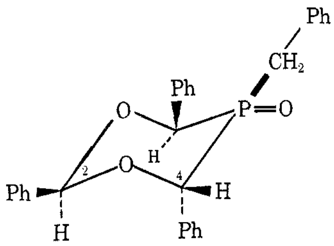
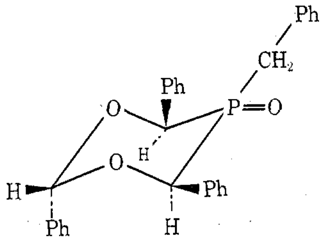


2a

expected to give symmetrical nmr spectra since they each have a plane of symmetry through the 2,5-ring positions. However, an examination of molecular models showed isomers IV and VIII to be extremely crowded with severe 1,3 interactions between the phenyl groups at C_4 and C_6. These interactions would favor the diequatorial configuration at C_4 and C_6. The proton at C_2 shows a doublet (J = 2 Hz). The only coupling which would give a doublet would be to phosphorus. This long-range coupling would be expected to be greater than 1 Hz only if the proton were equatorial.[17,18] Thus, the structure of **2s** is that of



2s

isomer V. Again two of the three phenyl groups attached to carbon are in the equatorial positions.

The two isomers isolated are the only ones which have two bulky groups equatorial and two axial. All the rest have three bulky groups, either axial or equatorial.

The reasons for obtaining only these two isomers and the mechanism necessary to produce the meso ring system from *d,l* starting material are now under investigation and will be reported in a subsequent publication.

Experimental Section

Reagent grade chemicals were used as supplied. Phosphine was generated by addition of water to a suspension of aluminum phosphide in dioxane. The benzene and benzaldehyde were dried over Linde Molecular Sieve 4A. Ir spectra were run as KBr disks on a Perkin-Elmer 137 with NaCl optics; nmr spectra were run in $CDCl_3$ on a Varian A-60.

Benzylbis(α-hydroxybenzyl)phosphine Oxide.—The preparation was carried out identically with Buckler's work.[2] However, after running the experiment several times, the maximum yield of crystalline solid was 35%: mp 150–152°; nmr (DMSO-d_6) δ 3.18 (m, 2 H, PCH_2Ph), 5.17 (d, J = 9 Hz, 1 H, HC(O)P), 5.3 (d, J = 12 Hz, 1 H, HC(O)P), 6.48 (m, 2 H, OH), 6.73–7.78 (m, 15 H, aromatics).

5-Benzyl-2,4,6-triphenyl-1,3,5-dioxaphosphorinane 5-Oxide (2).—A solution of 35 ml of benzaldehyde, 120 ml of dry benzene, and a crystal of *p*-toluenesulfonic acid was prepared and 17.6 g (0.05 mol) of **1** was added. The mixture was heated under reflux until the water in the Dean-Stark trap did not increase over several hours reflux. Only 0.55 ml of water was collected (theoretical, 0.90 ml), and this took 7 days of reflux (Buckler reported 20 hr). The resulting solution was dried *in vacuo* and the residue mixed with 150 ml of anhydrous ether. The white solid present was collected (11.6 g, 52.8% yield), mp 158–200°, as a mixture of isomers **2**. The pure isomers were obtained by mixing **2** with 450 ml of ethyl acetate, heating, and filtering. The ethyl acetate soluble material after crystallization was recrystallized further from 2-propanol (three times) to yield 2.32 g of a white solid: mp 198–200° (**2a**); nmr ($CDCl_3$) δ 2.9 (m, 2 H, PCH_2Ph), 5.36 (d, $J_{P\text{-}H}$ = 17 Hz, 1 H, eq HC(O)P), 5.50 (d, $J_{P\text{-}H}$ = 16 Hz, 1 H, ax HC(O)P), 6.25 (s, 1 H, HC(O)O), 7.87–6.78 (m, 20 H, aromatics).

The ethyl acetate insoluble portion was then recrystallized four times from dioxane to yield 0.3 g of a white solid: mp 216–220° (**2s**); nmr ($CDCl_3$) δ 3.5 (d, $J_{P\text{-}H}$ = 16 Hz, 2 H, PCH_2Ph), 5.32 (d, $J_{P\text{-}H}$ = 14 Hz, 2 H, HC(O)P), 6.02 (d, $J_{P\text{-}H}$ = 2 Hz, 1 H, HC(O)O), 7.85–6.88 (m, 2 OH aromatics).

Registry No.—**1**, 36871-68-8; **2a**, 36871-89-3; **2s**, 36871-90-6.

Use of Polymethylhydrosiloxane as a Selective, Neutral Reducing Agent for Aldehydes, Ketones, Olefins, and Aromatic Nitro Compounds

Jonathan Lipowitz* and Sheryl A. Bowman

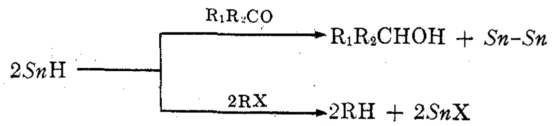
Research Department, Dow Corning Corporation, Midland, Michigan 48640

Received August 3, 1972

Several reports of the reductions of a variety of functional groups by silyl hydrides under mild conditions and in high yields prompted this work. The present study was aimed at determining the scope and utility of siloxane hydrides as general reducing agents for organic compounds under mild, neutral conditions.

Recently Grady and Kuivila[1] reported reductions of halocarbons and a ketone by tin hydrides, generated *in situ* from reaction of polymethylhydrosiloxane (PMHS) and organostannoxanes. Stoichiometric quantities of stannoxane were required. Earlier work of Nitzsche and Wick[2] had described reductions of several ketones and aromatic nitro compounds with methylhydrosiloxanes and catalytic quantities of dialkyltin diacylates or other organometallics in protic solvents. In view of Grady and Kuivila's work[1] and earlier reports of the reactions of stannoxanes and alkoxystannanes with silyl hydrides,[3] it is likely that tin hydrides are the active reducing agents, being rapidly consumed and regenerated *in situ*.

$$\mathit{Sn}O\mathit{Sn} + \frac{2}{n}[\mathrm{MeHSiO}]_n \longrightarrow \frac{2}{n}[\mathrm{MeSiO}_{1.5}]_n + 2\mathit{Sn}\mathrm{H}$$



Sn = organotin

The organotin hydrides are versatile reagents which reduce a variety of functional groups.[4] However,

---

(1) G. L. Grady and H. G. Kuivila, *J. Org. Chem.*, **34**, 2014 (1969).

(2) S. Nitzsche and M. Wick, *Angew. Chem.*, **69**, 96 (1957); U. S. Patent 3,061,424 (1962).

(3) (a) K. Hayashi, J. Iyoda, and I. Shiihara, *J. Organometal. Chem.*, **10**, 81 (1967); (b) K. Itoi and S. Kumano, *Kogyo Kogoku Zasshi*, **70**, 82 (1967); (c) B. Bellegarde, M. Pereyre, and J. Valade, *Bull. Soc. Chem. Fr.*, 3082 (1967).

(4) (a) H. G. Kuivila, *Advan. Organometal. Chem.*, **1**, 47 (1964); (b) *Synthesis*, **2**, 499 (1970), and references cited therein; (c) W. P. Neumann, "The Organic Chemistry of Tin," Interscience, New York, N. Y., 1970, Chapter 10, and references cited therein; (d) R. C. Poller, "The Chemistry of Organotin Compounds," Academic Press, New York, N. Y., 1970, Chapter 7.

difficulty in the preparation and storage of tin hydrides, especially the reactive dihydrides, and the use of stoichiometric quantities of reagent have hindered widespread use of this unique class of reducing agent. Some examples of marked selectivity are known. Thus, progesterone is reduced to the carbinol preferentially at the 3-carbonyl by tin hydrides whereas sodium borohydride reduces preferentially at the 20-carbonyl.[4a]

We find that PMHS[5] and an organotin catalyst, bis(dibutylacetoxytin) oxide (DBATO),[6] in a protic solvent functions as a mild, convenient reagent for the specific reduction of aldehydes and ketones to carbinol in high yield.

$$R_1R_2CO + \frac{1}{n}[MeHSiO]_n + ROH \xrightarrow{\text{DBATO}} R_1R_2CHOH + \frac{1}{n}[MeSi(OR)O]_n$$

One equivalent of siloxane hydride per mole of substrate is required, with the solvent contributing a proton to complete reduction to the carbinol. Reduction takes place under mild, neutral conditions during reaction and work-up.[8] Exclusion of air and water is not necessary. Table I lists reductions which have been carried out in refluxing 95% ethanol (80°) using 2 mol % DBATO and a 10% excess of PMHS.

TABLE I

PMHS REDUCTIONS WITH 2 MOL % DBATO[a]

Substrate	Registry no.	Product	Yield, %
Ph_2CO	119-61-9	Ph_2CHOH	80[b]
PhCOMe	98-86-2	PhCHOHMe	81[b,d]
PhCHO	100-52-7	$PhCH_2OH$	100[c]
Me_2CO	67-64-1	Me_2CHOH	100[c]
$CH_2{=}CHCOMe$	78-94-4	$CH_2{=}CHCHOHMe$	65[c]
		EtCOMe	35[c]
4-*tert*-Butylcyclohexanone	98-53-3	*trans*-4-*tert*-Butylcyclohexanol	65[b] (100[c])
p-Benzoquinone	106-51-4	Hydroquinone	81[b]

[a] At 80° in refluxing 95% ethanol. [b] Isolated yield. [c] Glc yield, using an internal standard. [d] 1-Hr reflux was required after PMHS addition.

Table II lists representative esters, lactones, amides, carboxylic acids, nitriles, alkyl halides, and nitro compounds which are not reduced. In some cases, noted in Table II, reduction takes place approximately stoichiometrically with catalyst, especially in 2-ethylhexanol at 130°. Thus, 2 mol % catalyst gave about 2% amine (or ammonia) with nitriles and nitro compounds at 130°. Benzyl chloride reduction gave a 2% yield of toluene. Nitzsche and Wick[2] reported quantitative reductions of nitrobenzene and *p*-dinitrobenzene to the amines at higher temperature in refluxing 2-ethylhexanol (bp 184°).

TABLE II

UNSUCCESSFUL REDUCTIONS WITH PMHS AND 2 MOL % DBATO[a]

$PhNO_2$[b]
$EtCHNO_2CH_2OH$[b]
m-$NO_2C_6H_4COMe$[b]
PhCN[b]
EtCN[b]
$PhCH_2Cl$[b]
$MeCO_2Et$
$MeCO_2Bu$
γ-Butyrolactone
n-$BuCHEtCO_2H$
$HCONMe_2$

[a] Little or no reduction at 80 (in ethanol) or 130° (in 2-ethylhexanol). [b] Reduction is approximately stoichiometric with catalyst at 130°.

The following reaction scheme appears likely for reduction of carbonyl groups using catalytic stannoxane.

Catalyst formation

$$\mathit{Sn}O\mathit{Sn} + \mathit{Si}H \longrightarrow \mathit{Sn}H + \mathit{Si}O\mathit{Sn} \tag{1}$$

$$\mathit{Si}O\mathit{Sn} + ROH \longrightarrow \mathit{Si}OH + \mathit{Sn}OR \tag{2}$$

Reductive cycle

$$\mathit{Sn}H + R_1R_2CO \longrightarrow \mathit{Sn}OCHR_1R_2 \tag{3}$$

$$\mathit{Sn}OCHR_1R_2 + ROH \rightleftarrows \mathit{Sn}OR + R_1R_2CHOH \tag{4}$$

$$\mathit{Sn}OR(\mathit{Sn}OCHR_1R_2) + \mathit{Si}H \longrightarrow \mathit{Sn}H + \mathit{Si}OR(\mathit{Si}OCHR_1R_2) \tag{5}$$

Reactions of PMHS with stannoxanes (reaction 1) and alkoxystannanes (reaction 5) are rapid and exothermic.[3,9] Solvolyses of siloxystannanes (reaction 2) are well known.[10] Reaction of tributyltin hydride with ketones in methanol has recently been reported to lead directly to the carbinol *via* reactions 3 and 4.[11]

The active reducing agent in the system is either dibutylacetoxytin hydride or dibutyltin dihydride. The acetoxytin hydride is known to undergo rapid disproportionation, favoring the dihydride and the diacetate.[12] Evidence for the presence of dihydride is obtained by ir spectroscopy. A mixture of PMHS and DBATO leads to rapid formation of an ir band at 1830 cm^{-1}.[13] The presence of dibutylacetoxytin hydride in the reaction mixture is indicated by slow formation of 1,1,2,2-tetrabutyl-1,2-diacetoxyditin, the

---

(5) PMHS (Dow Corning® XZ8-5486 chemical reducing agent) is distributed by Aldrich Chemical Co., Inc. PMHS is an easily handled, chemically inert liquid in uncatalyzed form; the structure is $Me_3SiO(MeHSiO)_n$-$SiMe_3$, where $n \approx 35$.

(6) DBATO, mp 57°, is the stable hydrolysis product of dibutyltin diacetate under neutral or mildly basic conditions and is readily prepared by alkaline hydrolysis of dibutyltin diacetate,[7] by reaction of dibutyltin diacetate and dibutyltin oxide,[7] or most conveniently by reaction of dibutyltin oxide and acetic acid (*cf.* Experimental Section). DBATO is a more active catalyst than dibutyltin diacetate for the reduction of ketones and is more resistant to reduction to metallic tin.

(7) D. L. Alleston, A. G. Davies, M. Hancock, and R. F. M. White, *J. Chem. Soc.*, 5469 (1963).

(8) Nitzsche and Wick[2] worked up reactions using aqueous mineral acid to hydrolyze carbinol product which had been incorporated in the siloxane as alkoxysiloxane. We find that hydrolysis of product which has been incorporated in the polysiloxane and formation of an easily filtered, granular, methylsilsesquioxane gel will take place simply by addition of water with heating and stirring. The DBATO which is present functions as a hydrolysis catalyst.

$$\frac{1}{n}[MeSi(OR)O]_n + R_1R_2CHOH \underset{}{\overset{\text{Sn catalyst}}{\rightleftarrows}} \frac{1}{n}[MeSi(OCHR_1R_2)O]_n + ROH$$

$$\frac{2}{n}[MeSi(OR')O]_n + H_2O \longrightarrow \frac{2}{n}[MeSiO_{1.5}]_n + 2R'OH$$

(9) Siloxystannanes also react with PMHS.[3a] Addition of PMHS too rapidly during reaction leads to an increase in PMHS concentration. The excess PMHS may then react with siloxystannane in a reaction competitive with reaction 2, leading to methylsilsesquioxane gel formation before reduction is complete: $\mathit{Si}O\mathit{Sn} + \mathit{Si}H \rightarrow \mathit{Si}O\mathit{Si} + \mathit{Sn}H$.

(10) P. G. Harrison, *Organometal. Chem. Rev.*, **4**, 415 (1969), and references cited therein.

(11) M. Pereyre and J. Godot, *Tetrahedron Lett.*, 3653 (1970); M. Pereyre, J. Quintard, J. Godot, and J. Valade, *Organometal. Chem. Syn.*, **1**, 269 (1971).

(12) A. K. Sawyer and H. G. Kuivila, *J. Org. Chem.*, **27**, 613 (1962).

(13) Dibutyltin dihydride exhibits an ir band, ν(SnH), at 1832 cm^{-1}.[12]

thermal decomposition product of the acetoxytin hydride.[12] Evidence for the intermediacy of dibutylacetoxytin hydride was provided by formation of dibutylacetoxychlorotin and chloroform in the reaction of PMHS and DBATO in CCl_4. Tin hydrides are known to react rapidly and exothermally with CCl_4.[4,14] It is possible, however, that dibutyltin dihydride was trapped by CCl_4 to give dibutyltin dichloride, which can subsequently undergo exchange with diacetate.[15]

Differences are observed between our results and previous reductions using dibutyltin dihydride. Reduction of methyl vinyl ketone gives 65% methyl vinyl carbinol and 35% methyl ethyl ketone (Table I). The latter product arises by 1,4 addition of a tin hydride followed by solvolysis.[16] However, Kuivila and Beumel[17] reported reduction only to methyl vinyl carbinol in 31% yield by dibutyltin dihydride. We obtained exclusively *trans*-4-*tert*-butylcyclohexanol in reduction of 4-*tert*-butylcyclohexanone whereas Kuivila and Beumel[17] obtained a 7:1 trans-cis mixture using dibutyltin dihydride. The differences observed between reductions with dibutyltin dihydride and the PMHS-DBATO reagent, although not pronounced, are considered to be great enough to suggest that the reactive intermediate in the present case is dibutylacetoxytin hydride. This tin hydride seems to be somewhat more reactive towards carbonyl groups than the dihydrides,[16,17] although its selectivity and stereospecificity remains largely unexplored.

Hydrogenations using a Pd-on-charcoal catalyst provide additional examples of the versatility of PMHS as a reducing agent under mild conditions. High yields have been reported in room temperature hydrogenolyses of aryl chlorides and bromides and reactive alkyl chlorides.[18,19] We find that hydrogenations of

$$R_3SiH + R'X \xrightarrow{Pd/C} R_3SiX + R'H$$

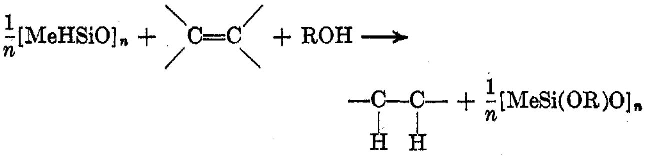
terminal and cis olefins, aromatic nitro compounds and aromatic aldehydes proceed readily in ethanol with Pd on charcoal (Table III). Similar reductions by trialkylsilyl hydrides and siloxane hydrides have been observed in aqueous dioxane.[20]

TABLE III

HYDROGENATION WITH PMHS AND Pd/C IN EtOH, 40–60°

Compound	Registry no.	Time, (hr)	Product	Yield, %
$PhNO_2$	98-95-3	1	$PhNH_2$	89[a]
PhCHO		1	$PhCH_3$	84[a]
1-Octene	111-66-0	1	*n*-Octane	88[b]
2-Nonene	6434-77-1	1	*n*-Nonane	25[a,c]
Cyclohexene	110-83-8	1	Cyclohexane	100[a]
$CH_2{=}CHCOMe$		2	EtCOMe	100[a]

[a] Glc yield, using an internal standard. [b] Distilled yield. [c] 100% cis isomer reduction, no trans isomer reduction.



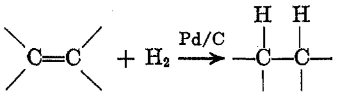
$$\frac{1}{n}[MeHSiO]_n + \rangle C{=}C\langle + ROH \longrightarrow \underset{H}{-\overset{|}{C}}-\underset{H}{\overset{|}{C}}- + \frac{1}{n}[MeSi(OR)O]_n$$

$$\frac{2}{n}[MeHSiO]_n + ArCHO + 2ROH \longrightarrow ArCH_3 + \frac{2}{n}[MeSi(OR)O]_n + H_2O$$

$$\frac{3}{n}[MeHSiO]_n + ArNO_2 + 3ROH \longrightarrow ArNH_2 + \frac{3}{n}[MeSi(OR)O]_n + 2H_2O$$

Reductions using PMHS and Pd/C constitute a safe, convenient form of low-pressure hydrogenation. Although the observed pattern of hydrogenations are similar to those obtained with hydrogen and Pd/C at 1 atm and room temperature,[21] reaction *does not* proceed simply by the known[22] Pd/C catalyzed solvolysis of silyl hydride, followed by olefin hydrogenation. Thus, in the reduction of 2-nonene containing a 75:25 ratio of trans/cis isomers, only the cis isomer is reduced. No hydrogen evolution is observed even though 77% of the silyl hydride remains unreacted. However, hydrogenation of 1-octene proceeds with vigorous hydrogen evolution throughout even though reduction if rapid and 91% complete (9% isomerized octenes are obtained). The absence of a correlation between the extent of hydrogen evolution and the extent of reduction indicates that reaction does not take place *via* the above scheme.

$$\mathit{Si}H + ROH \xrightarrow{Pd/C} \mathit{Si}OR + H_2$$



$$\rangle C{=}C\langle + H_2 \xrightarrow{Pd/C} -\underset{|}{\overset{H}{C}}-\underset{|}{\overset{H}{C}}-$$

The versatility of the PMHS reagent is illustrated by quantitative reduction of methyl vinyl ketone to methyl ethyl ketone with Pd/C catalyst whereas catalysis by DBATO gives a 65% yield of methyl vinyl carbinol. Additional reactions in which the utility of silyl hydrides have been demonstrated include the Pd/C catalyzed reduction of acid chlorides to aldehydes.[23] Reductions of phosphine oxides, and phosphoric acid esters to phosphines by PMHS are also known.[24]

Experimental Section

Melting and boiling points are uncorrected.

Bis(dibutylacetoxytin) Oxide (DBATO).—A mixture of 10.0 g of dibutyltin oxide (40 mequiv) and 2.4 g of acetic acid (40 mmol) in 15 ml of ethanol was heated at 60° with stirring. In 30 min, the solution had become homogeneous and functioned as well as recrystallized DBATO in reduction of acetophenone. Evaporation of solvent and recrystallization from acetone at −20° gave DBATO, 10.3 g (86%), mp 54–57° (lit.[7] mp 56–60°), ir (CCl_4) 1570, 1640 cm^{-1} (C=O).

---

(14) D. H. Lorenz and E. I. Becker, *J. Org. Chem.*, **27**, 3370 (1962).

(15) A. K. Sawyer and H. G. Kuivila, *Chem. Ind. (London)*, 260 (1961).

(16) A. J. Leusink and J. G. Noltes, *Tetrahedron Lett.*, 2221 (1969).

(17) H. G. Kuivila and O. F. Beumel, Jr., *J. Amer. Chem. Soc.*, **83**, 1246 (1961).

(18) J. D. Citron, J. E. Lyons, and L. H. Sommer, *J. Org. Chem.*, **34**, 638 (1969).

(19) Hydrogenolyses by siloxane hydrides with Pd/C proceed in high yield in hydrocarbons or without solvent; private communication from Dr. G. H. Barnes, Jr.

(20) Private communication from Dr. G. H. Barnes, Jr.

(21) R. L. Augustine, "Catalytic Hydrogenation," Marcel Dekker, New York, N. Y., 1965.

(22) G. H. Barnes, Jr., and N. E. Daughenbaugh, *J. Org. Chem.*, **31**, 885 (1966); L. H. Sommer and J. E. Lyons, *J. Amer. Chem. Soc.*, **89**, 1521 (1967).

(23) J. D. Citron, *J. Org. Chem.*, **34**, 1977 (1969).

(24) H. Fritzsche, U. Hasserodt, and F. Korte, *Chem. Ber.*, **97**, 1988 (1964); *ibid.*, **98**, 1681 (1965).

Dibutylacetoxychlorotin was prepared[15] by heating 3.5 g of dibutyltin diacetate and 3.0 g of dibutyltin dichloride at 80–90° for 5 min. Recrystallization from pentane gave 5 g of the acetoxytin chloride, mp 59–62° (lit.[15] mp 63–65°), ir (CCl_4) 1590 cm^{-1} (C=O).

PMHS Reduction with DBATO.—A solution of the organic substrate (1 mol) and 12 g of DBATO (0.02 mol) in 700 ml of 95% ethanol was heated to reflux (80°).[25] PMHS,[5] 70 g (1.1 equiv), was added dropwise slowly enough to maintain gentle reflux.[26] In most cases, reduction was complete when all the PMHS was added. Completion of reduction was determined by disappearance of carbonyl absorption using ir analysis. Water, 800 ml, was added and the reaction mixture was stirred at 80° until a granular methylsilsesquioxane gel was obtained (about 1 hr). The gel was filtered and the filtrate and gel were extracted with chloroform. The combined chloroform extracts were distilled, recrystallized, or analyzed by glc with addition of toluene or xylene as an internal standard. Products on which glc yields are reported were identified by tandem glc–mass spectroscopy. Isolated products were characterized by melting point or boiling point, and ir spectroscopy. Isomeric purity of *trans*-4-*tert*-butylcyclohexanol was determined by ir spectroscopy.[27] *p*-Hydroquinone was isolated as the quinhydrone.[17] Reductions that failed were carried out similarly, using 700 ml of 2-ethylhexanol as solvent in the 130° runs. The reductions of nitro compounds and nitriles at 130° gave traces of amines (or ammonia) as evidenced by alkalinity during attempted distillation. In addition, approximately 2% yields of aniline and toluene were obtained, by glc mass spectroscopy, in reductions of nitrobenzene and benzyl chloride, respectively.

Reaction of Polymethylhydrosiloxane and Bis(dibutylacetoxytin) Oxide.—A solution of 0.19 g of PMHS (3 mequiv) and 1.8 g of DBATO (3 mequiv) in 25 ml of dry cyclohexane was prepared under dry N_2. An ir spectrum, obtained immediately, showed a band at 1830 cm^{-1} attributable to ν(SnH) of dibutyltin dihydride [lit.[12] ν(SnH) 1832 cm^{-1}]. After storage overnight, a band appeared at 1550 cm^{-1} attributable to 1,1,2,2-tetrabutyl-1,2-diacetoxyditin [lit.[12] ν(C=O) 1553 cm^{-1}], which is a decomposition product of dibutylacetoxytin hydride.[12]

A solution of 0.20 g of PMHS and 1.8 g of DBATO in 20 ml of CCl_4 was refluxed for 2 hr. Infrared analysis during the reaction showed the disappearance of silyl hydride [ν(SiH) 2160 cm^{-1}] and the formation of chloroform [δ(CH) 1210 cm^{-1}] and dibutylacetoxychlorotin [ν(C=O) 1590 cm^{-1}].

PMHS Reductions with Pd on Charcoal. A 10% excess of PMHS was added to a mixture of the organic substrate (0.1 mol) and 0.05 g of 5% Pd on charcoal in 40 ml of 95% ethanol containing 1 drop of concentrated HCl.[28] For reduction of olefins, benzaldehyde, and nitrobenzene, 0.11, 0.22, and 0.33 equiv respectively of PMHS were used. The reaction mixture was swirled occasionally, and the temperature was maintained at 40–60° by cooling or heating, depending on substrate reactivity. Methyl vinyl ketone, which did not exotherm, was heated at 40–60° for 2 hr. Other substrates were heated for about 30 min after the exotherm, which required cooling, had subsided. The catalyst was removed by filtration, 80 ml of water was added, and the product was extracted from the aqueous mixture with pentane. The pentane extract was dried ($CaCl_2$) and products were identified by tandem glc–mass spectrometry. Yields were determined by addition of toluene or xylene as a glc internal standard to the pentane extract. Distillation of the 1-octene reduction product gave *n*-octane, bp 125°, containing 7% isomerized olefins. Isomerized olefins were also detected by glc in the 2-nonene reduction product.

Registry No.—**1**, 9004-73-3; **2**, 5967-09-9; Pd, 7440-05-3.

Acknowledgment.—We thank John Coutant and Ron Robinson for glc–mass spectroscopy analyses and Jerry Garner for glc analyses of isomerized olefins.

(25) The rate of reduction can be increased by increasing DBATO concentration or by increasing reaction temperature by use of a higher boiling alcohol.

(26) Premature gelation before completion of reduction may occur if PMHS concentration is allowed to build up by too rapid addition.

(27) R. S. Ro, Ph.D. Thesis, University of Notre Dame, 1957; E. L. Eliel and R. S. Ro, *J. Amer. Chem. Soc.*, **79**, 5992 (1957).

(28) *Caution.* PMHS should be added in small portions to reactions run on an appreciably larger scale to control the exotherm.

Carbonyl Compounds and Secondary Amines from Diarylhydroxylamines *via* Nitroxides

YUL YOST AND H. R. GUTMANN*

Laboratory for Cancer Research, Veterans Administration Hospital and Department of Biochemistry, University of Minnesota, Minneapolis, Minnesota 55417

Received August 7, 1972

In previous work we have described the preparation of *N*-phenyl-*N*-fluorenylhydroxylamines by the reaction of nitrofluorenes with phenylmagnesium bromide in a nitrogen atmosphere.[1] In the presence of air the hydroxylamines were transformed to products that have now been identified. The work presented here shows that *N*-phenyl-*N*-fluoren-2-ylhydroxylamine in the presence of air gives rise to 2-anilinofluoren-9-one and *N*-phenylfluoren-2-amine and that a nitroxide is the intermediate, as shown in Scheme I. Similarly, *N*-phenyl-*N*-fluoren-3-ylhydroxylamine yielded the corresponding diaryl ketone and diarylamine. 1-Anilinofluoren-9-one and *N*-phenylfluoren-1-amine, isolated from the reaction of 1-nitrofluorene and phenyl Grignard in air, undoubtedly arose from the intermediate *N*-phenyl-*N*-fluoren-1-ylhydroxylamine. The course of these reactions may be rationalized by a mechanism similar to that proposed by Calder and Forrester.[2] According to these workers, *N*,*N*-alkylarylhydroxylamines disproportionate to carbonyl compounds and arylamines *via* intermediate nitroxides. The applicability of this mechanism to diarylhydroxylamines was supported by the oxidation of *N*-phenyl-*N*-biphenyl-4-ylhydroxylamine to a stable nitroxides and by the conversion of the nitroxide to *p*-benzoquinone biphenyl-4-ylimine *N*-oxide and *N*-phenylbiphenyl-4-ylamine.

Another reaction which yields fluoren-9-ones from fluorenes is the oxidation of the methylene group involving intermediate peroxides.[3] This pathway may have contributed to the formation of fluorenones, since 2- and 3-anilinofluoren-9-one were obtained in minor amounts by air oxidation of the respective secondary amines.

Experimental Section

Melting points were taken with a Fisher-Johns apparatus. Ir spectra were recorded with a Beckman IR-10 spectrophotometer. The uv spectra were taken with a Beckman DK-2 spectrophotometer and the absorbancies at λ_{max} were read with a Gilford digital absorbance meter on a DR Beckman monochromator. Mass spectra were recorded with a Hitachi Perkin-Elmer RMU-6 spectrometer. Silica gel GF_{254} for tlc was obtained from Brinkman Instruments, Inc., Westbury, N. Y.

2-Anilinofluoren-9-one.—*N*-Fluoren-2-yl-*N*-phenylhydroxyamine[1] (1.50 g, 5.50 mmol) in ethanol (60 ml) and 2.5 *N* NaOH (2.5 ml) were stirred in an open flask for 12 hr at 40°. The colorless mixture turned red, then yellow, and finally green. A red precipitate was dissolved by addition of dimethylformamide (25 ml). The solution was treated with gaseous ammonia (9 min) and hydrogen sulfide (20 min) and stirred at room temperature for 1 hr. The volume of the solution was reduced by 50%. Ice–water was added and the resulting red precipitate was collected and washed with water (1.22 g). A portion (80 mg) was chromatographed (tlc) on silica gel with benzene. The

---

(1) Y. Yost, H. R. Gutmann, and C. Muscoplat, *J. Chem. Soc.*, 2119 (1971).

(2) A. Calder and A. R. Forrester, *J. Chem. Soc. C*, 1459 (1969); A. R. Forrester and S. P. Hepburn, *ibid.*, 1277 (1971).

(3) Y. Sprinzak, *J. Amer. Chem. Soc.*, **80**, 5449 (1958); E. F. Pratt and L. E. Trapasso, *ibid.*, **82**, 6405 (1960).