the extent of 0.2 ml. per 0.1 mole run, along with 2 g. of palladium-barium sulfate catalyst.[4] The reduction started more rapidly when the catalyst was added *after* the flask containing the xylene-poison mixture had been heated to boiling for ten minutes with a slow stream of dry hydrogen passing through the solution. When the heating bath was at 175°, the acid chloride was added through the top of the condenser. Reduction proceeded best at 175-180° (bath temperature) and was complete in two to three hours as evidenced by the cessation of hydrogen chloride evolution. After removal of the catalyst by filtration and of the xylene by distillation under reduced pressure the residue was fractionated *in vacuo* through a six-inch Vigreux column. Methyl phthalaldehydate was collected at 136-138° (13 mm.) or 146-147° (17 mm.)[3] as a colorless liquid having a pleasant odor; yield, 13.1-13.8 g. (80-84%); $n^{20}\text{D}$ 1.5411. (Auwers and Heinze[3] have reported values ranging from 1.5410 to 1.5423.)

The semicarbazone of methyl phthalaldehydate crystallized from dilute methanol in clusters of white, elongated prisms melting sharply at 194.5°.

Anal. Calcd. for $C_{10}H_{11}O_3N_3$: C, 54.29; H, 5.01; N, 19.00. Found: C, 54.19; H, 4.74; N, 18.88.

Hydrolysis of Methyl Phthalaldehydate.—Methyl phthalaldehydate (5.0 g., 0.0305 mole) was refluxed for twelve hours with 25 ml. of 6 *N* hydrochloric acid. The solution was concentrated by removing the water and hydrochloric acid under reduced pressure. The residue crystallized on cooling. It was recrystallized from 20 ml. of water to yield 4.1 g. (90%) of phthalaldehydic acid melting at 93-96° (dried in a vacuum desiccator). A second recrystallization raised the melting point to 96-97°. The semicarbazone of the acid melted at 202° as reported in the literature.[8]

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[4] Mosettig and Mozingo in Adams, "Organic Reactions," Vol. IV, John Wiley and Sons, Inc., New York, N. Y., 1948, pp. 362 ff.

[5] H. Meyer, *Monatsh.*, **22**, 578 (1901).

[6] Melting and boiling points are uncorrected. Microanalysis by Micro-Tech Laboratories, Skokie, Ill.

[7] Goggans and Copenhaver, THIS JOURNAL, **61**, 2909 (1939).

[8] Liebermann, *Ber.*, **29**, 179 (1896).

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Brominations with Tetramethylammonium Bromide–Bromine Mixtures

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Recently the use of pyridine hydrobromide perbromide was suggested for certain brominations.[1] This note has prompted us to report some of our experiments, in which bromine was added to double bonds with the aid of tetramethylammonium bromide–bromine mixtures.

Tetramethylammonium bromide and bromine form two addition compounds with bromine, *viz.*, $(CH_3)_4NBr_3$ and $(CH_3)_4NBr_9$ with congruent melting points at 118.5 and 56.7°.[2]

These two compounds form a eutectic at 15.8° of the stoichiometric composition $(CH_3)_4NBr_{5.6}$; at 25°, in the composition range $(CH_3)_4NBr_{5.1}$ to $(CH_3)_4NBr_{6.2}$ the system is liquid and can be used for brominations. Particularly in such reactions which call for mild conditions, these liquids offer a number of advantages as brominating agents. Diluents and intensive cooling can be omitted. Weighing and dosage of the bromine in this form is simplified, and operations may be performed without a hood, because their bromine pressure at room temperature is only about 10 mm.

As an example, the preparation of 2,3-dibromopropanol will be described. The brominating agent contained 72.2% free bromine by weight, and was prepared as follows: 154 g. (1 mole) tetramethylammonium is dissolved in 500 g. of water, and 400 g. of (2.5 moles) bromine is added during a period of fifteen minutes under stirring. The temperature is maintained between 20 and 30° by cooling. A dark-red liquid (density, 2.33) is formed, which is drawn off the aqueous solution in a separating funnel. The yield is over 90%. However, if the aqueous solution is used again for the preparation of subsequent batches, a theoretical yield is practically achieved. To 58 g. (1 mole) of allyl alcohol, 222 g. of the brominating agent is slowly (within forty minutes) added under stirring.

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[1] Djerassi and Scholz, THIS JOURNAL, **70**, 417 (1948).

[2] The phase diagram of the system tetramethylammonium bromide and bromine has been studied in this Laboratory and the results will be published shortly.