worked up as described for VII. Recrystallization from ethanol gave product of m.p. 115°, $[\alpha]^{25}D$ +319.8° (*c* 1.26, chloroform). Reaction with TTC and SNP gave no color until after reduction with lithium aluminum hydride in diethyl ether.

Anal. Calcd for $C_{20}H_{30}O_{12}S_2$: S, 12.17; Rast mol. wt., 526. Found: S, 11.87; Rast mol. wt., 517.

Acknowledgment.—The authors gratefully acknowledge grants from the U. S. Department of Health, Education and Welfare and from the Corn Industries Research Foundation which helped support this work.

Reactions of Calcium with Organonitrogen Compounds and Aromatic Hydrocarbons[1]

Allen R. Utke and R. T. Sanderson[2]

Department of Chemistry, University of Iowa, Iowa City, Iowa

Received December 16, 1963

In a recent note[3] we described the reaction by which calcium in liquid ammonia and pyridine and methylpyridines form highly reactive compounds. We have also conducted exploratory investigations of reactions between ammonia solutions of calcium and other organonitrogen compounds, making similar observations. Following the suggestion that these reactions may involve electron addition to the aromatic rings by the calcium–ammonia system, we extended this investigation to aromatic hydrocarbons and observed similar reactions. Evaporation of the excess ammonia led to isolation of insoluble solid products that were mostly highly colored, easily hydrolyzed, and highly reactive with air. These products have not been well-characterized, but we wish to report them here in the hope of interesting others in studying them further.

Empirical compositions of the products together with color and general order of reactivity are given in Table I for the nitrogen compounds and in Table II for the hydrocarbons. Some evidence of reaction was also noted with ethylenediamine and piperidine, but not with benzene or tetrahydrofuran.

Experimental

Reagents.—Calcium metal was about 98% pure electrolytic lump from Fisher Scientific Co. Spectrographic analysis showed the major impurities to be magnesium and strontium, with minor amounts of manganese, aluminum, and copper and only a trace of iron. It was granulated in an inert atmosphere immediately before use. Ammonia was commercial liquefied anhydrous dried over solid potassium hydroxide. Ethylenediamine, 98–100%, was obtained from Matheson Coleman and Bell, stored over solid potassium hydroxide, and refluxed over barium oxide prior to distillation for use. Benzene from Fisher Scientific Co. and tetrahydrofuran from Matheson Coleman and Bell were dried over sodium wire before use. Acridine and 3-methylisoquinoline, both from Eastman, were recrystallized from ether, as were pyrene and 2,6-diaminopyridine from Reilly Tar and Chemical Corp. Indene, Eastman practical, was redistilled (b.p. 181°, lit. 182.4°). Diphenylethylene was a student preparation, boiling at 114° (1 mm.), as was tetraphenylethylene, m.p. 227–228°, lit. 227°. Freshly opened samples were used of phenanthrene and diphenyl from Matheson Coleman and Bell, purified naphthalene from Fisher Scientific Co., 1,10-phenanthroline and 2,2′-dipyridylamine from Aldrich Chemical Co., and Eastman triphenylmethane and 2,2′-dipyridine. Other reagents used as obtained from the suppliers were 2-aminopyridine from Matheson Co., m.p. 58–60°, chrysene and fluoranthene (95% minimum) from Reilly Tar and Chemical Corp., Eastman 2-amino-5-methylpyridine, anthracene, fluorene (98%), triphenylamine, and Paragon Testing Laboratories diphenylamine. Other chemicals used were standard laboratory reagents.

Table I

Calcium Organonitrogen Compositions and Properties

Reagent (R)	Empirical formula[a]	Color	Air reactivity[b]
Quinoline	$CaRA_{1.54}$	Red-brown	L
	$CaRA$	Black	L
	$CaR_{1.46}$	Black	L
	$CaR_2A_{0.52}$	Black	L
3-Methylisoquinoline	$CaRA_{1.88}$	Orange-brown	H
Phenanthridine	$CaRA_{1.78}$	Orange-brown	M
Acridine	$CaRA_{1.69}$	Tan	M
2,2′-Dipyridine	$Ca_2RA_{1.29}$	Violet-black	M
1,10-Phenanthroline	$CaRA_{0.74}$	Purple	M
2-Aminopyridine	$CaRA_{0.88}$	White	H
	CaR_2	White	L
2-Amino-5-methylpyridine	$CaRA_{0.72}$	White	M
2,2′-Dipyridylamine	$CaRA_{0.73}$	Yellow	H
	$CaR_2A_{0.33}$	Light green	L
Diphenylamine	$CaRA_{2.13}$	Light green	H
	$CaR_2A_{0.83}$	Tan	M
Triphenylamine	$CaRA_{1.44}$	Tan	L

[a] A = NH_3. [b] H = high reactivity, incandescence, sometimes throwing off sparks; M = medium reactivity, immediate color change with evolution of heat and smoke, sometimes setting fire to paper in contact with it; L = low reactivity, only slightly exothermic with air or water.

Table II

Calcium Hydrocarbon Compositions and Properties

Reagent (R)	Empirical formula[a]	Color	Air reactivity[b]
Diphenyl	$CaRA_{1.48}$	Orange-brown	L
Naphthalene	$CaRA_{2.07}$	Light red	H
	$CaRA_{1.62}$	Light red	H
Anthracene	$CaRA_{1.49}$	Light green	H
Phenanthrene	$CaRA_{1.84}$	Tan	L
Chrysene	$CaRA_{1.81}$	Violet	M
Pyrene	$CaRA_{2.04}$	Red-violet	M
Fluoranthene	$CaRA_{1.70}$	Orange-green	L
Diphenylethylene	$CaRA_{2.06}$	Green	L
Tetraphenylethylene	$CaRA_{1.44}$	Light red	L

[a] A = NH_3. [b] See footnote *b*, Table I.

Apparatus and General Procedure.—These were identical with those described in detail in our earlier note.[3] Briefly the nitrogen compound or hydrocarbon was added to the calcium–ammonia solution at about −70°, excess ammonia was evaporated at its boiling point, and after long evacuation of the residue at room temperature, its composition was estimated by weight difference

Quinoline–Calcium, 1:1.—Two experiments were run with similar results. Formation of a red-brown solid was observed after evaporation of the ammonia and evacuation, 39 hr. at 27° for one product and 22 hr. at 31° for the other. The compositions were $Ca(Q)(NH_3)_{1.52}$ and $Ca(Q)(NH_3)_{1.43}$ The first product did not react very obviously with air except to change to a yellowish tan. It reacted with water forming a yellow solid that dissolved in dilute hydrochloric acid. Analysis of this solution showed 48.9% of the original quinoline to be present.

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[1] Taken from the dissertation submitted to the University of Iowa by A. R. Utke in partial fulfillment of the requirements for a Ph.D. degree, 1963.

[2] To whom communications should be addressed; during the academic year 1963–1964, Department of Chemistry, Arizona State University, Tempe, Ariz.

[3] A. R. Utke and R. T. Sanderson, *J. Org. Chem.*, **28**, 3582 (1963).

The second product was heated at 100° *in vacuo* for 15 hr., which left a black solid of composition, $Ca(Q)_{0.99}$ $(NH_3)_{0.82}$. Evacuation for 2 hr. at 150° removed only a little of the ammonia to yield $Ca(Q)_{0.99}$ $(NH_3)_{0.73}$. A sample of this in air turned to an oily orange solid after 30 min. Hydrolysis by the ether–alcohol–water method produced orange products not further examined.

Quinoline–Calcium, 2:1.—Addition of the quinoline produced a precipitate which after evaporation of the ammonia and evacuation at 50° for 41 hr. was violet-black, of composition, $Ca(Q)_{1.99}(NH_3)_{0.52}$. On standing in air, this material changed in about 10 min. to an oily brown solid, which did not appear to undergo further change over another 5-hr. period. With water, the violet-black product became warm and turned yellow.

Quinoline–Calcium, 3:1.—Addition of the quinoline caused the mixture to turn green and then red-orange. Evaporation of the ammonia left a viscous red solution containing some red solid. This was subjected to evacuation at 60° for 140 hr., leaving a black solid. Assuming all the excess weight over that of calcium to be quinoline, the composition was $Ca(Q)_{1.46}$. By weight gain, the calcium content was 17.5%; by actual analysis of the black solid, it was 17.2% (theory for $Ca_2(Q)_3$, 17.9%). Exposed to air for 1 hr., this material changed completely to an oily orange solid and, after 24 hr. in the air, this solid was extracted with 250 ml. of ether, forming a yellow solution and leaving some orange insoluble matter. Evaporation of the ether filtrate left a very viscous orange-yellow oil.

3-Methylisoquinoline–Calcium, 1:1.—This amine is not very soluble in liquid ammonia. Its addition caused formation at once of a golden yellow precipitate. Evaporation of the ammonia left a yellow solid which became orange-brown after 6 hr. evacuation at 27°. Its composition was $Ca(Q)(NH_3)_{1.88}$. In air, it smoked, became incandescent, and turned light tan. With water, heat was evolved and the solid turned tan.

Phenanthridine–Calcium, 1:1.—This amine is colorless and insoluble in liquid ammonia. Five minutes after its addition, the blue calcium–ammonia color suddenly disappeared and an orange precipitate formed. Evaporation of the ammonia left an orange-brown solid, unchanged in color after 8-hr. evacuation at 28°. Its composition was then $Ca(phen)(NH_3)_{1.78}$. In air, it became very hot, smoked, and turned dark brown. In water it evolved heat and turned yellow but did not dissolve.

Acridine–Calcium, 1:1.—The acridine used was pale yellow even though recrystallized from ether and insoluble in ammonia. After about 15 min. of stirring the acridine with the calcium–ammonia solution, a pale green precipitate appeared Evaporation of the ammonia left an almost white solid which became light tan after evacuation for 18 hr. at 31°. This material, of composition $Ca(acr)(NH_3)_{1.69}$, became warm in air, smoking slightly, and turned first dark brown and then yellow-brown. With water a little heat was evolved, and the substance turned yellow.

2,2′-Dipyridine–Calcium, 1:2.—Dipyridine is colorless and insoluble in liquid ammonia. About 10 min. after its addition, a very dark violet color developed; no solid could be seen. Evaporation of the ammonia left a dark red-violet solid that turned dark violet-black when evacuated at 26° for 11 hr. The composition was $Ca_2(bipy)(NH_3)_{1.29}$. In air it became hot, smoked, and during about 5 min. turned pale yellow. In water it evolved heat and turned yellow-green.

1,10-Phenanthroline–Calcium, 1:1.—Phenanthroline is colorless and insoluble in liquid ammonia. It was added in two equal, separate portions. The first portion showed no reaction after 15 min. of stirring. Following addition of the second portion, a dark violet-red color developed. Evaporation of the ammonia left a purple solid which did not change appearance after evacuation at 31° for 11 hr. Its composition was then $Ca(phen)(NH_3)_{0.74}$. In air it became warm and smoked but required 15 min. to change color completely to yellow. In water it also turned bright yellow, with some heat evolved.

2-Aminopyridine–Calcium, 1:1.—Addition of this compound to the calcium–ammonia solution caused prompt appearance of a green precipitate. The color lightened as the ammonia was evaporated, becoming white. No more than a trace of hydrogen was evolved. After 6 hr. of evacuation at 28°, the composition was $Ca(AP)(NH_3)_{0.88}$. In air, this substance smoked and became incandescent, turning brown. With water, it formed a fluffy white precipitate and only a trace of hydrogen.

2-Aminopyridine–Calcium, 2:1.—The aminopyridine was added in two equal portions. Addition of the first caused appearance at once of a green suspension which soon became white. The second portion was then added, with no further visible change. Evaporation of the ammonia below 0° left a grayish white solid. This was extracted with 100 ml. of diethyl ether in which 2-aminopyridine is very soluble. Only a trace of solid was present in the evaporated extract. The insoluble solid was then dried in a stream of helium and analyzed. It seemed unreactive in air but reacted vigorously in water, forming a white precipitate and yellow solution. Calcium was determined as the oxalate: 18.1, 18.6%; theory for $Ca(AP)_2$, 17.7% Ca.

In a second experiment, the aminopyridine was added all at once, producing a white precipitate and removing the blue color of the ammonia solution. After evaporation of the ammonia and evacuation for 6 hr. at 28°, the composition was $Ca(AP)(NH_3)_{0.07}$. Analysis by ignition gave Ca 16.9, 17.0%, compared to 17.5% from the weights of reagents and 17.7% theory. This substance was hygroscopic, after 72 hr. in air being half-liquefied, but otherwise it seemed unreactive.

2-Amino-5-methylpyridine–Calcium, 1:1.—Addition of the pyridine derivative caused the blue ammonia solution to change to green, and a green precipitate appeared. Evaporation of the ammonia left a white solid which after evacuation for 15 hr. at 23° had the composition, $Ca(A)(NH_3)_{0.72}$. This became hot in air and smoked, turning dark brown. With water, heat was evolved, and a tan yellow solution with fluffy white precipitate was formed.

2-Amino-5-methylpyridine–Calcium, 2:1.—Addition of this compound caused immediate formation of a white precipitate. Evaporation of the ammonia and evacuation 14 hr. at 23° left a white solid of composition $Ca(A)_2(NH_3)_{0.31}$. No change in air was visible, but a sample gained 38% in weight after 24 hr. Only a color change from white to tan was observed with water. Analysis by ignition gave Ca 16.3, 16.8%, compared to 15.3% based on the original weights of reagents. Extraction with 100 ml. of ether separated only 4.9% of the original amine, identified by m.p. 62°, lit. m.p. 63°.

2,6-Diaminopyridine–Calcium, 1:2.—Initial addition of half the pyridine compound caused no visible change. Addition of the second half produced a dark gray precipitate. Cooling of the solution below the boiling point of ammonia permitted the observation of evolution of small gas bubbles—presumably hydrogen—which continued for an hour. Evaporation of the ammonia, followed by drying in a stream of nitrogen, left a ring of pink crystals halfway up the flask walls, and an olive green powder at the bottom. The pink crystals were removed and analyzed separately. They turned slightly brownish in air and seemed only slightly soluble in water, with no visible reaction. Calcium was determined as the oxalate: 6.1, 6.3%; theory for $Ca(C_5H_7N_3)_6$, 5.8%. The olive green solid turned brown in air in 10 min. In water it was largely soluble. Calcium was determined as the oxalate: 20.2, 21.1%.

2,2′-Dipyridylamine–Calcium, 1:1.—Addition of this substance caused the solution to turn dark green at once, and then an orange-yellow precipitate formed. Evaporation of the ammonia left a greenish orange solid which turned yellow after evacuation at 26° for 11 hr. Composition was $Ca(D)(NH_3)_{0.73}$. In air, the solid grew hot and smoked, with someparts becoming incandescent and turned a blackish brown. In water the color changed at once to yellow-green, and a strange odor was observed.

2,2′-Dipyridylamine–Calcium, 2:1.—Initial observations were the same as in the preceding experiment, but removal of the ammonia left a pale green solid which retained its color after 12 hr. evacuation at 26°. The composition was then $Ca(D)_2(NH_3)_{0.33}$. The solid turned white in air during 45 min. and gained 13% in weight in 24 hr. No reaction with water was visible except immediate loss of color. Analysis by ignition gave 11.3, 11.2% Ca; theory for the above-indicated composition, 10.3% Ca. Extraction of the bulk of the product with 100 ml. of ether separated a yellow, oily semisolid having the odor of dipyridylamine. The amount was 17% of the weight of the original amine. Water added to this oil caused it to crystallize. After air drying, this yellow-orange solid melted over a range of 55–70°, in contrast with the original amine, m.p. 88°.

Diphenylamine–Calcium, 1:1.—After about 30 min. following the addition of this amine, a clear blue-green solution was formed which suddenly changed to a clear yellow solution containing a tan precipitate. Evaporation of the ammonia left a pale green solid. After 3-hr. evacuation at 25°, this color was unchanged, and the composition was Ca(D)(NH$_3$)$_{2.13}$. In air this substance became dark green at once, then smoked, glowed red-hot, and turned black. In water it turned pink with some heat being evolved.

Diphenylamine–Calcium, 2:1.—A bright yellow-green precipitate appeared within 10 min. of the addition of the amine. The ammonia was evaporated, leaving a green solid which quickly turned light brown *in vacuo*. After 25 hr. evacuation at 25°, the tan residue had the composition, Ca(D)$_2$(NH$_3$)$_{0.83}$. In air, it promptly turned dark green and black, with evolution of smoke and heat. In water, some heat was evolved and the substance turned pink.

Triphenylamine–Calcium, 1:1.—This amine is colorless and insoluble in liquid ammonia. When it was added to the calcium solution, a clear green color slowly developed over 30 min., and then suddenly the solution became clouded with an orange precipitate. Evaporation of the ammonia left a bright orange solid which lightened perceptibly during the first few minutes of evacuation. After 5-hr. evacuation at 31°, the solid was light tan, of composition Ca(T)(NH$_3$)$_{1.44}$. In either air or water it turned brown but evolved little heat. Extraction of the bulk of the product with 100 ml. of ether separated a colorless, crystalline substance melting at 112° and containing no calcium, in amount corresponding to 94% of the initial triphenylamine (m.p. 126.5°).

Ethylenediamine–Calcium, 1:1.—No visible reaction occurred when the diamine was added to the calcium–ammonia solution, but evaporation of the ammonia left a deep royal blue solid, which *in vacuo* turned gray at once. After 19 hr. evacuation at 27°, the residual solid seemed to be a mixture of gray and yellow-green particles, represented by Ca(NH$_3$)$_{2.47}$ or Ca(en)$_{0.07}$ assuming either all ammonia or all ethylenediamine was attached to the calcium. The substance smoked in air, becoming incandescent in places, and turned dark brown. With water there was some effervescence and formation of a white solid.

Ethylenediamine–Calcium, 6:1.—Again no visible reaction occurred, but evaporation of the ammonia left a deep royal blue solid which turned gray during 2 hr. *in vacuo*. After 19 hr. at 27°, evacuation left white or gray particles similar to the preceding product in behavior toward air and water. The composition corresponded to Ca(NH$_3$)$_{3.07}$ or Ca(en)$_{0.87}$.

Piperidine.—Several experiments were run in which piperidine, in quantity ranging from equimolar to large excess, was added to calcium–ammonia solutions. In none did any visible reaction occur. Evaporation of the ammonia and excess piperidine, followed by evacuation to nearly constant weight, led in each experiment to isolation of a blue-gray solid containing from 18 to 36% calcium. Since calcium hexamine is unstable *in vacuo*, whereas these products were stable, it seems probable that they contained at least some piperidine, since a mixture of calcium metal and calcium amide would contain more than 55% calcium. In air these products became incandescent, smoking and throwing off sparks. They were also highly reactive with water.

Tetrahydrofuran.—Addition of tetrahydrofuran to a calcium–ammonia solution produced no observable change even when 2 moles per mole of calcium had been added. Evaporation of the ammonia and vacuum evaporation of the tetrahydrofuran left a gray powder presumed to be metallic calcium, with perhaps some calcium amide, since approximately complete recovery of the furan was obtained.

Benzene.—For each mole of calcium in ammonia solution, 1, 2, and then 3 moles of benzene added had no visible effect. Evaporation of the ammonia left a violet-gray slurry, from which the color quickly disappeared as the solid was dried *in vacuo*. This solid, a grayish white, had the composition Ca(NH$_3$)$_{1.86}$ or Ca(NH$_2$)$_2$ but was not further investigated since no stable benzene derivative seemed indicated.

Diphenyl–Calcium, 1:1.—After addition of the diphenyl, no visible change occurred for 15 min. The mixture was then cooled to −80° and an orange precipitate suddenly appeared. Evaporation of the ammonia left an orange-red solid which became orange-brown after 12 hr. *in vacuo* at 22°, having the composition Ca(D)(NH$_3$)$_{1.48}$. In air this became only slightly warm and turned pale pink. It evolved some heat in reaction with water, forming a white solid.

Naphthalene–Calcium, 1:1.—No immediate reaction was observed when the naphthalene, which is insoluble in liquid ammonia, was added. Dry tetrahydrofuran (2 ml.) was then added, whereupon the blue of the ammonia solution disappeared at once, and an orange solid precipitated which rapidly became bright green. Evaporation of the ammonia left a violet-red solid, which on further evacuation faded to a very pale pink after 3 hr. at 28°. The formula after 5 min. was Ca(N)(NH$_3$)$_{2.07}$; compositions after continued evacuation were not determined accurately because of volatilization of naphthalene as well as ammonia.

In another experiment, no tetrahydrofuran was added. After about 30 min. at temperatures near −34°, the mixture was cooled to −80° which appeared to initiate reaction. Evaporation of the ammonia left a violet-red solid which faded perceptibly in 5 min. of evacuation and became light red after 11 hr. at 22°. The composition was uncertain since the product weight indicated the loss of naphthalene. In air, the solid smoked and became incandescent in spots, turning dark brown. Water turned the solid white, and the odor of naphthalene was detected.

Anthracene–Calcium, 1:1.—Anthracene is insoluble in liquid ammonia and caused no visible change for 5 min., when an orange-green precipitate suddenly appeared. Evaporation of the ammonia and evacuation for 11 hr. at 28° left a light green solid of composition Ca(A)(NH$_3$)$_{1.49}$. In air this smoked, became incandescent, and turned tan. With water, a little heat was evolved and an insoluble tan solid remained.

Phenanthrene–Calcium, 1:1.—Phenanthrene is insoluble in liquid ammonia, but its addition caused the ammonia solution to turn green promptly, and in about 3 min. it changed again, a red precipitate appearing. Evaporation of the ammonia left an orange-red solid which was light tan after 7 hr. evacuation at 22° and of composition Ca(Ph)(NA$_3$)$_{1.84}$. This became pale pink in air without other visible reaction. With water it became warm and an insoluble solid remained.

Chrysene–Calcium, 1:1.—Almost at once, with the addition of this ammonia-insoluble compound, a purple-violet color began forming, and a purple precipitate appeared in about 5 min. Evaporation of the ammonia left a purple solid which changed to a violet powder after evacuation for 6 hr. at 22°. The composition was Ca(Ch)(NH$_3$)$_{1.81}$. In air this became slightly warm and turned greenish brown. The only visible change in water was to a yellow color.

Pyrene–Calcium, 1:1.—About 15 min. after addition of this compound no visible change had occurred. The mixture was then cooled to −80° and a bright red precipitate suddenly appeared. Evaporation of the ammonia left a bright red solid. This, after 7-hr. evacuation at 25°, became a bright violet-red powder, of composition, Ca(Py)(NH$_3$)$_{2.04}$. In air this substance at once evolved heat and smoke and turned yellow-green. Water turned it the same color.

Fluoranthene–Calcium, 1:1.—A few minutes after this ammonia insoluble hydrocarbon was added, a bright red precipitate suddenly appeared. After the ammonia was evaporated, the solid turned orange. Evacuation at 27° for 3 hr. left a greenish orange solid of composition, Ca(Fl)(NH$_3$)$_{1.70}$. This only became slightly warm in air, turning brown, and was largely insoluble in water.

Diphenylethylene–Calcium, 1:1.—This hydrocarbon, which is ammonia insoluble, was added with stirring. Slowly, over about 1-hr., the blue color changed to dark green, and then a bright orange precipitate suddenly formed. Evaporation of the ammonia left a moist blue-green solid which remained sludge-like even after 12 hr. *in vacuo* at 25°. The composition was Ca(Dip)(NH$_3$)$_{2.06}$. In air, this material quickly turned black; in water it turned white. No other reaction was observed.

Tetraphenylethylene–Calcium, 1:1.—After about 1 hr. following the addition of this hydrocarbon, the blue of the calcium–ammonia solution suddenly changed to a dark violet purple. No precipitate could be seen. Evaporation of the ammonia left a violet purple powder which changed *in vacuo* to light red. After 3-hr. evacuation at 25° the composition was Ca(T)(NH$_3$)$_{1.44}$. In air the solid warmed slightly and turned white; the reaction with water was similar.

Triphenylmethane–Calcium, 1:1.—An hour after addition of this ammonia insoluble compound, a bright red precipitate suddenly formed. Evaporation of the ammonia left a bright red solid that paled rapidly when evacuated. After 5 hr. at 27° a pink solid of composition Ca(Tr)(NH$_3$)$_{2.03}$ remained. This became white in air but seemed otherwise unreactive. The only change observed with water was to a brown color. Extraction of the product with 100 ml. of ether separated a colorless solid containing no calcium and amounting to 96% of the weight of the original triphenylmethane, melting at 82° (triphenylmethane, m.p. 92.5°).

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.

Acknowledgment.—The authors acknowledge with thanks the support of the National Science Foundation in this work.

Diphenylamino Derivatives of Carbon, Silicon, Germanium, and Phosphorus

GEORGE BAUM, WILLIAM L. LEHN, AND CHRIST TAMBORSKI

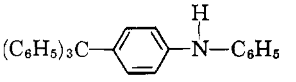
Nonmetallic Materials Division, Polymer Branch, Air Force Materials Laboratory, Wright-Patterson Air Force Base, Ohio

Received October 24, 1963

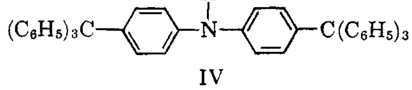
Wieland has reported the preparation[1a] of N-trityldiphenylamine (I), m.p. 172° dec., and the thermal rearrangement[1b] of I to *p*-trityldiphenylamine (III), m.p. 242° In a more recent paper, Chugunov[2] formulated the product resulting from the lithium condensation of trityl chloride and diphenylamine 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, $(C_6H_5)_{n-1}M^nN(C_6H_5)_2$.

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

or

$$(C_6H_5)_2NH + NaH \longrightarrow (C_6H_5)_2NHa + H_2$$

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

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

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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[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.

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