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HEXAMETHYLDITIN DEOXYGENATION OF ORGANIC OXIDES

I. REDUCTIVE COUPLING OF AROMATIC NITRO COMPOUNDS

F.P. TSUI and G. ZON*

Maloney Chemical Laboratory, The Catholic University of America, Washington, D.C. 20064 (U.S.A.)

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Summary

Heating nitroaromatics with hexamethylditin (Me_6Sn_2) at 150°C has been found to give, in most cases, moderately high yields of azoxy coupling products without significant amine production. Ultimate azoxy to azo conversion by Me_6Sn_2 occurs in a subsequent and relatively slow step. Oxidation by-products from Me_6Sn_2 are $Me_3SnOSnMe_3$, Me_4Sn, and a Me_2SnO-like polymer. The deoxygenation was found to obey a rate law which is first-order in both aromatic nitro compound and Me_6Sn_2. Pseudo first-order kinetic measurements with 4-nitrotoluene and 2-nitrotoluene revealed only a 1.5-fold deoxygenation rate retardation upon *ortho* substitution about the NO_2 group, while butyl for methyl substitution about the Sn—Sn bond led to a ca. 70-fold deceleration in reduction rate. Kinetic studies of 2-nitrobiphenyl deoxygenation with Me_6Sn_2 gave $\Delta H^{\ddagger} = 21.1$ kcal mol^{-1} and $\Delta S^{\ddagger} = -24$ cal mol^{-1} K^{-1}. Mechanistic schemes consistent with the experimental data are discussed.

Introduction

Deoxygenation of nitro compounds (RNO_2) has received considerable attention with regard to synthetic applications and mechanistic elucidation of derived nitrene ($R\ddot{N}$:) or nitrenoid intermediates [1,2]. By comparison, however, the search for novel classes of nitro group deoxygenating agents has been rather limited. Tricoordinate organophosphorus compounds [3] are most commonly employed for such reductions, with less frequent usage of transition metal chelates [4,5] and metal carbonyls [6,7].

We have recently reported [8] that hexaorganodisilanes (R_6Si_2) can likewise effect aromatic nitro compound ($ArNO_2$) deoxygenation (eqn. 1) but that reaction temperatures of ca. 240°C severely restrict the utility of this technique. Cognizance of the general tendency for organotin vs. organosilicon systems to

TABLE 1

DEOXYGENATION OF NITROAROMATICS ($ArNO_2$) WITH Me_6Sn_2[a]

Ar	Compound	Me_6Sn_2 (equivalent)	Product yield (%)[b]		
			ArN(O)=NAr	ArN=NAr	$ArNH_2$
C_6H_5	I	2	68	14	≤1[c]
	I	4	76	20	≤1
$4\text{-}MeC_6H_4$	II	2	73	6	≤1
	II	4	61	22	≤1
$4\text{-}ClC_6H_4$	III	2	62	14	[d]
	III	4	65	21	
2-Biphenylyl[e]	IV	2	0	42	5[f]

[a] Sealed ampoules at 150°C (16 h) with $[ArNO_2] = 0.7$ *M* using benzene solvent, except as indicated. [b] Isolated yield of purified product based on the amount of reacted $ArNO_2$ (ca. 90-100%), except as indicated. [c] Upper limit estimated from GLC. [d] Not determined. [e] *o*-Dichlorobenzene solvent: ca. 2% carbazole detected by GLC. [f] Quantitative GLC.

exhibit increased complexation and/or reaction with various oxygen-containing species [9] has therefore led to an evaluation of hexaorganoditin compounds (R_6Sn_2) as a class of more potent nitro group reducing agents. We now report product and kinetic studies which justify this expectation and demonstrate for the first time that nitroaromatics undergo relatively facile reductive coupling upon moderate heating with hexamethylditin (Me_6Sn_2).

$$ArNO_2 + 2\,R_6Si_2 \xrightarrow{240^\circ C} ArNH_2 + ArN{=}NAr + 2\,R_3SiOSiR_3 \tag{1}$$

Results and discussion

Deoxygenated products

Heating solutions of Me_6Sn_2 and various aromatic nitro compounds in either benzene or *o*-dichlorobenzene at 150°C for 16 h led to essentially complete reaction of $ArNO_2$ and yielded the respective products listed in Table 1. Inspection of Table 1 reveals that substrate coupling is the primary reaction mode, with little or no amine ($ArNH_2$) product being detected*. Use of the theoretical amount (2 equivalents) of Me_6Sn_2 necessary for complete $ArNO_2$ deoxygenation afforded, for compounds I-III, substantial amounts (ca. 70%) of azoxy coupling product ArN(O)=NAr and lesser quantities (ca. 20%) of fully reduced azo material ArN=NAr**. Only a small increase in the proportion of the latter product was noted with as much as a two-fold excess (4 equivalents) of Me_6Sn_2, indicating that ultimate azoxy→azo conversion is a slow process, relative to the initial nitro→azoxy transformation. This tentative conclusion was supported by independent reaction of azoxybenzene with 1 equivalent Me_6Sn_2 which led to only 32% conversion of starting material to azobenzene (85% yield, corrected) after 20 h at 150°C; excess Me_6Sn_2 (4 equivalents) and longer reaction time (43 h) gave 93% reaction and an 87% yield (corrected) of azobenzene. A suitable

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* Trace amounts of additional and as yet unidentified products were in evidence by TLC.

** In all cases, it is assumed that the thermodynamically more stable *trans*-azoxy and *trans*-azo products are obtained.

control experiment with aniline as a model reactant demonstrated that azo products do not arise from oxidative coupling of amines by reaction with Me_6Sn_2.

Results with 2-nitrobiphenyl (IV) are somewhat in contrast to those for I-III in as much as IV did not yield detectable amounts of azoxy product and IV was the only substrate which yielded its corresponding amine (5%). It is also interesting to note that Me_6Sn_2 reduction of IV afforded only a trace amount (ca. 2%) of carbazole, which markedly differs from results reported [8] for deoxygenation with Me_6Si_2 wherein this heterocycle was the major product*.

Currently available methods which can effect reductive coupling of nitroaromatics with minimal interference due to amine production include reaction with *(a)* Fe(salen)** in tetrahydrofuran at room temperature [5], *(b)* $Fe(CO)_5$ and CO at 200°C/200 atm [6], and *(c)* various metal oxalates at 250-300°C [4]. Consequently, the relatively low-temperature/low-pressure Me_6Sn_2 procedure presently reported represents a less drastic and more convenient synthetic method than *(b)* or *(c)*, but is not as efficient as that using Fe(salen).

Me_6Sn_2 oxidation products

By analogy to eqn. 1, it was anticipated that Me_6Sn_2 deoxygenation of $ArNO_2$ compounds would exclusively produce hexamethylditin oxide ($Me_3SnOSnMe_3$). Preliminary investigations regarding this expectation revealed that while $Me_3SnOSnMe_3$ is formed, substantial quantities of tetramethyltin (Me_4Sn) and an insoluble organotin oxide powder (m.p. >250°C) are also produced. Based on elemental composition and the striking similarity between the IR spectra of this powder and authentic dimethyltin oxide (Me_2SnO), we have concluded that the powder is a polymeric substance closely akin to Me_2SnO. Additional Me_6Sn_2 oxidation products were not in evidence.

Exact stoichiometric measurements for $ArNO_2$ deoxygenation by Me_6Sn_2 were not pursued because of difficulties associated with the hydrolytic instability [10] of $Me_3SnOSnMe_3$. However, semi-quantitative studies (see Experimental) were performed with 4-nitrotoluene (II) and Me_6Sn_2 at 150°C (16 h) as a model reduction system. Under these conditions it was found that only 50% of the theoretical amount of $Me_3SnOSnMe_3$ was present, with the material balance of $Me_3SnOSnMe_3$ being adequately accounted for by a near equal weight mixture of Me_4Sn and Me_2SnO-like powder. The mechanistic significance of these findings is discussed in a following section.

Kinetics

(a). Reaction order. Investigation of deoxygenation reaction order with respect to $ArNO_2$ and Me_6Sn_2 was carried out using compound IV as a model substrate. Three reaction mixtures containing various molar ratios of IV and Me_6Sn_2 were heated under identical conditions (150°C, 16.0 h) and comparison of relative amounts of unreacted IV indicated that, within experimental error, the disappearance rate for IV is given by $-d[IV]/dt = k[IV][Me_6Sn_2]$. This obedience to an overall second-order rate law is analogous to that reported [11] for deoxygenation of pyridine *N*-oxide with aryloxypentamethyldisilanes.

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* Control experiments verified that carbazole was stable under typical deoxygenation conditions employed in this study.

** salen = *N,N'*-ethylenebis(salicylideneiminato).

TABLE 2

PSEUDO FIRST-ORDER RATE CONSTANTS (k') AND HALF-LIVES ($\tau_{1/2}$) FOR DEOXYGENATION OF NITROAROMATICS ($ArNO_2$) WITH R_6Sn_2 ^{a}

Ar	Compound	R	T (°C)	$k' \times 10^5$ (sec^{-1})	$\tau_{1/2}$ (h)
4-MeC_6H_4	II	Me	120	8.66	2.2
2-MeC_6H_4	V	Me	120	5.67	3.4
2-Biphenylyl	IV	Me	120	8.65	2.2
	IV	Me	110	4.03	4.8
	IV	Me	100	1.96	9.8
	IV	Bu	120	0.13	153

^{a}[$ArNO_2$] = 0.1 M, [R_6Sn_2] = 2.0 M: benzene solvent for II and V, *o*-dichlorobenzene solvent for IV. Sealed ampoule technique using quantitative GLC analysis and linear least-squares analysis (±5-10% slope error) of data points collected over ca. 1-4 half-lives.

(b). Effect of $ArNO_2$ variation. In order to quantitatively evaluate the effect of $ArNO_2$ substrate changes on the rate of deoxygenation, psuedo first-order kinetic measurements were conducted on those nitro compounds listed in Table 2, using a molar ratio of $ArNO_2/Me_6Sn_2$ = 1/20. Least-squares treatment of data collected at 120°C indicated acceptable linearity over the monitored reaction period (ca. 2 half-lives) and passage through the origin. Comparison of half-life ($\tau_{1/2}$) values listed in Table 2 for II and V revealed that steric hindrance about the NO_2 functionality via *ortho* substitution with a methyl group leads to only a slight rate deceleration factor (1.5). Interestingly, *ortho* substitution with the bulkier phenyl group in IV does not suppress the reduction rate relative to II; attendant electronic differences at the NO_2 group which are effectuated by the proximate phenyl and methyl substituents may account for this apparent anomaly.

(c). Variation of the ditin reducing agent. A recent study [12] of hexaorganoditin oxidation by iron(III) complexes has provided a reactivity order in which hexabutylditin (Bu_6Sn_2) is significantly more reactive than the less bulky Me_6Sn_2 reagent. This seemingly unusual finding, which was rationalized [12] in terms of a rate-limiting outer sphere redox step, prompted our investigation of Bu_6Sn_2 as a potentially more reactive deoxygenating agent toward nitroaromatics, should an analogous redox process be involved. Deoxygenation of compound IV with Bu_6Sn_2 was studied and the results are summarized in Table 2. Comparison of appropriate $\tau_{1/2}$ values reveals that butyl for methyl substitution about the Sn—Sn bond results in a ca. 70-fold rate retardation, suggesting that accessibility to the Sn—Sn bond by the NO_2 function may play a dominant role in controlling the overall rate of $ArNO_2$ deoxygenation by R_6Sn_2 reagents. An analogous steric effect has been noted in the reduction of IV with hexaphenyldisilane [8].

With regard to deoxygenation product distribution, we add here that preparative scale reaction of IV with Bu_6Sn_2 gave a substantial increase in the proportion of amino product, relative to azo material, but that yields of these compounds were quite low (ca. 10 and 8%, respectively).

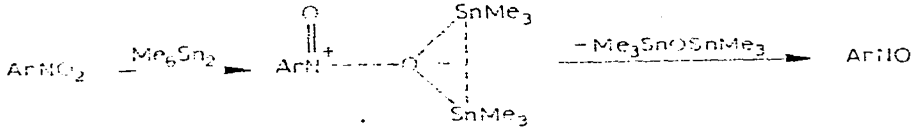
(d). Kinetic activation parameters. More detailed information concerning the mechanism of deoxygenation was obtained by measuring temperature de-

pendence of the pseudo first-order rate constant for reaction of model compound IV with Me_6Sn_2. Using the data given in Table 2 for temperatures of 120, 110 and 100°C, a linear plot (±4% slope deviation) of $\ln k'$ vs. $1/T$ was obtained from least-squares treatment, yielding $\Delta H^{\ddagger} = 21.1$ kcal mol^{-1} and $\Delta S^{\ddagger} = -24$ cal mol^{-1} K^{-1}, with $\Delta G^{\ddagger}_{100°} = 30.0$ kcal mol^{-1}.

Using the activation parameters measured for IV, and ignoring the relatively small effect of substrate variation on reduction rate (vide supra), we estimate that deoxygenation of I with Me_6Sn_2 at 220°C would be ca. 50000 times faster than deoxygenation of I with Me_6Si_2 ($\Delta G^{\ddagger}_{220°} = 41$ kcal mol^{-1} [8]). This impressive rate inequity, albeit only a rough approximation, supports our initial contention that R_6Sn_2 reagents are kinetically superior to their R_6Si_2 analogs in effecting nitro group deoxygenation.

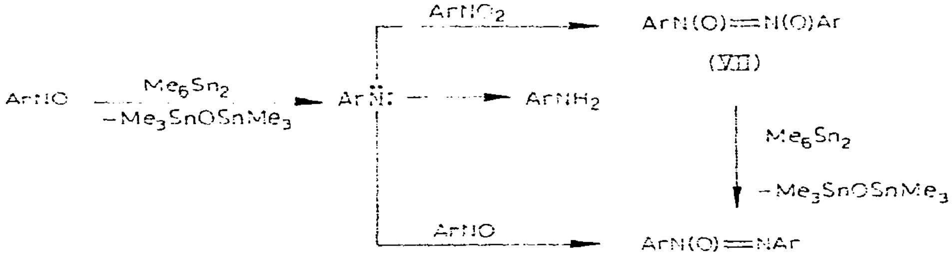
Mechanism

The aforementioned second-order rate law dependency together with the deoxygenation rate deceleration noted for Bu_6Sn_2, the thermal stability of Me_6Sn_2 per se (see Experimental), and the noteably large and negative value for $\Delta S^{\ddagger}$, are all consistent with rate-limiting involvement of a "highly ordered" activation complex between $ArNO_2$ and Me_6Sn_2. Structure VI is a reasonable representation of such a transition state, which then fragments into an intermediate



(VI)

(2)



(3)

$$2\,ArNO \rightleftharpoons VII \qquad (4)$$

$$ArN(O){=}NAr \xrightarrow[-Me_3SnOSnMe_3]{Me_6Sn_2} ArN{=}NAr \qquad (5)$$

$$Me_3SnOSnMe_3 \longrightarrow Me_4Sn + Me_2SnO \qquad (6)$$

nitroso compound (ArNO) and the observed $Me_3SnOSnMe_3$ by-product (eqn. 2)*. Subsequent and more rapid deoxygenation of ArNO to produce a transient nitrene ($Ar\ddot{N}$:) may then occur by an oxygen extrusion process similar to eqn. 2**. This reactive species can combine with $ArNO_2$ and/or ArNO yielding VII and/or azoxy product [3b], respectively, as well as lead to amine formation by H-abstraction*** (eqn. 3). Nitroso dimerization which bypasses $Ar\ddot{N}$: production and directly yields VII (eqn. 4) and hence ArN(O)=NAr is likewise a viable possibility. Ultimate transformation of azoxy→azo material by a relatively slow deoxygenation step (vide supra)☆ (eqn. 5) together with thermal and/or catalyzed disproportionation of $Me_3SnOSnMe_3$ (eqn. 6) [15] would then account for all of the remaining products which were observed.

A variety of alternative mechanistic rationale based upon consideration of schemes discussed [8] for $ArNO_2$ deoxygenation with R_6Si_2 are conceiveable. Consequently, we emphasize that while eqns. 2-6 economically encompass all of the experimental facts, they are heuristic in nature and further mechanistic studies are in order, especially with regard to the role (if any) played by nitrene intermediates. A similar caveat exists for any attempt at this stage to rationalize differences in product distribution obtained from deoxygenation with R_6Sn_2 vs. R_6Si_2 [8].

In summary, it has been shown that deoxygenation of nitroaromatics to give moderately high yields of azoxy coupling products can be effected by heating with Me_6Sn_2 at 150°C, while further reduction to azo products requires somewhat more vigorous conditions. This new synthetic method is superior to a number of existing techniques for reductive coupling of nitroaromatics, and may prove useful in extensions to other organic oxides. Results of our current investigations with sulfur and phosphorus oxides, ketones, and epoxides will be reported in the near future.

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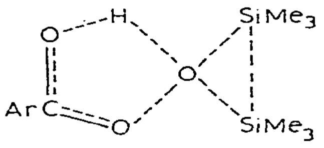
* Structure *i*, which is formally analogous to VI, has been discussed in a recent report [13] on the oxidation of Me_6Si_2 with *m*-chloroperbenzoic acid ($ArCO_3H$) in benzene solvent, for which $\Delta S^{\ddagger} = -26.8$ cal mol^{-1} K^{-1}. See ref. 14 for SO_2 insertion into a Sn—C bond ($\Delta S^{\ddagger} = -43$ cal mol^{-1} K^{-1}).



(*i*)

** Deoxygenation of nitrosobenzene with Me_6Sn_2 (see Experimental) at 90°C occurs with $\tau_{1/2}$ = 10.4 min. Comparison of this half-life with that calculated for IV at 90°C ($\tau_{1/2}$ = 22 h) suggests that ArNO compounds are roughly two orders of magnitude more reactive than their corresponding $ArNO_2$ derivatives.

*** *Note added in proof:* Hydrogen-abstraction by a nitrene could involve organotin and/or solvent molecules. Reduction of IV with Me_6Sn_2 in benzene-d_6 did not lead to detectable (IR) deuterium incorporation into 2-aminobiphenyl, while use of the relatively more efficient deuterium-donor solvent toluene-d_8 gave a sample of this amine having a weak N—D stretching absorption at ν 2530 cm^{-1}.

☆ While it is possible to evoke steric effects in rationalizing slower deoxygenation of intermediate azoxy species, relative to nitro starting material, it should be noted that azoxy group reduction by sulfoxides via nucleophilic *N*-oxide attack at sulfur is faster than corresponding reduction of a nitro group [16].

Experimental

All deoxygenation substrates were commercially available and were purified by either recrystallization or distillation before use. Solvents were purified by distillation under a nitrogen atmosphere and commercial grade (Alfa—Ventron) Me_6Sn_2, Bu_6Sn_2, Me_4Sn and Me_2SnO were used as received.

^1H NMR spectra were recorded on a Varian A-60 spectrometer using $CDCl_3$ solvent and TMS as an internal reference. IR spectra were obtained with Perkin—Elmer Model 137 and Model 337 instruments. Melting points were determined on a Thomas—Hoover capillary melting point apparatus and are uncorrected. Elemental analyses were performed by Chemalytics, Inc., and Alfred Bernhardt Mikroanalytisches Laboratorium. Preparative and analytical TLC utilized Analtek precoated 1000 and 250 μ Silica Gel GF plates, respectively. Column chromatography employed Baker Silica Gel (40-140 mesh). GLC analyses were carried out with Varian Aerograph Model 920 and 90-P thermal conductivity instruments using a flow rate of 60 ml He/min and Column A = 6 ft × 0.25 in 5% SE-30 on Chromosorb G (60/80 mesh); Column B = 5 ft × 0.25 in 3% SE-30 on Varaport 30 (100/120 mesh); Column C = 6 ft × 0.25 in 15% Apiezon L on Chromosorb W (60/80 mesh); Column D = 3 ft × 0.25 in 5% SE-30 on Chromosorb G (60/80 mesh).

Deoxygenations with Me_6Sn_2

General procedure. Solutions containing weighed amounts of the substrate to be deoxygenated and volumetrically delivered amounts of Me_6Sn_2 were sealed under vacuum in pre-dried and appropriately sized Pyrex tubes. After heating the submerged ampoules for 16 h in a constant temperature oil bath maintained at 150°C and then measurement of unreacted starting material by GLC analysis, the reaction solution was diluted with methylene chloride and separated from organotin oxide polymer which precipitated during the reduction. Concentration under reduced pressure was followed by analytical TLC and then column chromatography or preparative TLC isolation of products, which were ultimately purified for identification (m.p., TLC, IR, NMR) by recrystallization. Yields are listed in Table 1, with additional details and control studies given below.

Nitrobenzene (I). I (344 mg; 2.8 mmol) and Me_6Sn_2 (1.2 ml; 5.6 mmol) in benzene (1.20 ml) underwent complete reaction (Column A, 110°C) and led to TLC (5% ether in petroleum ether) isolation of *trans*-azobenzene and a somewhat slower eluting band of *trans*-azoxybenzene. IR and NMR spectra of these products were essentially superimposable on those obtained with authentic samples. A small amount (12 mg) of very slow eluting unidentified material was isolated as brown colored crystals, m.p. 55-58°C, and no aniline ($\leqslant$1%) was detected by GLC and TLC.

4-Nitrotoluene (II). II (384 mg; 2.8 mmol) was reacted (93%, Column A, 110°C) and processed in the same manner as I to yield *trans*-4,4'-dimethylazobenzene, m.p. 141-142°C (lit. [17] m.p. 144-145°C) and *trans*-4,4'-dimethylazoxybenzene, m.p. 68°C (lit. [18] m.p. 70°C). No 4-aminotoluene ($\leqslant$1%) was detected by GLC/TLC and trace by-products (TLC) were not isolated in sufficient quantity to allow identification.

4-Chloronitrobenzene (III). III (440 mg; 2.8 mmol) underwent 96% reaction (Column A, 110°C) when deoxygenated in the manner of I. Product isolation as above gave *trans*-4,4'-dichloroazobenzene, m.p. 180°C (lit. [4] m.p. 181.5-182.5°C) and *trans*-4,4'-dichloroazoxybenzene, m.p. 152-153°C (lit. [4] m.p. 155°C). Evidence (TLC) for the likely [4] by-product 2,7-dichlorophenazine (lit. [4] m.p. 267-268°C) was not obtained.

2-Nitrobiphenyl (IV). IV (560 mg; 2.8 mmol) and 2 equivalents of Me_6Sn_2 in *o*-dichlorobenzene (1.20 ml) were found (Column B, 170°C) to have undergone 94% reaction to give (GLC) 2-aminobiphenyl (5%) and carbazole (ca. 2%). Column chromatography using petroleum ether with increasing proportions of ether (0-50%) yielded *trans*-2,2'-azobiphenyl, m.p. 142-143°C (lit. [19] m.p. 144-145°C). (Found: C, 86.25; H, 5.43; N, 8.79. $C_{24}H_{18}N_2$ calcd.: C, 86.20; H, 5.43; N, 8.38%.) No 2,2'-azoxybiphenyl (lit. [19] m.p. 157-158°C) was isolated.

Separate solutions of 2-aminobiphenyl (0.35 *M*) and carbazole (0.35 *M*) in *o*-dichlorobenzene with 2 equivalents of Me_6Sn_2 were heated at 150°C for 20 and 8 h, respectively. Subsequent GLC analyses failed to reveal a change in substrate concentration, within experimental error. An additional control experiment, which involved heating a 1.1 *M* solution of Me_6Sn_2 in *o*-dichlorobenzene at 150°C for 16 h and then quantitative GLC analysis (Column C, 100°C) for Me_6Sn_2, confirmed the thermal stability of Me_6Sn_2 by failing to indicate a change in concentration.

Nitrosobenzene (143 mg; 1.4 mmol) and 1 equivalent of Me_6Sn_2 were reacted in benzene (2.8 ml) at 90°C for 20 min. GLC analysis (Column C, 80°C) indicated the absence of starting material and TLC led to isolation of azoxybenzene (68%), with only a trace amount (1%) of azobenzene.

Azoxybenzene solutions of 0.35 *M* concentration in benzene were heated with 1 and 4 equivalents Me_6Sn_2 at 150°C for 20 and 43 h, respectively. Quantitative GLC analyses (Column D, 172°C) indicated 32 and 93% conversion of starting material to 27 and 81% yields (uncorrected) of azobenzene, respectively. A minor by-product was detected by TLC as a slow eluting yellow band, but insufficient quantities of this material precluded identification.

Deoxygenation of IV with Bu_6Sn_2

A solution of IV (560 mg; 2.8 mmol) and Bu_6Sn_2 (2.29 ml; 5.6 mmol) in *o*-dichlorobenzene (1.8 ml) which had been heated at 150°C for 126 h was found (Column A, 200°C) to contain 10% unreacted IV. Preparative GLC of a portion of the reaction mixture led to isolation of 2-aminobiphenyl (10%, corrected), identified by IR, and approximately half as much of a yet unidentified material, which coincidentally had the same retention time as carbazole. TLC of the remaining reaction mixture led to isolation of *trans*-2,2'-azobiphenyl (8%, corrected). Low material balance (ca. 30%) was attributed to polymer formation, which was evident by TLC.

Determination of Me_6Sn_2 oxidation products

Preliminary analyses of reaction mixtures obtained from II and Me_6Sn_2 under the usual reaction conditions led to GLC (Column C, 82°C) identification of Me_4Sn, based on retention time comparison with authentic material, and isolation of $Me_3SnOSnMe_3$ as a colorless oil. The identity of this oil was established by its exposure to air, which led to immediate solidification via spontaneous hydrolysis [10] to hydroxytrimethyltin (Me_3SnOH), m.p. 110-121°C (lit. [10] m.p. 118°C). The IR spectrum of this sample of Me_3SnOH was essentially identical to that reported [10]. The Me_2SnO-like polymer (m.p. >250°C) that precipitated during deoxygenation was collected as a white powder, which was insoluble in methylene chloride, acetone, dimethyl sulfoxide, and pyridine, but which could be dissolved in concentrated hydrochloric acid. The IR spectrum of this material was similar to that of authentic Me_2SnO and featured the following absorptions: $\nu(CH_3)$ 2990, 2920, 1200, 1181; ν(SnOSn) 751; ν(SnC) 552 cm^{-1}. (Found: C, 15.08; H, 3.76; Sn, 76.06. C_2H_6SnO calcd.: C, 14.58; H, 3.67; Sn, 72.04%.) Additional oxidized products of Me_6Sn_2 were not detected by GLC or TLC.

Semi-quantitative stoichiometric data were obtained by heating a solution of II (2.8 mmol) and Me_6Sn_2 (5.6 mmol) in benzene (2.8 ml) at 150°C for 16 h. Under these conditions, essentially all of II was consumed and isolated yields of azoxy and azo product were 80 and 6%, respectively, which agrees reasonably well with GLC detection (Column C, 82°C) of 2.1 mmol unreacted Me_6Sn_2. Based on the amount of consumed Me_6Sn_2 (3.5 mmol), and assuming equal thermal conductivity response factors for Me_6Sn_2 and $Me_3SnOSnMe_3$, GLC analyses (Column C, 82°C) further indicated the presence of 1.9 mmol $Me_3SnOSnMe_3$ or 55% of the theoretical amount (1.9/3.5 × 100). The material balance of $Me_3SnOSnMe_3$ was accounted for by eqn. 6 (45% disproportionation), since quantitative GLC (Column C, 82°C) measurement of Me_4Sn (1.1 mmol) and isolation of the Me_2SnO-like polymer (200 mg) were both ca. 75% of their respective theoretical values. Lack of closer agreement with theory was ascribed to the aforementioned thermal conductivity approximation.

Kinetics

Reaction order. Three aliquots of each of three stock solutions of IV and Me_6Sn_2 in *o*-dichlorobenzene were sealed under vacuum in Pyrex ampoules and the nine samples were then simultaneously heated at 150°C for 16.0 h. For stock solution A: $[IV] = 0.59\,M$, $[Me_6Sn_2] = 1.40\,M$; for B: $[IV] = 0.70\,M$, $[Me_6Sn_2] = 0.70\,M$; for C: $[IV] = 0.70\,M$, $[Me_6Sn_2] = 0.35\,M$. GLC (Column B, 175°C, identical sample injection volumes) comparison of the peak area of IV for each stock solution with the average value of the peak area of unreacted IV for the three corresponding reaction aliquots led to calculation of "one point reaction rates" expressed as the decrease in [IV]. The found ratio of reaction rates for A/B = 1.62; theoretical ratio = 1.69 calculated on the assumption that $-d[IV]/dt = k[IV][Me_6Sn_2]$. The found ratio of reaction rates for B/C = 1.81; theoretical ratio = 2.00.

Determination of pseudo first-order rate constants. Five aliquots of each stock solution of II, IV, and V (0.1 *M*) with excess R_6Sn_2 (2.0 *M*) were sealed in vacuo and were then heated in a constant temperature oil bath which was controlled at ±0.1°C. Tubes were removed, cooled in an ice bath, and were then directly analyzed by GLC (Column A, 110°C for II and V; Column B, 170°C for IV) for the concentration of unreacted starting material ($[SM]_t$) using identical sample injection volumes for all aliquots, as well as for the remaining stock solutions ($[SM]_i$). Values of pseudo first-order reaction rate constants (k'), and hence half-life values ($\tau_{1/2}$), were obtained from a linear least-squares fit of $\ln([SM]_t/[SM]_i)$ vs. time; see Table 2.

Deoxygenation of nitrosobenzene (0.1 *M*) with Me_6Sn_2 (1.0 *M*) in benzene at 90°C was studied over 99% reaction in the same manner as described above (Column A, 75°C). The value for $k' = 1.11 \times 10^{-3}$ sec^{-1} (±7% slope error) and $\tau_{1/2}$ = 10.4 min.

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