52.36; H, 6.05; OCH_3, 8.33, 8.05; mol. wt. (Rast), 395, 398; sapn. equiv., 246, 242.

Isolation of Verbenalol.—Verbenalin (2 g.) was dissolved in 100 ml. of water containing 2.5 g. of crude emulsin, 25 ml. of citrate buffer (*p*H 4.5) added, and allowed to stand at 24° for one week. From the mixture which had turned dark brown, the aglucone was extracted continuously with ether, the yellow ether extract washed with water, dried, and concentrated to 5 ml. Crystalline verbenalol which separated on standing was recrystallized from ethyl acetate, acetone and alcohol to yield colorless rods, m. p. 133–134° (dec.); yield, 0.7 g. (58%); $[\alpha]^{24}D$ −20 to 21° (alcohol). When a drop of freshly prepared ferric chloride solution was added to a solution of 5 mg. of pure verbenalol in 1 ml. of water an immediate strong violet color was produced.

Anal. Calcd. for $C_{11}H_{14}O_5$: C, 58.40; H, 6.19; OCH_3, 13.71; mol. wt., 226; sapn. equiv., 226. Found: C, 58.54, 58.56; H, 6.14, 6.10; OCH_3, 14.73, 14.14; mol. wt. (Rast), 220, 216; sapn. equiv., 161, 155.

Verbenalol-2,4-dinitrophenylhydrazone.—2,4-Dinitrophenylhydrazine (0.25 g.) was dissolved in 25 ml. of warm absolute methanol, 0.25 g. of verbenalol added, and the solution refluxed on the steam-bath for one-half hour and allowed to cool. The microscopic crystals which separated (0.2 g.) were recrystallized from methanol to yield reddish-brown crystals, m. p. 179° (dec.).

Anal. Calcd. for $C_{23}H_{22}O_{11}N_8$: N, 19.11. Found: N, 19.83, 19.87.

Action of Bromine on Verbenalol.—Verbenalol (0.1143 g.) was dissolved in 50 ml. of chloroform, 25 ml. of 0.05 *N* bromine and 5 ml. of hydrochloric acid added, the mixture shaken and kept in the dark for two hours with shaking from time to time. Then 1.0 g. of potassium iodide was added and the liberated iodine titrated with 0.05 *N* thiosulfate. Upon standing after the end-point was reached the mixture continued to liberate iodine slowly.

Anal. Calcd. (for one mole of bromine absorbed): 20.22 ml. of 0.05 *N* Br. Found: 20.74 ml.

Methylation of Verbenalol.—To an absolute methanol solution of verbenalol (1.0 g. in 5 ml.) was added an ether solution (100 ml.) of diazomethane prepared from 10 g. of nitrosomethylurea. After keeping in the refrigerator for one week, incomplete methylation was indicated and the methylation was repeated on the residue with two additional portions of diazomethane prepared from 10-g. portions of nitrosomethylurea. The viscous brown residue obtained upon slow evaporation of the ether gave no coloration with ferric chloride but could not be crystallized. It was distilled at 175–180° (0.002 mm.).

Anal. Calcd. for $C_{10}H_{10}O_3(OCH_3)_2$: OCH_3, 25.83. Found: OCH_3, 22.22, 23.00.

Hydrogenation of Verbenalin.—5.01 g. of verbenalin was dissolved in 60 ml. of water, 1.0 g. of platinum oxide catalyst added, and shaken for five hours at room temperature in a bomb at a beginning pressure of 45 lb. p. s. i. The net pressure fall was approximately equivalent to two moles of hydrogen.[5] In another experiment 5.5 g. of verbenalin, dissolved in 250 ml. of absolute alcohol, was shaken with hydrogen in the presence of 1.0 g. of platinum oxide catalyst at room temperature and atmospheric pressure. The absorption of hydrogen proceeded smoothly during a period of eleven hours, the net amount (620 cc. at 0°, 760 mm.) corresponding very closely to two moles. From the latter hydrogenation mixture the catalyst was centrifuged off, the clear supernatant solution concentrated to 5 ml. and diluted with 50 ml. of chloroform, when the crude, amorphous product separated (4.5 g., m. p. 158–170°). Recrystallizations from ethyl acetate yielded colorless, glistening plates of tetrahydroverbenalin (2.8 g.), m. p. 173–174.5°. Tetrahydroverbenalin gave no color with ferric chloride, no iodoform test, did not reduce Fehling solution, but gave a beautiful silver mirror with ammoniacal silver nitrate.

Anal. Calcd. for $C_{17}H_{28}O_{10}$: C, 52.04; H, 7.14; OCH_3 7.91. Found: C, 52.48; H, 6.91; OCH_3, 8.12.

Tetrahydroverbenalol.—A mixture of tetrahydroverbenalin (2.0 g. in 75 ml. of water), crude emulsin (2.0 g.) and 20 ml. of citrate buffer (*p*H 4.5) was allowed to stand at room temperature for one week and the dark brown mixture then extracted continuously with ether. The residue, upon evaporation of the ether and crystallization from ethyl acetate and then acetone, yielded colorless plates of tetrahydroverbenalol, m. p. 123.5–124°; yield, 0.7 g. (60%). Tetrahydroverbenalol gave no color with ferric chloride, no iodoform test, did not reduce Fehling solution, but gave a beautiful silver mirror with ammoniacal silver nitrate. Its solution in aqueous alkali remained colorless during forty-eight hours and upon acidification the original tetrahydroverbenalol could be recovered.

Anal. Calcd. for $C_{11}H_{18}O_5$: C, 57.39; H, 7.83; OCH_3, 13.48. Found: C, 57.69, 57.54; H, 7.89, 7.85; OCH_3, 13.84.

Acetylation of Tetrahydroverbenalol.—A solution of tetrahydroverbenalol (0.28 g.) in 2.2 ml. of acetic anhydride and 0.3 ml. of pyridine was refluxed for two hours and poured into iced water. The separated solid was extracted with ether, and the ether extract evaporated to yield colorless crystals, which crystallized from ethyl acetate and then acetone in colorless plates (0.28 g.), m. p. 109–109.5°.

Anal. Calcd. for $C_{11}H_{16}O_3(OCOCH_3)_2$: sapn. equiv., 105.3. Found: sapn. equiv., 103.3, 99.3.

SCHOOL OF PHARMACY
UNIVERSITY OF WISCONSIN
MADISON, WISCONSIN
RECEIVED JANUARY 24, 1949

---

[5] We are indebted to Prof. Homer Adkins for this hydrogenation.

Triphenylmethyl Derivatives of Diphenylamine

BY DAVID CRAIG

The reaction of triphenylchloromethane (trityl chloride) with diphenylamine in boiling benzene was reported by Wieland and others[1] to yield *p*-trityldiphenylamine. Campbell,[2] working in this Laboratory, found that the reaction when conducted in the presence of aluminum chloride went to completion to form not only the monotrityl derivative but also a high melting by-product. To this he assigned the structure *p*-anilino-*p'*-diphenylmethyldiphenyl. More recent work has shown that Campbell's assignment of structure was based in part on an incorrect analysis for carbon. Our analyses now show that the empirical formula for this compound is $C_{50}H_{39}N$ corresponding to the composition of a ditrityldiphenylamine. The reaction of the compound with phenol in the presence of zinc chloride formed *p*-tritylphenol. Based on this reaction and the known tendency of aromatic amines to tritylate in the para-position,[3] it is inferred that the $C_{50}H_{39}N$ compound is *p,p'*-ditrityldiphenylamine. This inference is supported by the strong infrared absorption band at 2.9 microns which was found for the ditrityl as well as for the monotrityl derivative. This band is characteristic of the $>NH$ group.

---

[1] Wieland and others, *Ber.*, **52**, 893 (1919).

[2] U. S. Patent 1,902,115, March 21, 1933; U. S. Patent 1,950,-079, Mar. 14, 1934; Compare Groggins "Unit Processes in Organic Synthesis," McGraw-Hill, Inc., New York, N. Y., 1947, p. 747.

[3] (a) Iddles and Hussey, THIS JOURNAL, **63**, 2768 (1941); (b) Witten and Reid, *ibid.*, **69**, 973 (1947).

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%).

B. F. GOODRICH RESEARCH CENTER
BRECKSVILLE, OHIO
RECEIVED FEBRUARY 5, 1949

Trimeric Phosphonitrilic Dibutyl and Dimethyl Ester

BY BENJAMIN DISHON

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, $n^{28.6}\mathrm{D}$ 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.

---

[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).

DANIEL SIEFF RESEARCH INSTITUTE
WEIZMANN INSTITUTE OF SCIENCE
REHOVOTH, ISRAEL
RECEIVED JULY 20, 1948

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

BY ERNEST L. ELIEL AND ALBERT W. BURGSTAHLER

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]

---

[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).