Triphenylmethane–Calcium, 2:1.—Similar observations to those above. Evaporation of the ammonia and evacuation for 5 hr. at 27° left a pale pink solid of composition $Ca(Tr)_2(NH_3)_{1.74}$. This would correspond to 7.2% Ca. Analysis by ignition gave 5.8% Ca. Extracted by 100 ml. of ether was a colorless crystalline solid amounting to 91% of the weight of initial triphenylmethane, melting at 88°.

Indene–Calcium, 1:1.—About 20 min. after addition of the indene, the blue calcium–ammonia color suddenly disappeared and a tan precipitate appeared. (This experiment was terminated by accident and not repeated.)

Fluorene–Calcium, 1:1.—During 30 min. of stirring, the mixture gradually turned dark green, and then a dark red precipitate suddenly appeared. This change appeared to be promoted by cooling. Evaporation of the liquid ammonia left a bright red solid which became orange-yellow in 5 min. of evacuation and was bright yellow after 16 hr. *in vacuo* at 24°. Its composition was $Ca(Fl)(NH_3)_{1.46}$. In air, the solid became hot and smoked, turning dark brown. Water turned it tan without other visible change. An oily yellow-orange semi-solid was removed by extraction with 100 ml. of ether, in amount corresponding to 16% of the original fluorene. Fluorene melts at 116° in contrast to 70° for complete melting of the orange material. This material contained no calcium.

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Diphenylamino Derivatives of Carbon, Silicon, Germanium, and Phosphorus

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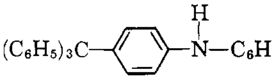
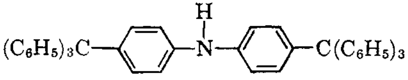
Wieland has reported the preparation[1a] of N-trityldiphenylamine (I), m.p. 172° dec., and the thermal rearrangement[1b] of I to *p*-trityldiphenylamine (III), m.p. 242° In a more recent paper, Chugunov[2] formulated the product resulting from the lithium condensation of trityl chloride and diphenylamine in refluxing toluene as I, but gave a melting point of 249–250°. In the same paper, Chugunov reports the preparation of N-triphenylsilyldiphenylamine (II) and gives a melting point of 224–225°.

$$\underset{\text{I}}{(C_6H_5)_3CN(C_6H_5)_2} \qquad \underset{\text{II}}{(C_6H_5)_3SiN(C_6H_5)_2}$$

We have confirmed that the lower melting product reported by Wieland is indeed I and find that the trityl derivative obtained by Chugunov is the isomer, *p*-trityldiphenylamine (III). Compound III and *p,p'*-ditrityldiphenylamine (IV) have been prepared by Craig[3] *via* the acid-catalyzed tritylation of diphenylamine by triphenylcarbinol. Compounds I and III may be clearly distinguished by their infrared absorption spectra. Compound III exhibits absorption bands at 3300 and 840 cm.$^{-1}$ which have been assigned[4] to the N–H stretching frequency and to the out-of-plane C–H deformation for *para*-substituted aromatic compounds, respectively. The spectrum of I does not exhibit an N–H band nor those bands characteristic of disubstituted aromatic compounds.


III


IV

When Chugunov's procedure for the preparation of N-triphenylsilyldiphenylamine (II) was repeated, a silylamine melting at 163° was obtained in poor yield. The melting point given by Chugunov (224–225°) for II is nearly identical with the melting point of hexaphenyldisiloxane (226°). Hexaphenyldisiloxane is often found as a by-product in organometallic reactions of triphenylhalosilanes.

We now report an improved general synthesis procedure for the preparation of N-substituted diphenylamines of the general type, $(C_6H_5)_{n-1}M^nN(C_6H_5)_2$.

$$(C_6H_5)_2NH + C_4H_9Li \longrightarrow (C_6H_5)_2NLi + C_4H_{10}$$

$$\text{or} \qquad (C_6H_5)_2NH + NaH \longrightarrow (C_6H_5)_2NHa + H_2$$

$$(C_6H_5)_2NLi(Na) + (C_6H_5)_{n-1}M^nCl \longrightarrow (C_6H_5)_2NM^n(C_6H_5)_{n-1}$$

$$M = C, Si, Ge, P$$

By this procedure, a 70% yield of N-trityldiphenylamine (I) was obtained along with 3% of isomer III. Similarly, a product which we propose to be N-triphenylsilyldiphenylamine (II), m.p. 162–163°, was obtained in 68% yield. N-Triphenylgermanyldiphenylamine, m.p. 153.5–155°, and N-diphenylaminodiphenylphosphine,[5] m.p. 131–132.5°, were also prepared by this route. Attempts to isolate the N-diphenylaminotriphenyltin were unsuccessful. Bis(triphenyltin) oxide which may have resulted from hydrolysis of the expected product[6] was found in the reaction mixture.

Experimental[7]

N-Lithiodiphenylamine.—A solution of 16.0 g. (0.01 mole) of diphenylamine in 70 ml. of anhydrous ether was added to an ice-cooled solution of 0.01 mole of butyllithium in 50 ml. of ether. The reaction was stirred for several hours until Color Test I[8] was negative, indicating the absence of butyllithium.

Preparation of N-Substituted Diphenylamine.—The preparation of **N-trityldiphenylamine** (I) from N-lithiodiphenylamine and from N-sodiodiphenylamine are described as examples of the procedures used.

Method A.—A solution of 0.10 mole of N-lithiodiphenylamine was added dropwise at room temperature to a stirred solution of 27.9 g. (0.10 mole) of trityl chloride in 75 ml. of THF. The reaction was mildly exothermic and became red-brown. The reaction was held at 35° for 1.5 hr. and was subsequently filtered. THF was replaced by benzene and 1.25 g. (3.2%) of *p*-trityldiphenylamine identical with III precipitated from solution. From the benzene solution, 28.8 g. (70%) of I was isolated. Two recrystallizations from ethyl acetate gave pure I, m.p. 175–177° dec.

Anal. Calcd. for $C_{31}H_{25}N$: C, 90.47; H, 6.12; N, 3.40. Found: C, 90.15; H, 6.09; N, 3.56.

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[1] (a) H. Wieland, *Ann.*, **381**, 200 (1911); (b) H. Wieland, B. Dolgow, and T. J. Albert, *Ber.*, **52**, 893 (1919).

[2] V. S. Chugunov, *J. Gen. Chem. USSR*, **20**, 2765 (1956).

[3] D. Craig, *J. Am. Chem. Soc.*, **71**, 2250 (1949).

[4] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1958.

[5] H. H. Sisler and N. L. Smith, *J. Org. Chem.*, **26**, 611 (1961).

[6] Organotin nitrogen compounds have been reported to be easily hydrolyzed [*cf.* K. Sisido and S. Kozima, *ibid.*, **27**, 4051 (1962); E. W. Abel, D. Brady, and B. R. Lerwill, *Chem. Ind.* (London), 1333 (1962)].

[7] All melting points are uncorrected. All reactions were performed under an atmosphere of dry, oxygen-free nitrogen. Tetrahydrofuran (THF) was distilled from CaH_2 prior to use.

[8] H. Gilman and F. Schulz, *J. Am. Chem. Soc.*, **47**, 2002 (1925).

Upon concentration of the benzene solution, 4.4 g. (17%) of triphenylcarbinol was also isolated.

Method B.—A solution of 5.57 g. (0.02 mole) of trityl chloride and 3.38 g. (0.02 mole) of diphenylamine in 30 ml. of THF was added to a slurry of 0.48 g. (0.02 mole) of a 52% dispersion of sodium hydride in mineral oil with stirring at room temperature. After the addition was complete, the reaction was refluxed for 4 hr. and a red-brown color slowly developed. The reaction mixture was allowed to stand overnight, 100 ml. of benzene then was added, and the reaction mixture was filtered. THF was driven off and replaced by hot petroleum ether (b.p. 30–60°). Upon cooling, 5.42 g. (66.2%) of crude I, m.p. 170–172° dec., precipitated from solution.

N-Triphenylsilyldiphenylamine (II). Method A.—The addition of triphenylchlorosilane to an equivalent amount of N-lithiodiphenylamine gave II in 68% yield, m.p. 162–163° after recrystallization from ethyl acetate.

Anal. Calcd. for $C_{30}H_{25}NSi$: C, 84.26; H, 5.89; N, 3.27; Si, 6.56; mol. wt., 427.6. Found: C, 84.23; H, 5.89; N, 3.20; Si, 6.7; mol. wt., 431.

From the reaction mixture, 5.2% of hexaphenyldisiloxane was isolated also, m.p. 225–226°, lit.[9] m.p. 226°. Identification was based on mixture melting point and comparison of its infrared spectrum with that of an authentic sample.

Method B.—The addition of triphenylchlorosilane and diphenylamine to an equivalent amount of sodium hydride gave II in 56% yield and 11% of hexaphenyldisiloxane.

Hydrolysis of N-Triphenylsilyldiphenylamine (II).—A solution of 1.0 g. (0.00234 mole) of II in 30 ml. of 95% ethanol and 2 ml. of concentrated hydrochloric acid was refluxed for 80 min. The hot solution was poured into water and the aqueous layer was extracted with ether. The ether layer was dried, evaporated to dryness, and the residue was recrystallized from petroleum ether (b.p. 60–90°) to give 0.49 g. (77.2%) of triphenylsilanol identified by mixture melting point and comparison of its infrared spectrum with that of an authentic sample.

N-Diphenylaminodiphenylphosphine (V). Method A.—The addition of N-lithiodiphenylamine to an equivalent amount of diphenylchlorophosphine gave 58% of V, m.p. 131–132.5 after recrystallization from ethyl acetate, lit.[5] m.p. 130–132°.

Anal. Calcd. for $C_{24}H_{20}NP$: C, 81.56; H, 5.70; N, 3.96; P, 8.77. Found: C, 80.13; H, 5.74; N, 4.10; P, 8.98.

Method B.—A solution of 5.07 g. (0.030 mole) of diphenylamine in 35 ml. of THF was added dropwise with stirring to 0.036 mole of sodium hydride (52% dispersion in mineral oil). The reaction mixture was refluxed for 2 hr. A solution of 6.62 g. (0.030 mole) of diphenylchlorophosphine in 30 ml. of THF was added dropwise to the hot reaction mixture. The resulting mixture was refluxed for 2 hr., cooled, filtered, and the filtrate was concentrated under reduced pressure. The residue was recrystallized from ethyl acetate to give 7.46 g. (70.3%) of V.

N-Triphenylgermanyldiphenylamine (VI). Method A.—The addition of triphenylchlorogermane to an equivalent amount of N-lithiodiphenylamine gave 23% of crude VI, m.p. 130–153°. Two recrystallizations from petroleum ether (b.p. 60–90°) gave VI, m.p. 153.5–155°.

Anal. Calcd. for $C_{30}H_{25}GeN$: C, 76.32; H, 5.34; N, 2.97. Found: C, 76.59, 76.75; H, 5.31, 5.29; N, 2.66, 2.60.

Method B.—A solution of 3.38 g. (0.020 mole) of diphenylamine in 30 ml. of THF was added to 0.020 mole of sodium hydride (48% dispersion in mineral oil) with stirring. The reaction mixture was refluxed for 0.5 hr., cooled, and to it a mixture of 6.78 g. (0.020 mole) of triphenylchlorogermane in 40 ml. of THF was added. The reaction mixture was refluxed for 2 hr. and filtered hot. The filtrate was concentrated and extracted with a small amount of petroleum ether (b.p. 60–90°) to remove unchanged diphenylamine. The residue was extracted with ethanol, and the alcohol soluble material was recrystallized several times from petroleum ether (b.p. 60–90°) to give VI in 25.2% yield.

***p*-Trityldiphenylamine (III) and *p,p′*-Ditrityldiphenylamine (IV).**—The procedure used was essentially that of Craig.[3] A solution containing 2.79 g. (0.0174 mole) of diphenylamine, 4.84 g. (0.0174 mole) of tritylchloride, 10 ml. of concentrated hydrochloric acid in 100 ml. of glacal acetic acid was refluxed for 3 hr. The cooled reaction mixture was diluted with water and 10 ml. of diethyl ether was added. The mixture was filtered and the precipitate was extracted with benzene to give 2.4 g. (33.5%) of III, m.p. 248–255°, lit.[3] m.p. 245–248°.

Anal. Calcd. for $C_{31}H_{25}N$: C, 90.47; H, 6.12; N, 3.40. Found: C, 90.64; H, 5.92; N, 3.35.

The benzene insoluble material was washed with carbon tetrachloride and afforded 3.3 g. (61.5%) of IV, m.p. 350–356°, lit. m.p. 350–351°.

Anal. Calcd. for $C_{50}H_{39}N$: C, 91.84; H, 6.01; N, 2.14. Found: C, 91.00; H, 5.92; N, 2.18.

The procedure of Chuganov[1] was repeated. A mixture of 14.0 g. (0.050 mole) of trityl chloride, 9.0 g. (0.056 mole) of diphenylamine, and 1.4 g. (0.203 g.-atom) of freshly cut lithium wire in 50 ml. of toluene was refluxed with stirring under nitrogen for 22 hr. From the reaction mixture, the following products were isolated: 0.50 g. (5.8%) of diphenylamine; 8.6 g. (41.5%) of III, mixture melting point showed no depression and infrared spectrum was superimposable with that of III described above; and 1.74 g. (13.9%) of triphenylcarbinol identified by mixture melting point and comparison of its infrared spectrum with that of an authentic sample.

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Base-Metal Sulfides as Reductive Alkylation Catalysts

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Base-metal sulfides[1] have been investigated as catalysts for the preparation of secondary amines by the reductive alkylation[2] of primary amines with ketones in the presence of hydrogen. It was hoped to minimize

$$RNH_2 + O{=}C< + H_2 \xrightarrow{\text{cat.}} RNH{-}CH< + H_2O$$

the nuclear hydrogenation of aromatic rings, an important and undesirable side reaction in nickel[3] and in platinum-metal-[4,5] catalyzed reductive alkylations of aryl amines.

The sulfides of rhenium, iron, cobalt, nickel, molybdenum, tungsten, and nickel–tungsten showed activity in the reductive alkylation of primary amines, or their nitro precursors, with aliphatic ketones. Good results were obtained with both alkyl and aryl amines.

The desired absence of nuclear hydrogenation with aryl amines was realized. In addition, there was little or no cleavage of carbon–nitrogen bonds such as caused by platinum-metal catalysts.[4–6] Such cleavage probably involves the hydrogenolysis of an unsaturated amine formed during an intermediate stage of nuclear hydrogenation.[7] That an allylic amine is the active intermediate is suggested by the hydrogenolysis

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