

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 $C_{20}H_{15}N$: 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. Wissemann,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 chloride⁴ 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_D^{25} 1.4473; d_4^{25} 1.0342. (*Anal.* Calcd. for $(C_4H_9O_2NP)_3$: 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 $(C_2H_5O_2NP)_3$: 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 phosphates⁵) and 4.10 for nitrogen (as in $C-N=C$ compounds),⁶ one arrives at a theoretical value of 152.76.

(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 Phthalaldehyde and Phthalaldehydic Acid by the Rosenmund Reduction¹

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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 iodide³ since other methods of esterification yield the pseudo-ester.³

(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.*, **62**, 595 (1919).

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

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

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