The prepared isopulegone was treated with mercuric acetate as previously described. The acetoxy ketone fraction obtained in 25% yield was found to be identical in infrared and n.m.r. spectra, and in its gas chromatogram with the product obtained from (+)-pulegone. The gas chromatogram of the residue showed only the presence of 80% pulegone and 20% isopulegone.

Reductions with Triphenyltin Hydride

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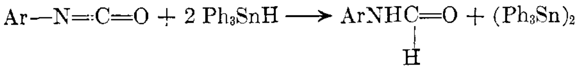
As part of a continuing study on the scope of hydrogenolyses with triphenyltin hydride we are reporting on the reactions of organo-isocyanates, isothiocyanates, and Schiff bases with triphenyltin hydride.

When phenyl isocyanate or α-naphthyl isocyanate was treated with two equivalents of triphenyltin hydride, the corresponding arylformamides were produced in 40–50% yield. This is distinctly different from the reaction of isocyanates with lithium aluminum hydride[4] which produces the corresponding N-methylamines. Another advantage of this reaction is that no hydrolysis step is required as in the case of lithium aluminum hydride reactions.



$$\mathrm{Ar{-}N{=}C{=}O} + 2\,\mathrm{Ph_3SnH} \longrightarrow \mathrm{ArNH}\underset{\mathrm{H}}{\underset{|}{\mathrm{C}}}\mathrm{{=}O} + (\mathrm{Ph_3Sn})_2$$

Ar=Ph, α-Naphthyl

The reaction of phenyl isothiocyanate with triphenyltin hydride takes a different course. From this reaction mixture, hexaphenylditin, and bis-(triphenyltin) sulfide were isolated and identified by mixture melting points with known samples. This indicates that the carbon–sulfur bond is more labile than the carbon–oxygen bond to hydrogenolysis by triphenyltin hydride. In addition to the above products a basic liquid mixture which had a strong odor of an isocyanide was obtained. Infrared spectra indicated the presence of an aryl isocyanide and aromatic amines. Diazotization of the distilled reaction products and treatment with β-naphthol gave an orange product indicating the presence of a primary aromatic amine. Strong, but not completely conclusive, evidence for the identification of the products were the vapor phase chromatographs, using two different columns and three different temperatures, which showed three bands whose retention times in all cases matched those of known samples of aniline, N-methylaniline and phenyl isocyanide.

These reductions of the isothiocyanates by triphenyltin hydride may be contrasted with the reduction with lithium aluminum hydride which reacts with aryl isothiocyanates to give the corresponding N-methylamines.[5]

Since the presence of aniline in the reaction of triphenyltin hydride with phenyl isothiocyanate suggested the presence of a Schiff base as a possible intermediate, benzalaniline was treated with triphenyltin hydride. The product N-phenylbenzylamine was isolated in 35% yield. The low yield of the amine is probably due to decomposition of the hydride by the amine formed. This amine decomposition has been noted by a number of workers.[6] The other product of the reaction was hexaphenylditin, which was identified by mixture melting point with a known sample.

Experimental

α-Naphthyl Isocyanate with Triphenyltin Hydride.—α-Naphthyl isocyanate (3.38 g., 0.02 mole) was added to 14 g. (0.040 mole) of triphenyltin hydride and heated at 80° for 1 hr. Extraction of the cooled, completely solidified, reaction mixture with hot chloroform followed by filtration and cooling afforded a white solid, m.p. 210–220°. An additional crop, m.p. 200–210°, was obtained from the mother liquor. The chloroform was finally removed under vacuum leaving a yellow-white solid, melting at 118–124°. This solid was washed with ethanol leaving behind a white solid, m.p. 220–225°. The ethanol solution was concentrated depositing a white solid, m.p. 190–200°. Water was added to the hot ethanol solution until cloudy, and on cooling a needle-like crystalline product was obtained, m.p. 116–128°. This product was dissolved in hot ethanol (charcoal), and cooled to give a white product, m.p. 123–126°. Recrystallization from benzene–heptane gave 1.43 g. (41%) of colorless α-naphthylformamide, m.p. 137.8–138.5°, whose infrared spectrum was superimposable upon that of known α-naphthylformamide. A mixture melting point with authentic α-naphthylformamide showed no depression (1:1 mixture, m.p. 137.8–138.8°).

The combined solids melting around 200° were recrystallized four times from benzene–heptane to give hexaphenylditin, m.p. 228–231°. A mixture melting point with known hexaphenylditin showed no depression.

Phenyl Isocyanate with Triphenyltin Hydride.—A mixture of 2.4 g. (0.02 mole) of phenyl isocyanate and 15 g. (0.043 mole) of triphenyltin hydride was heated at 100° for 4 hr. On cooling, the reaction mixture solidified. It was extracted overnight with water in a Soxhlet extractor. Distillation of the water *in vacuo* gave a yellow oil, which was recrystallized from ether–pentane to give a product, m.p. 45.4–47.0°. Recrystallization from ether–pentane (charcoal) did not alter the melting point, 1.35 g. (55%). The infrared spectrum was superimposable upon that of known N-phenylformamide and admixture melting point with a known sample of N-phenylformamide showed no depression (1:1 mixture, m.p. 45.6–47.1°).

The hexaphenylditin left after extraction was recrystallized from benzene–heptane to give a product, m.p. 230–231°, showing no depression upon admixture with a known sample of hexaphenylditin.

Phenyl Isothiocyanate with Triphenyltin Hydride.—A mixture of 2.8 g. (0.02 mole) of phenyl isothiocyanate and 28 g. (0.080 mole) of triphenyltin hydride was heated at 90° for 3 hr. Upon cooling, the reaction mixture solidified. It was then heated to 170° under vacuum and the vapors were collected in a flask in a Dry Ice–acetone bath. Vapor phase chromatography of the liquid product, which smelled strongly of an isocyanide, showed three bands which were identified as aniline, N-methylaniline and phenyl isocyanide by comparison with the vapor phase chromatographic behavior of known standards, using two different columns [K-polyethylene glycol (Carbowax 1500), R-polyglycol (Ucon LB-550-X)] and three different temperatures (179°, 189°, 194°) for comparison. The infrared spectrum showed the presence of aromatic amines and an aromatic isocyanide [NH stretch 3450 cm.$^{-1}$ and 3400 cm.$^{-1}$ (shoulder), C—N 1345 cm.$^{-1}$ (primary amine) and 1265 cm.$^{-1}$ (secondary amine), R—N=C 2145 cm.$^{-1}$]. Diazotization of the distilled reaction products and treatment with α-naphthol gave rise to an orange product indicating the presence of a primary aromatic amine.

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[2] To whom inquiries should be sent.

[3] Sponsored by the U. S. Army Research Office (Durham), whose support we are happy to acknowledge.

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The solid reaction mixture left after the distillation was extracted with hot chloroform and filtered. On cooling it deposited a white solid melting 200–210°. Recrystallization of this solid from chloroform and then from benzene–heptane raised the melting point to 228–231°, which showed no depression on admixture melting point with known hexaphenylditin.

The chloroform filtrate was evaporated *in vacuo* and the resulting yellow solid was washed with ethanol leaving a white solid, m.p. 120–130°, and a yellow ethanol solution. Recrystallization of this white solid from benzene–heptane gave a product melting 143.5–145.0°. A mixture melting point with a sample of known bis-(triphenyltin) sulfide showed no depression.

Benzalaniline with Triphenyltin Hydride.—Benzalaniline (1.81 g., 0.10 mole) was mixed with 10.5 g. (0.030 mole) triphenyltin hydride and heated at 124° for 22 hr. On cooling, the reaction mixture solidified and was extracted with hot methanol. The solid remaining was recrystallized from chloroform and an admixture melting point with hexaphenylditin showed no depression.

The methanol solution was evaporated under vacuum leaving a brownish oil, which was taken up in ether and extracted with 10% hydrochloric acid. Treatment with 10% sodium hydroxide, extraction with ether, drying the ether layer over sodium sulfate, and distillation of the ether left a brownish red oil to which pentane was added. Upon standing in a refrigerator overnight, a solid was obtained, m.p. 32.6–35.3°. Recrystallization from ethanol–water gave 0.65 g. (35%) of colorless product, 35.4–36.5° (lit. 37°).

The **phenylthiourea derivative** was prepared by mixing 0.185 g. of the N-phenylbenzylamine with 0.135 g. of phenyl isothiocyanate and allowing the mixture to stand overnight. Addition of hexane with cooling and scratching gave a white solid with a melting point of 80–83°. Recrystallization from ethanol–water gave colorless crystals, m.p. 104.6–105.6° (lit. 103°).

Multi-nuclear Ferrocenes. I. Biferrocenyl[1a,b]

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In its initial isolation, biferrocenyl (I) was obtained in small yield during distillation of the reaction products produced from treatment of a mixture of lithio- and dilithioferrocene with tri-*n*-hexylbromosilane[2,3]; since publication of a preliminary account of this work,[4] a number of additional reports concerning biferrocenyl have appeared.[5–9] Russian workers prepared biferrocenyl *via* reaction of ammoniacal silver oxide with ferroceneboronic acid,[5,10] and by catalytic pyrolysis of diferrocenylmercury.[6,11] Shechter and Helling[8] have shown that biferrocenyl may be obtained from ferrocenyl Grignard reagents, while still another method for preparation of biferrocenyl parallels the Ullmann procedure for biaryls in that iodoferrocene is heated in the presence of activated copper bronze.[7,9]

Because of the increasing interest in biferrocenyl, and because our spectral data[13] have been used to establish identity of biferrocenyl obtained by various methods,[8,9,12] we wish to report the experimental evidence upon which our original structural assignment to biferrocenyl was based, and present additional evidence in confirmation of that structure.

Initial data (combustion analysis, molecular weight determinations, and infrared C—H stretching absorption)[4] were clearly consistent with the biferrocenyl formulation, and comparison of absorption intensities (absorbance) of the 9- and 10-bands[14] of biferrocenyl with those of ferrocene showed the unsubstituted ring content of the former to be equal to that of the latter (Table I).

TABLE I

9–10-BAND ABSORBANCE OF FERROCENE AND BIFERROCENYL[a]

Molarity × 10^{-3}	9-Band		10-Band	
	Ferrocene	Biferrocenyl	Ferrocene	Biferrocenyl
3.41	0.054	0.061	0.056	0.054
5.08	.082	.076	.082	.076
8.49	.134	.141	.136	.123
11.1	.176	.179	.177	.165
14.1	.222	.218	.223	.200

[a] Measurements carried out in carbon disulfide solution.

The possibility of fortuitous agreement in this case was ruled out by examining similarly the 9–10 infrared absorption of a variety of known ferrocene derivatives (see Experimental). For each compound a Lambert–Beer plot was made of absorbance *vs.* molarity (carbon disulfide solution). Straight line relationships were obtained, while upper limits of concentration were determined for ferrocene, palmitoylferrocene, and hexadecylferrocene. Deviations from linearity for these compounds occurred above concentrations of 14 × 10^{-3} *M* for the 9-band, and above concentrations of 22 × 10^{-3} *M* for the 10-band. Working concentrations for all compounds, therefore, were kept below these limits. Difficulties due to base-line variations were overcome by use of the so-called base-line technique introduced by Wright.[15] A more serious limitation, however, lay in the fact that in some cases the 9- and/or the 10-band may be greatly distorted by the close proximity of other absorption. In such cases quantitative use of the 9–10 Rule is not applicable. For this reason the

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(3) Formation of biferrocenyl, as described in this work, was first observed in 1957 by D. W. Mayo (Wright Air Development Center technical report 57-62, Part II, February, 1958; ASTIA document no. 150979). Efforts to accumulate additional material for investigation were aided by a subsequent preparation carried out by M. D. Rausch. In that case, tri-*n*-dodecylbromosilane was used instead of the tri-*n*-hexylbromosilane employed in the original and in subsequent runs.

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