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

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

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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TABLE I

REDUCTIVE ALKYLATIONS[a]

Catalyst		Amine or nitro compd.		Ketone		Temp., °C.	Pressure, p.s.i.g.	Time, hr.	Products, mole % yield
Compd.	Wt., g.	Compd.	moles	Compd.	moles				
Re sulfide	2.5	Aniline	0.75	Acetone	2.25	140	1200–1400	4.4	N-Isopropylaniline, 90%[b, c]
Mo sulfide	10.0	Aniline	0.75	Acetone	2.25	185	1400–1600	3.5	N-Isopropylaniline, 91%[b]; aniline, 4%[b, d]
Ni–W sulfide	10.0	Aniline	0.75	Acetone	2.25	185	1400–1600	2.8	N-Isopropylaniline, 90%[b, e]; aniline, 8%[b, e]
Mo sulfide	20.0	N-Phenyl-*p*-phenylenediamine	0.80	Acetone	4.5	180–190	500–700	5.5	N-Isopropyl-N'-phenyl-*p*-phenylenediamine, 100%[f]
Ni sulfide	[g]	N-Phenyl-*p*-phenylenediamine	0.50	Acetone	2.18	210	1000–1800	6.3	N-Isopropyl-N'-phenyl-*p*-phenylenediamine, 77%[h]; N-phenyl-*p*-phenylenediamine, 19%[i, j]
W sulfide	16.0	N-Phenyl-*p*-phenylenediamine	0.75	Methyl ethyl ketone	3.0	245	1900–2550	2.5	N-Phenyl-N'-*sec*-butyl-*p*-phenylenediamine, 86%[b]; N-phenyl-*p*-phenylenediamine, 7%[i, k]
Fe sulfide	10.0[l]	Nitrobenzene	0.20	Acetone	2.72	180	1600–1800	3.6	N-Isopropylaniline, 12%[b]; aniline, 48%[b]; nitrobenzene, 30%[b]
Co sulfide	11.5[l]	*p*-Nitroaniline	0.30	Methyl ethyl ketone	1.80	110–150 180	1200–1400	0.1 6	N,N'-Di-*sec*-butyl-*p*-phenylenediamine, 94%[b]
Mo sulfide	10.0	Cyclohexylamine	0.50	Cyclohexanone[m]	0.50	190	1150–1700	5	Dicyclohexylamine, 88%[b]
Ni sulfide[n]	15.0	Cyclohexylamine	1.0	Cyclohexanone	1.90	180	1400–1700	14	Dicyclohexylamine, 95.5%[o]

[a] Each experiment was run in a 600-ml. Magne-Dash autoclave or a 1-l. stirred autoclave with a turbine impeller. [b] Determined by gas–liquid chromatographic analysis (g.l.c.). [c] Hydrogen absorption was *ca.* 280% of theory; g.l.c. analysis of the distillate showed that most of the excess acetone had been reduced to isopropyl alcohol. [d] No isopropyl alcohol, cyclohexylamine, or N-isopropylcyclohexylamine (determined by g.l.c.); negligible isopropylamine and diisopropylamine (determined by titration of distillate for base). [e] Weight % of topped residue product. [f] Topped residue product, m.p. 67–77.5° (mostly 70.5–77.5°); pure compound, m.p. 79.5–80°. The distillate was shown by titration for base to contain little or no aliphatic amines, and by g.l.c. to contain little or no isopropyl alcohol. [g] Prepared *in situ* from *ca.* 10 g. (on dry basis) of Raney nickel and 0.64 g. of sulfur. [h] Identified and analyzed by infrared. [i] Identified by infrared and analyzed by colorimetric determination of reaction product with salicylaldehyde in glacial acetic acid. [j] Distillate shown by titration for base to contain *ca.* 2 mole % yield of aliphatic amines, and by g.l.c. to contain *ca.* 10 mole % yield (based on acetone) of isopropyl alcohol. [k] Distillate shown by titration for base to contain *ca.* 1 mole % yield of aliphatic amines, and by g.l.c. to contain *ca.* 13.5 mole % yield (based on methyl ethyl ketone) of *sec*-butyl alcohol. [l] Weight given on dry basis. [m] Xylene (150 ml.) added as solvent. [n] Girdler T-920. [o] Isolated and identified by infrared as the hydrochloride. Chlorine analysis of 15.5% (theory is 16.3%) indicates 95% purity and actual yield of 91 mole %.

of benzyl amines[8] and the salts of allylic and propargylic amines.[9]

The use of rhenium sulfide resulted in hydrogenation of excess ketone to the corresponding alcohol. Little or no ketone reduction, a major disadvantage of copper chromite catalysts,[10] was observed with the other sulfides except under rather severe reaction conditions with nickel sulfide and with tungsten sulfide.

Rhenium sulfide appears to be the most active, and iron sulfide and tungsten sulfide the least active of the catalysts tested. However, variations both in reaction conditions and methods of catalyst preparation preclude all but gross qualitative comparisons.

Base-metal sulfides often will be the catalysts of choice for reductive alkylations because of their extreme resistance to poisoning[1] and their ability to minimize nuclear hydrogenation, carbon–nitrogen cleavage, and, in most cases, ketone reduction.

Experimental

Rhenium heptasulfide was prepared as described in the literature.[1] Cobalt polysulfide was prepared as described in the literature[11] and used as an isopropyl alcohol paste containing 13.5 wt. % solids. Iron sulfide was prepared by the addition of a solution of 40.4 g. (0.10 mole) of ferric nitrate, $Fe(NO_3)_3\cdot 9H_2O$, in 200 ml. of water to a solution of 24.0 g. (0.10 mole) of sodium sulfide, $Na_2S\cdot 9H_2O$, and 6.4 g. (0.20 mole) of sulfur in 200 ml. of water at *ca.* 40°. The black precipitate was filtered and washed several times with water and then twice with isopropyl alcohol. The iron sulfide was used as an isopropyl alcohol paste containing 42% solids. It was observed to turn rust brown on exposure to air.

A powdered tungsten disulfide (Sylvania TTC-657) was obtained from Sylvania Electric Products, Inc. Powdered 20% molybdenum sulfide on alumina (Girdler T-318) was obtained from the Chemetron Corp. Nickel–tungsten sulfide on alumina (6% Ni, 19% W, Harshaw Ni-4405E) was obtained from the Harshaw Chemical Co. as $^1/_8$-in. extrusions and was powdered before use. Nickel sulfide on activated Montmorillonite clay suspended in hardened cottonseed oil and containing 15% Ni (Girdler T-920) was obtained from the Chemetron Corp. A second nickel sulfide catalyst was prepared *in situ* from about 10 g. (on a dry basis) of Raney nickel and 0.64 g. of sulfur.

The results are summarized in Table I. A detailed description of one experiment is given to illustrate the experimental procedure.

To a 1-l. stainless steel autoclave fitted with a turbine agitator were added 147 g. (0.80 mole) of N-phenyl-*p*-phenylenediamine, 261 g. (4.5 moles) of acetone, and 20.0 g. of 20% molybdenum sulfide-on-alumina catalyst (Girdler T-318). The autoclave was sealed and purged first with nitrogen and then with hydrogen; hydrogen was added to a pressure of 500 p.s.i.g. The reaction

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(8) W. H. Hartung and R. Simonoff, "Organic Reactions," Coll. Vol. 7, John Wiley and Sons, Inc., New York, N. Y., 1953, p. 263.

(9) R. Epsztein, M. Olomucki, and I. Marszak, *Bull. soc. chim. France*, 779 (1952).

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(11) M. S. Farlow, M. Hunt, C. M. Langkammerer, W. A. Lazier, W. J. Peppel, and F. K. Signaigo, *J. Am. Chem. Soc.*, **70**, 1392 (1948).

mixture was heated with agitation for 5.5 hr. at 180–190° and 500–700 p.s.i.g. There was little or no hydrogen absorption in the last 0.5 hr. The autoclave was cooled and depressurized and its contents were filtered to remove the catalyst. The filtrate was concentrated under reduced pressure until the pot temperature reached 185° at 22 mm. The residue product consisted of 182 g. (quantitative yield) of N-isopropyl-N′-phenyl-*p*-phenylenediamine, m.p. 67–77.5° (mostly 70.5–77.5°), identified by its infrared spectrum. The distillate was shown by titration to contain little or no aliphatic amines, indicating the absence of carbon–nitrogen cleavage, and was shown by gas–liquid chromatographic analysis to contain little or no isopropyl alcohol, indicating the lack of ketone reduction.

Organotin Chemistry. IV.[1] Reduction of Hexaorganoditins with Lithium Aluminum Hydride

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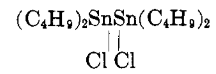
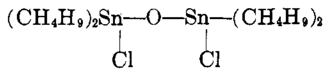
Noltes and van der Kerk[2] have reported the reductive cleavage of the tetrabutyldichloroditin (I), re-


$$\underset{\text{Cl}}{(C_4H_9)_2Sn}\underset{\text{Cl}}{Sn(C_4H_9)_2}$$

I

ported by Johnson and Fritz,[3] to yield dibutyltin dihydride. Subsequently, I has been reformulated as bistetrabutyldichlorotin oxide (II).[4]


$$(CH_4H_9)_2\underset{\text{Cl}}{Sn}—O—\underset{\text{Cl}}{Sn}—(CH_4H_9)_2$$

II

Therefore, the work of Noltes and van der Kerk must be taken as evidence for reduction of the tin–oxygen bond. This hypothesis was further strengthened by the work of Considine and Ventura[5] who reduced bistributyltin oxide with lithium aluminum hydride and obtained good yields of tributylin hydride.

It, therefore, seemed appropriate to determine whether the Sn–Sn bond was, in fact, cleaved by lithium aluminum hydride.

The cleavage of ditins with reagents such as lithium in tetrahydrofuran is well-known. Both hexabutylditin and hexaphenylditin have been reduced with the above reagent to yield the corresponding triorganotin hydride.[6]

Table I

Reaction of Hexabutylditin with Lithium Aluminum Hydride

Solvent	Temp., °C.	Time, hr.	Products after work-up (%)
Ether	35	18	Recovered ditin (90), Bu_3SnH (4)
Tetrahydrofuran	64	18	Recovered ditin (73), Bu_3SnH (18)
Tetrahydrofuran	64	168	Recovered ditin (71), Bu_3SnH (19)
Dioxane	100	3	Recovered ditin (85), Bu_3SnH (10)
Dioxane	100	6.5	Recovered ditin (80), Bu_3SnH (10) (remainder tar)
Dioxane	100	21	Recovered ditin (26), Bu_3SnH (5), Bu_2SnO (33), Sn metal (5) (remainder tarry products)
Diglyme	135	2.5	Recovered ditin (20), Bu_3SnH (19), Bu_2SnO (22), Sn metal (17) (remainder tar)

Hexabutylditin was treated with a large excess of lithium aluminum hydride in various solvents at different temperatures for different time periods. The results are shown in Table I. The reaction is complex. It appears to be an equilibrium reaction at lower temperatures giving, as the major cleavage product, tributyltin hydride. Presumably, the first step in the reaction is cleavage of the ditin by hydride ion (or its equivalent) as indicated below.

$$(C_4H_9)_3SnSn(C_4H_9)_3 \overset{H^-}{\rightleftharpoons} (C_4H_9)_3SnH + (C_4H_9)_3Sn^-$$

The anion is neutralized by a cation such as Li^+ or its equivalent to form tributyltin lithium or its equivalent. Hydrolysis of this compound would give additional amounts of tributyltin hydride as well as regenerating starting material. The reverse reaction involved in the equilibrium, the regeneration of starting hexabutylditin, could be the attack of the tributyltin anion on tributyltin hydride. Gilman[7] has demonstrated in the phenyltin series the reaction of phenyllithium with triphenyltin hydride to give tetraphenyltin and lithium hydride.

Tributyltin lithium was prepared by the procedure of Gilman and Rosenberg[8] from stannous chloride and butyllithium. The reagent was hydrolyzed with ammonium chloride solution to yield 38% tributyltin hydride and 55% dibutyltin oxide. Coates[9] was unable to detect any tributyltin hydride among the hydrolysis products of tributyltin lithium prepared by the above method, while Tamborski[10] reported a 54% yield of tributyltin hydride and a 29% yield of hexabutylditin from hydrolysis of tributyltin lithium prepared from tributyltin chloride and lithium in tetrahydrofuran. It, therefore, appears that the hydrolysis products of tributyltin lithium vary, depending on the method of preparation as well as on the reaction solvent.

An equilibrium reaction is also indicated by the data in Table I which show that both 18- and 168-hr. reflux in tetrahydrofuran gave identical yields (20%) of tributyltin hydride. In a subsequent experiment, 20 mole % of tributyltin hydride was added to hexabutylditin, and the mixture reacted with lithium aluminum hydride. Instead of the expected 40% yield of tributyltin hydride, there was only obtained a 27% total yield showing that the equilibrium had been displaced to the left by the inclusion in the reaction of one of the products.

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