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GENERATION OF 1,2-DEHYDROBENZENE FROM THE DEHALOSILYLATION OF (*o*-HALOPHENYL)TRIMETHYLSILANES

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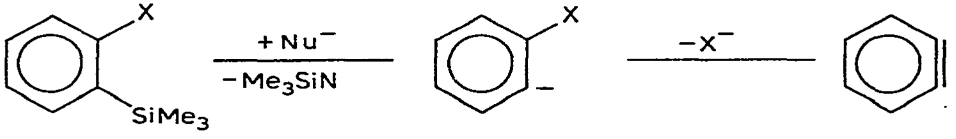
SUMMARY

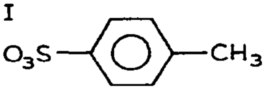
(*o*-Halophenyl)trimethylsilanes afford products expected from the generation of 1,2-dehydrobenzene when treated with potassium tert-butoxide or tetramethylammonium fluoride in aprotic solvents such as hexamethylphosphoric triamide and diglyme. The dehalosilylation leading to 1,2-dehydrobenzene appears to proceed by a stepwise process which involves the initial formation of an *o*-halophenyl carbanion resulting from heterolytic cleavage of the aryl–silicon bond.

INTRODUCTION

The observation that (2-chlorovinyl)trimethylsilanes undergo dechlorosilylation to acetylene under aprotic nucleophilic conditions[1] led us to examine the potential of *ortho*-substituted arylsilanes (I) to serve as precursors to 1,2-dehydrobenzene (benzyne) (III). In principle, 1,2-dehydrobenzene can arise from nucleophilic attack on (I) by either a concerted 1,2-elimination or in a stepwise fashion via the carbanion (II) (shown)*.



(I) (II) (III)

a , X = Cl
b , X = Br
c , X = I
d , X =  (OTs)

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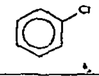
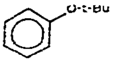
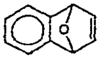
* It has recently been reported that potassium fluoride in dimethyl formamide cleaves aryl–silicon bonds to generate (presumably) various di- and poly-halophenyl carbanions, trapped as their benzaldehyde adducts[2]. Under protic conditions, nucleophilic attack at silicon appears to be concerted with electrophilic attack by proton at carbon, and discrete carbanions are not generated[3].

RESULTS AND DISCUSSION

The effect of a variety of nucleophiles (Nu^-) on (*o*-chlorophenyl)trimethylsilane (Ia) as a model substrate was determined using a number of aprotic solvents (Table 1). Both potassium tert-butoxide and tetramethylammonium fluoride were found to be potent reagents for effecting the dechlorosilylation of (Ia), and (Ib–d) also underwent facile elimination by alkoxide. In the presence of furan as the dehydrobenzene trap, compounds (IV)–(VII) (Nu = O-t-Bu) were produced from potassium tert-butoxide and (I)*, while similar treatment of (Ia) with tetramethylammonium fluoride led to the formation of chlorobenzene, (VI) and (VIII)*.

TABLE 1

REACTION OF VARIOUS REAGENTS WITH (*o*-CHLOROPHENYL)TRIMETHYLSILANE (Ia)[a,b,c]

Run	*Reagent*	*Solvent*				*Reaction time* (*h*)
1	BuLi	Ether				18[d]
2	LiO-t-Bu	Ether				154[d]
3	KF[e]	DMSO[f]				72[d,g]
4	KF[e]	HMPT[h]				72[d]
5	AgF[e]	DMSO				20[d]
6	$Et_4NF \cdot 2H_2O$[i]	DMSO	90	[j]	Trace	0.1
7	Et_4NCN[e]	HMPT				68[d]
8	LiF[e]	HMPT				148[d]
9	Me_4NF	HMPT	12	[j]	31	0.1[k]
10	Me_4NF[e]	Furan	39	[j]	32	240[l]
11	NaSPh	HMPT				19[d]
12	KO-t-Bu	HMPT	18	4	18	0.2[m]
13	KO-t-Bu	HMPT	11	6	16	0.2[m,n]
14	KO-t-Bu	HMPT	0	13	0	0.2[m,o]
15	KO-t-Bu	HMPT	4	2	32	0.2[m,p]
16	KO-t-Bu	HMPT	18	2	36	0.2[q]
17	KO-t-Bu	HMPT	2	14		0.2[m,r]
18	KO-t-Bu[e]	Furan				18[d]
19	KO-t-Bu	CH_3CN				23[d]
20	KO-t-Bu	Diglyme[s]	7	14	25	0.3[m]
21	KO-t-Bu	Diglyme	13	12	40	0.3[t]

[a] At 25° unless noted otherwise. [b] Yields [% based on (Ia)] were determined by quantitative GLC after isolation of products. [c] Furan as trapping agent. [d] No reaction. [e] Insoluble or sparingly soluble in solvent shown. [f] Dimethyl sulfoxide. [g] Trace of chlorobenzene after 29 h at 145°. [h] $(Me_2N)_3PO$. [i] Eastman Organic Chemicals "Et_4NF"; analysis showed this to be the dihydrate. [j] No fluorobenzene was detected. [k] 12% (VIII) also formed. [l] 29% (VIII) also formed; 90% complete in 120 h. [m] (Ia) added dropwise to reactants at 0°. [n] Commercial (unsublimed) KO-t-Bu. [o] No furan present. [p] Addition of (Ia) followed immediately by trimethylchlorosilane. [q] KO-t-Bu in HMPT added dropwise to reactants at 0°. [r] Anthracene as trapping agent (sparingly soluble); no adduct formed. [s] Bis(2-methoxyethyl) ether. [t] KO-t-Bu added dropwise to reactants at −20° followed by trimethylchlorosilane; 4% (VIII) also formed.

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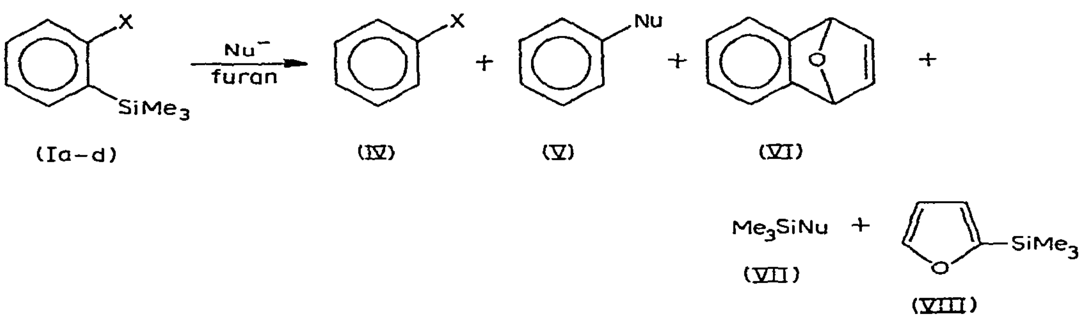
* In reactions employing HMPT as solvent, traces of *N,N*-dimethylaniline were also produced.



Consumption of (o-chlorophenyl)trimethylsilane (Ia) was found to be extremely fast when either tetramethylammonium fluoride or potassium tert-butoxide in HMPT was employed, and GLC analysis of these reaction mixtures immediately after (Ia) had been added showed complete disappearance of starting material. The reaction of potassium tert-butoxide with (Ia) in diglyme was only slightly slower, and was complete within 10 minutes of addition. In general, dehalosilylation appears to be promoted by those solvents which not only dissolve the reagents employed, but also enhance the ionic character of these species by coordination (HMPT) and chelation (diglyme) at the cationic center. Although the insolubility of some reagents undoubtedly lends to their ineffectiveness (the metal fluorides, for example), homogeneity is not of itself a sufficient condition for elimination, even for potassium tert-butoxide when dissolved in acetonitrile. It is worthy of note that the nucleophiles found effective in elimination are those which form the strongest bonds to silicon (fluoride, alkoxide)[4].

Optimum yields (30–40%) of dehydrobenzene adduct (VI) in both HMPT and diglyme solvents were realized when a solution of potassium tert-butoxide was slowly added to a cold mixture of the other reactants, or when tetramethylammonium fluoride was employed as the nucleophile source in HMPT or neat furan. In most runs employing alkoxide, the presence of chlorobenzene and phenyl tert-butyl ether significantly detracted from the output of dehydrobenzene adduct. The ether must arise from addition of alkoxide or tert-butyl alcohol to dehydrobenzene itself[5], while chlorobenzene can result from proton capture by the o-chlorophenyl carbanion (II). The absence of chlorobenzene from the products of run 14 (Table 1) suggested that furan was serving as the ultimate source of labile protons*. Although trimethylchlorosilane derivatization of an alkoxide elimination carried out in HMPT (Table 1, run 15) afforded no 2-(trimethylsilyl)furan (VIII), this compound was obtained after run 21 (in diglyme) was treated in a similar fashion. Moreover, significant amounts of (VIII) were isolated from eliminations induced by tetramethylammonium fluoride (Table 1, runs 9 and 10). These results suggest that the o-chlorophenyl carbanion (II) is a discrete intermediate in these reactions, and is the precursor to chlorobenzene by way of proton abstraction from furan. Subsequent reaction of the 2-furyl anion

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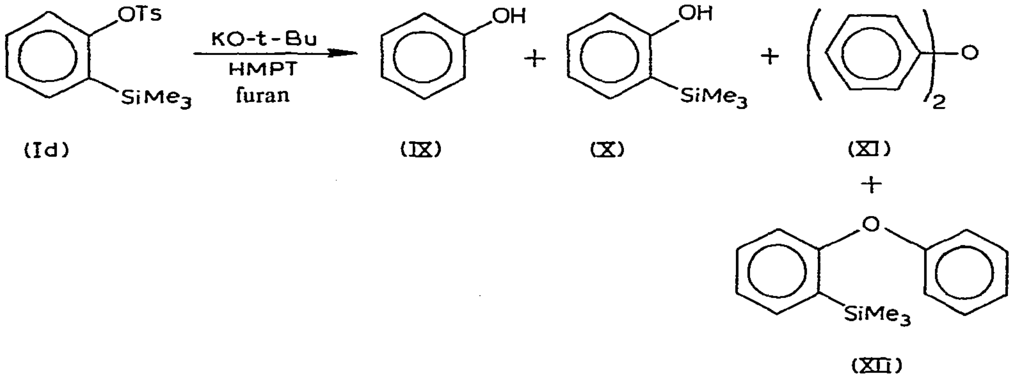
* The analogous potassium tert-butoxide/DMSO system has been employed to measure the rate of 2-proton exchange in furan[6]. It has been reported that the hydrogens of HMPT are completely unreactive towards strongly basic reagents[7].

thus formed with added trimethylchlorosilane then affords (VIII)*. In neat furan containing fluoride ion as nucleophile, (VIII) presumably results from the *in situ* capture of the 2-furyl anion by the trimethylfluorosilane produced upon elimination.

In an effort to speed halide loss from the carbanion (II) relative to proton capture** (Ib–d) were prepared and subjected to standard elimination conditions (Table 2). No improvement in the yields of cycloaddition product (VI) was observed. The use of DMSO as solvent for the elimination of (*o*-tosyloxyphenyl)trimethylsilane (Id) led mainly to protonation of the intermediate carbanion (IId). (DMSO is a much better proton donor than is HMPT[8].) In HMPT, the reaction of potassium tert-butoxide with (Id) produced only the compounds (IX)–(XII) in low yield. The first two of these are indicative of ester exchange at sulfur*** (with and without prior desilylation), while (XI) and (XII) may arise from the reaction of dehydrobenzene with (IX) and (X) or their phenoxides.



Since the tosylate (Id) appeared to have a geometry that might facilitate thermal 1,2-elimination via a cyclic transition state, its pyrolytic behavior was investigated. In contrast to expectations, (Id) was quite stable to high temperatures and did not undergo decomposition until pyrolyzed at 650°. No products attributable to a dehydrobenzene intermediate could be isolated from these attempts.

The present technique affords an alternative to known base-promoted generation of dehydrobenzene in the ease and regiospecificity of elimination. Under the conditions used, dehydrohalogenation is not detectably competitive with dehalosilylation. Mixtures of potassium tert-butoxide, HMPT and either bromobenzene†

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* Control experiments in which potassium tert-butoxide was contacted with furan in both HMPT and diglyme followed by addition of trimethylchlorosilane showed only a trace of (VIII), assumed to arise from a small equilibrium concentration of the 2-furyl anion under these conditions.

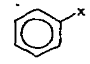
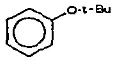
** For a discussion of relative rates of halide loss from intermediates such as (II), see ref. 5, pp. 43–60.

*** The other product of this exchange, tert-butyl tosylate, is unstable under ambient conditions[9].

† Interestingly, it has been reported[10] that in DMSO, potassium tert-butoxide converts bromobenzene to tert-butyl phenyl ether in 86% yield after 15 h at 25°. Several reports are pertinent to our negative findings in HMPT relative to this information. First, solutions of potassium tert-butoxide in DMSO have been shown to contain appreciable concentrations of potassium methanesulfinylmethyl carbanion (KCH_2SOCH_3) at equilibrium[11]. Secondly, Mac and Parker have suggested that KCH_2SOCH_3 is a stronger hydrogen base than KO-t-Bu in DMSO[12]. An attractive suggestion is that dehydrobenzene formation in the KO-t-Bu/DMSO system is initiated by proton removal from bromobenzene by the methanesulfinylmethyl carbanion, but that in the far less acidic HMPT, the only active (and less potent) hydrogen base available is the tert-butoxide ion.

TABLE 2

ELIMINATION OF (2-SUBSTITUTED PHENYL)TRIMETHYLSILANES WITH KO-t-Bu IN HMPT/FURAN

Substrate			
X = Br	2	18	9
I	0^a	25	20
OTs	60	15	5^b
OTs	0	0	0^c

[a] In the absence of furan, iodobenzene gives phenyl tert-butyl ether under these conditions. [b] DMSO as solvent. [c] See experimental section.

or chlorobenzene showed no consumption of aryl halide after 18 h at 25°, although only 25% of iodobenzene remained after ½ h of this treatment. However, none of the substrates (Ia–d) afforded detectable amounts of cycloaddition products incorporating the trimethylsilyl function.

EXPERIMENTAL

All solvents and furan were purified before use by distillation from calcium hydride. Commercial potassium tert-butoxide was sublimed (150°/0.5 mm). Lithium tert-butoxide was prepared in ether by adding a 10% excess of n-butyllithium in hexane to anhydrous tert-butyl alcohol. Sodium benzenethiolate was prepared in HMPT by the addition of benzenethiol to an excess of sodium hydride previously freed of mineral oil by a pentane wash; the thiolate solution was then filtered from excess hydride before use. Tetraethylammonium cyanide[13], triptycene[14], biphenylene[14], 1,4-dihydro-1,4-epoxynaphthalene[15], 2-(trimethylsilyl)furan[16], phenyl tosylate and tert-butoxytrimethylsilane were prepared by standard methods. Transfers of highly hygroscopic materials were carried out in a dry-box, and subsequent reactions performed in tightly sealed flasks.

Gas chromatographic (GLC) analyses were carried out using a 5 ft. 3% or 20% SE-30 on 60/80 mesh Chromosorb W stainless steel column; the separation of (IVa) from (VIII) required a 10 ft. FFAP column. Infrared data were obtained on neat films using a Beckman IR-8 spectrophotometer. NMR spectra were obtained on CCl_4 solutions with CH_3CN as internal standard using a Varian A60-A spectrometer. Analytical data were provided by Galbraith Laboratories, Knoxville, Tennessee, and by Mr. G. Martinie of this Department.

(*o-Chlorophenyl*)*trimethylsilane* (*Ia*)

This material was prepared from *o*-chloroiodobenzene[17] by the method of Eaborn in 60% yield, b.p. 90–96°/18 mm (lit.[18] b.p. 89°/15 mm).

(*o-Bromophenyl*)*trimethylsilane* (*Ib*)

A mixture of 5.4 g (0.78 g-atom) of lithium wire (1% Na) and 100 ml anhydrous ether was agitated with a high-speed stirrer in a Morton flask under helium, while

18.4 g (0.10 mole) of (*o*-chlorophenyl)trimethylsilane was slowly added. After stirring 4 h, the flask was cooled to −78°, and 16.0 g (0.10 mole) of bromine in 25 ml ether added. An aqueous workup followed by distillation gave 7.6 g (33%) of (Ib), b.p. 120°/18 mm (lit.[19] b.p. 77°/3.5 mm). The yield obtained is not indicative of the method's potential, as a leak in the helium line led to products (phenyltrimethylsilane and 1,3,5-tribromophenol) indicative of moisture and oxygen introduction. IR: 3.22w, 3.35m, 3.41w, 6.30w, 6.41w, 6.88w, 7.10m, 8.00s, 8.90m, 9.05m, 9.82m, 11.95s, 13.50s, 14.15m, 14.51w, 15.49w μm. NMR: δ 7.2–7.8c, 0.6s.

(o-Iodophenyl)trimethylsilane (Ic)

This material was prepared in the same fashion as (Ib) from 3.5 g (0.50 g-atom) lithium and 18.4 g (0.10 mole) of (Ia), followed by 63.5 g (0.50 mole) iodine. Workup gave 18.6 g (67%) of (Ic), b.p. 80–82°/2 mm (lit.[19] b.p. 77°/3.5 mm). IR: 3.23w, 3.32m, 3.41w, 6.34w, 6.43w, 6.89w, 7.05m, 7.99s, 8.91m, 9.10w, 9.60w, 9.93m, 11.90s, 13.48s, 14.35m, 14.51w, 15.60w μm. NMR: δ 6.8–8.0c, 0.6s.

(o-Tosyloxyphenyl)trimethylsilane (Id)

A mixture of 21.2 g (0.128 mole) *o*-(trimethylsilyl)phenol[20], 30.0 g (0.157 mole) *p*-toluenesulfonyl chloride and 50 ml pyridine was heated at 100° for 12 h. The solution was then poured into water, extracted with ether, and the organic layer washed with dilute acid and potassium carbonate solution. After drying ($MgSO_4$), distillation gave 28.8 g (73%) of (Id), b.p. 148°/0.06 mm. (Found: C, 59.94; H, 6.34. $C_{16}H_{20}O_3SSi$ calcd.: C, 59.96; H, 6.29%.) IR: 3.20w, 3.31m, 3.38w, 6.25w, 6.79w, 6.99w, 7.25s, 7.98m, 8.34s, 8.45s, 8.88w, 9.15w, 9.34m, 11.40s, 11.92s, 13.10w, 13.61m, 13.95w, 15.25m μm. NMR: δ 7.0–8.0c, 2.5s, 0.4s.

Reaction of nucleophiles with (Ia–d)

The following procedure employing (Ia) is typical of the runs carried out with potassium t-butoxide in HMPT and diglyme.

Sublimed potassium tert-butoxide was weighed into the reaction flask in a dry-box (6.2 g, 0.055 mole), 100 ml HMPT added, and the mixture stirred at 25° until solution had been achieved (ca. $\frac{1}{2}$ h). Furan (13.5 g, 0.20 mole) was then added, the flask cooled in an ice bath, and 9.2 g (0.050 mole) (Ia) added dropwise over 10 min. to the rapidly stirred solution. A GLC analysis of the dark solution was made immediately after addition was complete and subsequently compared to GLC traces obtained on the isolated product mixture; no significant change in product composition was observed. Workup consisted of steam distillation* followed by ether extraction of the distillate and removal of ether and furan by distillation through an 8″ vigreux column. The residue was analyzed by GLC (internal standards and comparison with solutions of authentic samples of known concentrations were both used) and found to contain tert-butoxytrimethylsilane (44%), chlorobenzene (18%), tert-butyl phenyl ether (4%) and 1,4-dihydro-1,4-epoxynaphthalene (18%).

When inverse addition was employed, the same quantities of materials were used, but the alkoxide was first dissolved in 50 ml HMPT and then slowly added to the other reactants in 50 ml HMPT.

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* This was far superior to separation by either exhaustive pentane extraction of the hydrolyzed solution or complexation of HMPT with anhydrous magnesium chloride followed by filtration. Even volatile products could not be cleanly separated from HMPT by simple distillation.

Runs using tetramethylammonium fluoride were carried out in a similar fashion. About 5 g of this material dissolved in 100 ml HMPT upon stirring for 20 h at 25°.

Conditions as described in Table 1 which led to no reaction were monitored by GLC both for the appearance of potential products and (quantitatively) for disappearance of starting (Ia).

The reaction of 8.0 g (0.025 mole) (Id) with 3.2 g (0.028 mole) KO-t-Bu and 6.8 g (0.10 mole) furan in 50 ml HMPT (worked up by acidification and ether extraction) led to no detectable amounts of (IVd), (V) or (VI). Instead, GLC analysis indicated the presence of phenol (4%), *o*-(trimethylsilyl)phenol (4%), diphenyl ether (4%) and (*o*-phenoxyphenyl)trimethylsilane (11%). The (*o*-phenoxyphenyl)tritrimethylsilane was identified by spectral data (IR: 3.23w, 3.36w, 3.42w, 6.29m, 6.39m, 6.71m, 6.82m, 6.98m, 8.18s, 8.63w, 8.90w, 9.31w, 11.96s, 12.50w, 13.37m, 13.90w, 14.51w μm. NMR: δ 6.8–7.7c, 0.45s), n_D^{24} 1.5503 (lit.[21] n_D^{20} 1.5525) and analysis (Found: C, 74.49; H, 7.74. $C_{15}H_{18}OSi$ calcd.: C, 74.33; H, 7.49).

Thermolysis of (o-tosyloxyphenyl)trimethylsilane (Id)

A mixture of 6.4 g (0.020 mole) (Id) and 10.7 g (0.060 mole) anthracene was heated under nitrogen at 240° for $5\frac{1}{2}$ h. Workup of the reaction mixture showed no triptycene by GLC analysis, and gave an almost quantitative recovery of starting materials.

In another run, neat (Id) was added to a 7-in. tube filled with 0.25-in. pyrex helices and heated to 390° under slow nitrogen flow. Only starting material and a small quantity of low boiling material was present in the pyrolysate obtained from the −78° trap; no biphenylene was present. When the pyrolysis was repeated at 650°, about half of the initial mass was collected in the trap. No biphenylene was present; 10–20% of this material was identified as toluene.

Control experiments

The reaction products (IVa–c)–(VII) (Nu=O-t-Bu) were all independently subjected to the reaction conditions employed in the KO-t-Bu/HMPT runs (but without furan). Chlorobenzene, bromobenzene, and tert-butoxytrimethylsilane showed no reaction (as determined by quantitative GLC analysis) after 18 h at 25°. Consumption of iodobenzene was 75% complete after $\frac{1}{2}$ h, and led to tert-butyl phenyl ether as the only isolable product. tert-Butyl phenyl ether was itself monitored for 6 h and found to be completely stable. Bromobenzene did undergo 90% reaction after 19 h at 125° to give a 22% isolated yield of tert-butyl phenyl ether. Adduct (VI) underwent no reaction at 25° after 5 days.

A mixture of 6.1 g (0.054 mole) KO-t-Bu, 50 ml HMPT and 3.4 g (0.050 mole) furan was stirred for 17 h at 25°. Trimethylchlorosilane (6.5 g, 0.060 mole) was then added at once. GLC analysis showed that only a trace of (VIII) was present. A similar run employing diglyme as solvent gave identical results.

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