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Benzylic C-H functionalisation by [Et_3SiH + KO^{t}Bu] leads to radical rearrangements in *o*-tolyl aryl ethers, amines and sulfides

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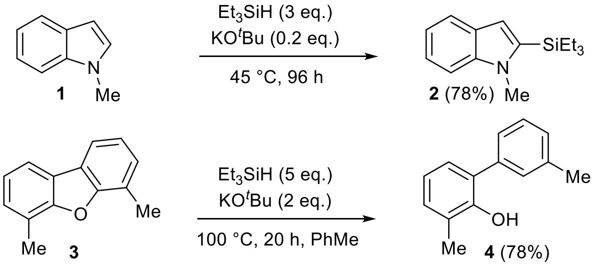
Abstract. Reaction of Et_3SiH + KO^{t}Bu with diaryl ethers, sulfides and amines that feature an *ortho* alkyl group leads to rearrangement products. The rearrangements arise from formation of benzyl radicals, likely formed through hydrogen atom abstraction by triethylsilyl radicals. The rearrangements involve cyclisation of the benzyl radical onto the partner arene, which, from computation, is the rate determining step. In the case of diaryl ethers, Truce-Smiles rearrangements arise from radical cyclisations to form 5-membered rings, but for diarylamines, cyclisations to form dihydroacridines are observed.

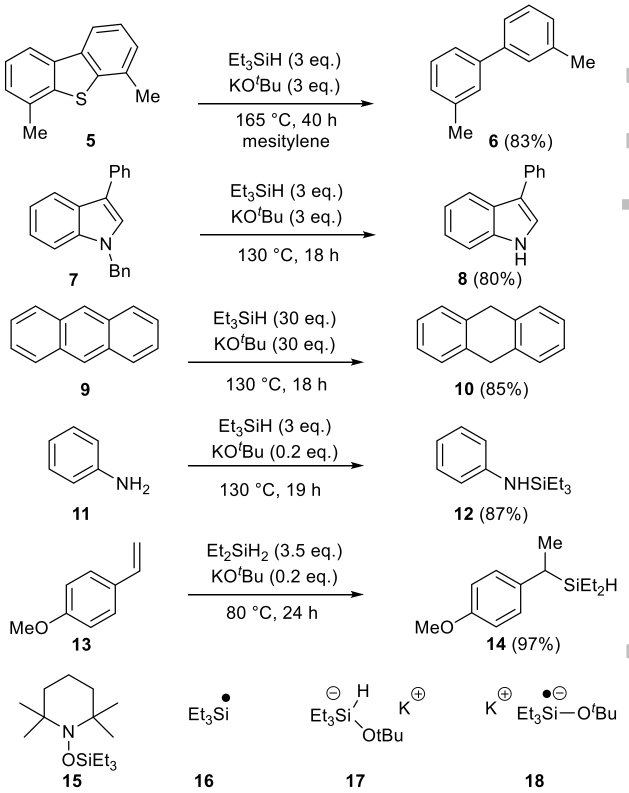
Keywords: radical; Truce-Smiles rearrangement; silane; KO^{t}Bu.

Introduction

In 2013, Grubbs *et al.* reported[1] that heating Et_3SiH with KO^{t}Bu afforded a novel reagent which has since been shown to carry out a wide range of chemical transformations.[1-11] (Schemes 1 and 2). This versatile reagent achieves regioselective silylation reactions of indoles **1** and other heterocycles.[1,3,5,6] at lower temperatures, cleavage of Ar-O bonds in aryl ethers **3**,[1] and Ar-S bond cleavage in thioethers **5** [4] at higher temperatures. In addition, the reagent debenzylates N-benzylindoles, **7**,[7] reduces fused aromatic hydrocarbons, (*e.g.* **9**) to their dihydro counterparts,[7] and converts primary and secondary amines, e.g. **11** to their silylated derivatives,[9,10] in this case, **12**. The analogous silane, Et_2SiH_2, (and less efficiently, Et_3SiH) in combination with KO^{t}Bu, converts styrenes, e.g. **13** to their hydrosilylated derivatives, in this case, **14**.[8]



Scheme 1. Early transformations with Et_3SiH + KO^{t}Bu.



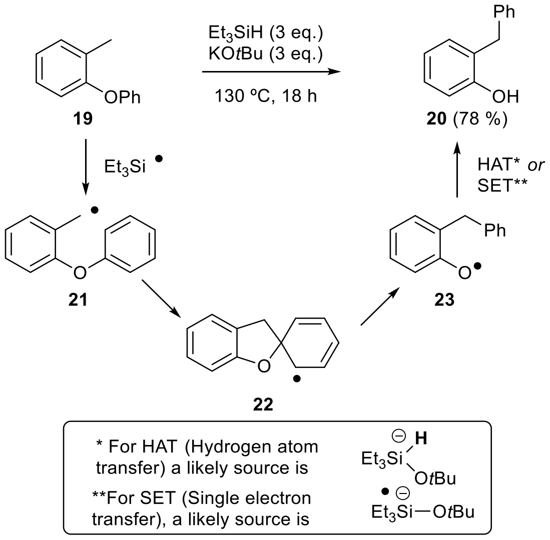
Scheme 2. Recent transformations by Et_3SiH + KO^{t}Bu.

It appears that many different types of reactive species may be produced from heating Et_3SiH with KO^{t}Bu, and the nature of the reactive species present in this mixture is really not fully understood. Houk, Stoltz *et al.* detected[5] TEMPO-$SiEt_3$, **15**, following addition of TEMPO, which provides evidence for triethylsilyl radicals **16**, and Jeon *et al*. have proposed K^+ $[Et_2Si(H)_2O^tBu]^-$ and analogue **17** as hydrogen atom transfer agents (and ultimately, hydrosilylation agents).[8] The radical anion **18** has also been proposed to play an active role.[1,7] As an indication of the range of mechanisms under consideration, both radical[5] and non-radical[6] mechanisms have been proposed for the silylation reactions of indoles **1**. Our recent efforts have reported novel reactions that provide new information on the diverse pathways open to this reagent.[7,10,11]

As mentioned above, diaryl ethers were studied by Grubbs *et al.* who reported Ar-O bond cleavages, e.g. **3**→**4**. The more recently published proposal[4] for the mechanism involves *ipso* silyl radical addition to an aryl ring at the site of substitution, *i.e*. at the carbon involved in the Ar-O bond, followed by fragmentation of the C-O bond. In principle, electron transfer from a species such as **18** to the π^* system of a diaryl ether, might also produce cleavage of the aryl ether,[1] and our original experiments were designed to explore the nature of the cleavages. This paper now reports our results.

Results and Discussion

When substrate **19**, (substrates were routinely synthesised *via* standard reactions, such as Ullmann or Chan-Lam coupling reactions. For details of their preparation and characterisation, see S.I.), was subjected to our standard Et_3SiH/KO^tBu reaction conditions (3 eq. of both reagents at 130 ºC for 18 h) in the absence of solvent, rearranged product **20** (78%) was isolated (Scheme 3). Control thermal reactions (i) with KO^tBu but with no Et_3SiH, (ii) with Et_3SiH but with no KO^tBu and (iii) with neither reagent (a purely thermal rearrangement is known at 320 ºC[12]) returned only starting material, which confirmed that the combination of Et_3SiH and KO^tBu was essential for the transformation.



Scheme 3. Truce-Smiles rearrangement of radical **21**.

Given the evidence for triethylsilyl radicals in these reaction mixtures, this rearrangement looks to be a radical-induced Truce-Smiles rearrangement.[13-18] Hydrogen atom abstraction from the methyl group of **19** forms radical **21**. This radical then undergoes rearrangement via the spirocyclic radical **22**, which rearomatises in forming phenoxyl radical **23** that is quenched in due course.

Efforts then focused on optimisation of the reaction with substrate **19** through variation of temperature, reaction time, nature of the silane and nature of the base and solvent, prior to using those optimised conditions to study the scope of the reaction with a variety of substrates. Initially, a temperature study was conducted at 70 °C, 100 °C and 150 °C, but all proved inferior to our standard 130 °C (see Table 1).

Table 1. Effect of varying temperature on aryl migration reaction of **19**.

Entry	Temperature, T (° C)	**20** (%)[a]	**19** (%)[a]
1[b]	130	78	0
2	70	0	86
3	100	57	28
4	150	75	0

[a]% yield determined by internal NMR standard (1,3,5-trimethoxybenzene); [b]isolated by column chromatography

A survey of reaction times showed that yields suffered when the reaction was conducted for a shorter period than 18 h (Table 2).

Table 2. Effect of varying reaction time on rearrangement of **19**.

Entry	Reaction Time	**20** (%)[a]	**19** (%)[a]
1[b]	18 h	78	0
2	10 min	3	74
3	30 min	54	25
4	6 h	63	17

[a]% yield determined by internal NMR standard (1,3,5-trimethoxybenzene); [b] isolated by column chromatography

Varying the nature of the silane showed that tri-*n*-alkylsilanes as well as methyldiphenylsilane and phenyldimethylsilane worked comparably well (Table 3).

Table 3. Effect of varying silane on aryl migration reaction of **19**.

Entry	Silane	**20** (%)[a]	**19** (%)[a]
1[b]	Et_3SiH	78	0
2	Ph_3SiH	35	38
3	Ph_2MeSiH	73	0
4	$PhMe_2SiH$	77	0
5	$(^iPr)_3SiH$	0	100
6	$^nPr_3SiH$	74	0
7	Et_2SiH_2	43	27

[a]% yield determined by internal NMR standard (1,3,5-trimethoxybenzene); [b] isolated by column chromatography

On the other hand, triphenylsilane was much less effective and tri*iso*propylsilane gave no conversion at all, suggesting that substantial stabilisation of the silyl radical in triphenylsilyl radical, or substantial steric hindrance around silicon, in the tri*iso*propyl radical, adversely affected the rearrangement. Interestingly, the reagent that Jeon et al. found to work most effectively in their hydrosilylation reactions,[8] diethylsilane, Et_2SiH_2, was much less effective in this transformation (Entry 7).

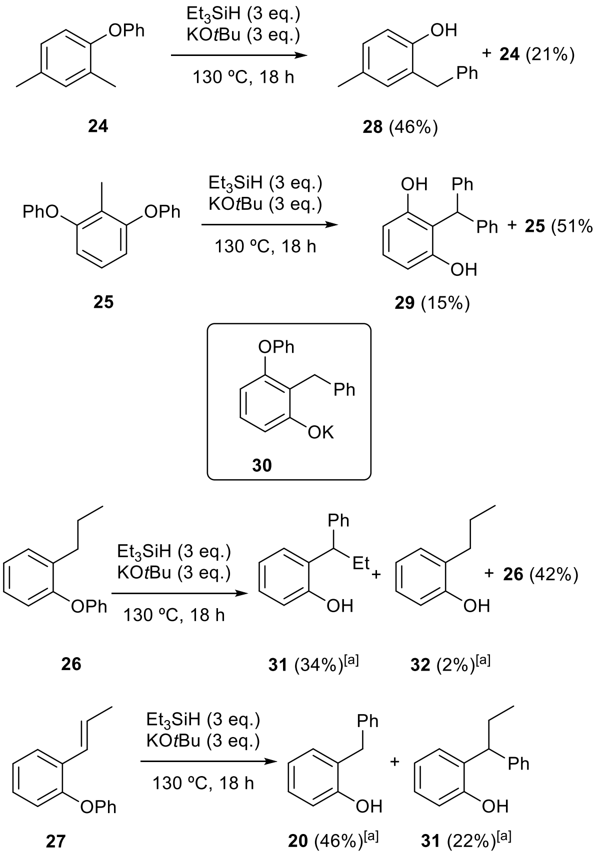
Table 4. Effect of varying the base on rearrangement reaction of **19.**

Entry	Base	**20** (%)[a]	**19** (%)[a]
1[b]	KO^{t}Bu	78	0
2	NaO^{t}Bu	0	90
3	NaH	0	100
4	KH	18	30
5[c]	KH	0	80
6	KOH	0	89
7	KOEt	13	31
8[c]	KOEt	0	100
9	KHMDS	0	83
10	LDA	0	100

[a]% yield determined by internal NMR standard (1,3,5-trimethoxybenzene); [b] isolated by column chromatography; [c]reaction conducted in the absence of triethylsilane.

In a study of the influence of different bases on the reaction, KO^{t}Bu was effective for the aryl migration of substrate **19** to phenol **20** (Entry 1, Table 4). Switching to NaO^{t}Bu only yielded starting material **19** (Entry 2). Similarly, no conversion was seen when using NaH as the base (Entry 3). However, with KH, rearranged product **20** was observed, albeit to a lesser extent than with KO*t*Bu (Entry 4). A control experiment (absence of Et_3SiH) showed that KH alone cannot cause aryl migration to occur (Entry 5). These results show the great importance of the potassium ion present in the base for the rearrangement of **19** to **20** and, more generally, for the silane-base system. This was consistent with results from the Grubbs, Stoltz and Jeon groups in their study of different reactions as well as with our earlier studies.[1,2-4,6,8] KOH, which was employed for C(sp)-H bond silylation by Grubbs *et al.*,[19] gave no conversion of substrate **19** (Entry 6). KOEt (Entry 7) gave only a 13 % yield of phenol **20** from compound **19** and KHMDS and LDA both proved ineffective (Entries 9 and 10).

With these results, the diaryl ethers, **24**-**27** were prepared and tested under the optimum solvent-free conditions (Scheme 4). Xylylphenyl ether **24** afforded rearranged product **28** (46%) together with some starting material (21%). Symmetrical resorcinol diphenyl ether **25** gave benzhydryl-substituted resorcinol **29** (15%), together with starting material (51%). The double-migration observed in forming **29**, and the absence of a product showing a single-migration, such as **30**, is in line with the fact that while **30** would be an intermediate in the process, C-H abstraction from a CH_2 benzylic position in **30** is easier than from the CH_3 group in **25**, and so **30** is selectively activated for conversion to **29**. The sensitivity of substrates to the alternative and simpler fragmentative mode of reaction witnessed by Grubbs *et al.* was seen with propylphenyl phenyl ether **26**, where the simple fragmentation product **32** was seen in low yield (2%), alongside the rearrangement product **31** (34%) and starting material **26** (42%).

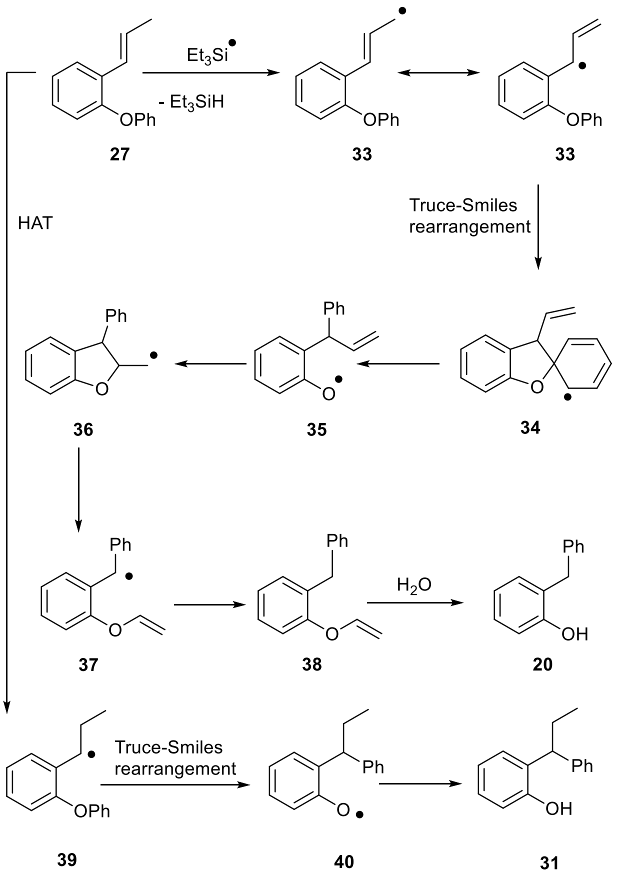


[a]% yield determined by NMR internal standard (1,3,5-trimethoxybenzene)

Scheme 4. Probing the scope of the rearrangement.

Substrate **27** provided useful information on the routes to activation for rearrangement. It does not feature an easily abstractable benzylic H-atom, as C-H bonds to sp^2-carbons are so strong, but the terminal sp^3-methyl group C-H bonds in cinnamyl compound **27** should have similar bond strength to the benzylic C-H in **19**. Abstraction of the cinnamyl C-H would form radical **33**. Scheme 5 shows the evolution of radical **33** to the unexpected product **20**. Radical **33** undergoes a Truce-Smiles rearrangement to give radical **35**. Cyclisation to give **36** followed by a fragmentation and hydrogen atom abstraction via benzyl radical **37** leads to vinyl ether **38**, and then facile hydrolysis of the vinyl ether would afford the observed product **20**.

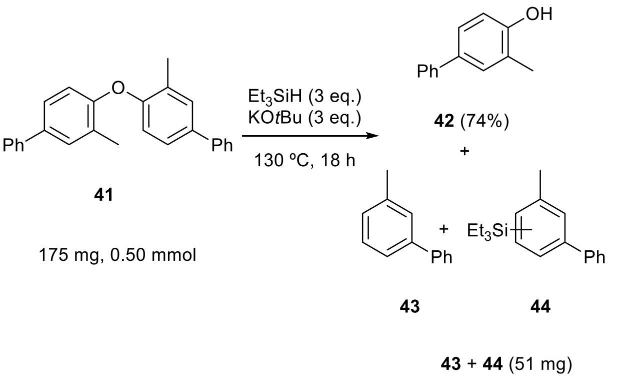
Alternatively, a benzyl radical **39** could be reached by a different route, namely through hydrogen atom transfer (HAT), as proposed in Jeon's work. In Jeon's examples, the benzyl radical that is formed by HAT to the styrene undergoes silylation (as seen in **13**→**14**, Scheme 1). In this case, that benzyl radical **39** has an alternative exit via a Smiles rearrangement, resulting in phenol **31**.



Scheme 5. Proposal for the formation of phenols **20** and **31** from substrate **27**.

A point of concern for us was the mass balance in our reactions. With so many likely types of reactive species present, it was not surprising that a range of alternative products might be formed, but we wondered whether some products might be volatile. Accordingly, substrate **41** was selected (Scheme 6). This substrate has the advantage of being derived from a phenyl-substituted phenol, and therefore the products arising should not be volatile. Also, this substrate is symmetrical and this should limit the number of by-products. In this case, reaction under our standard conditions afforded the phenylcresol **42** (74%), and an inseparable mixture of *m*-methylbiphenyl **43** and silylated counterparts **44**. Interestingly, no product of Smiles rearrangement was observed.

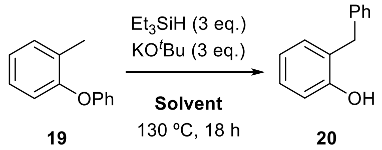
Continuing our exploration of the scope of the reaction, substrates **45** and **46** were now assessed (Scheme 7). Although they differed from substrate **19** only by a single alkyl group, their reactions took completely different courses than **19**, under analogous conditions. Thus, **45** gave the two phenols that would result from simple fragmentation, **50** (5%) and **51** (64%). Likewise, the *p*-cresol derivative **46** gave **50** (11%) and **53** (38%).



Scheme 6. Fragmentation of substrate **41**.

At that stage, we decided to explore one remaining parameter relating to our parent case **19**→**20**, *i.e.* the effect of solvent. Table 5 shows that THF was the solvent of choice. Accordingly, we returned to substrates **45** and **46**, and compared their reactivity in THF with that under solvent-free conditions. Scheme 7 shows that the addition of THF has a profound effect on the outcome of the reactions of these substrates, leading to rearranged products **52** (53%) and **54** (34%) respectively.

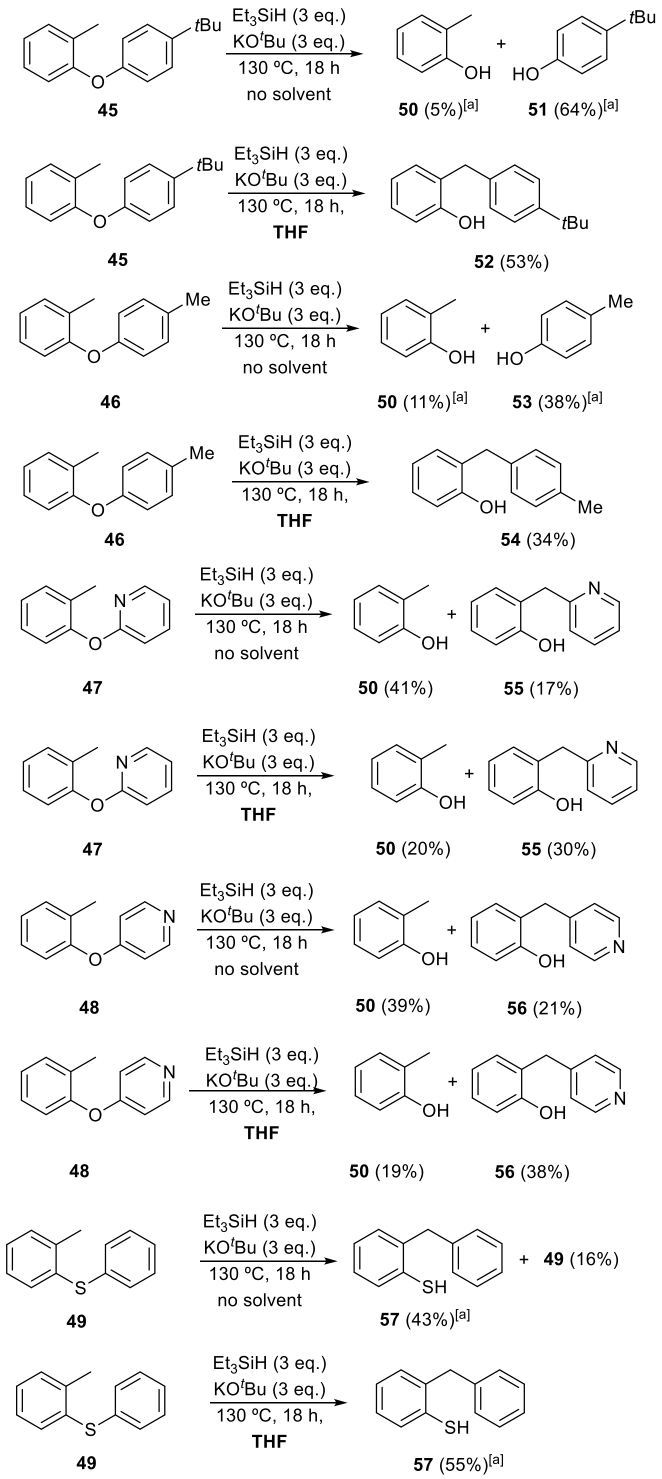
Table 5. Effect of solvent on aryl migration reaction of **19**.



Entry	Solvent[a]	**20** (%)[b]	**19** (%)[b]
1[c]	-	78	0
2	Hexane	16	24
3	Toluene	8	30
4	THF	88	0
5[d]	THF	58	3
6	1,4-Dioxane	0	91

[a] 5 mL of solvent used; [b] % yield determined by internal standard (1,3,5-trimethoxybenzene); [c] isolated by column chromatography; [d] 2 mL of THF used

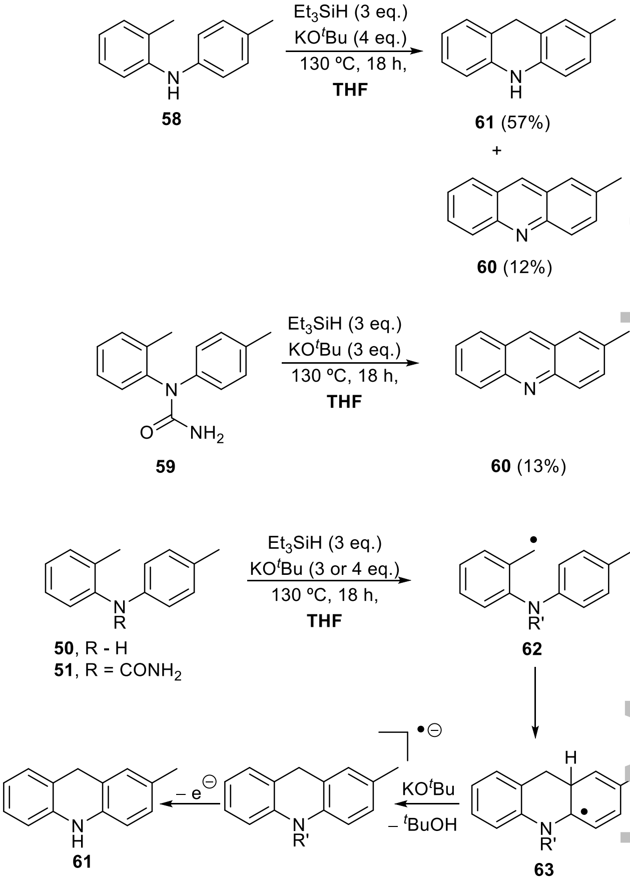
The pyridine substrates **47** and **48** were next examined. In these cases, the rearrangement products **55** and **56** respectively, as well as *o*-cresol, **50**, were obtained under solvent-free and THF conditions. At this stage, it is not possible to define the role of THF. It is clear that potassium ions are of critical importance for this reagent, so it is not too surprising that the nature of its solvation should also be important.



Scheme 7. Rearrangements in THF as solvent, compared to solvent-free conditions

The formation of *o*-cresol **50** as the sole 'simple fragmentation' product of these substrates (no pyridones were observed) would be consistent either with selective addition of a radical (H atom or triethylsilyl radical) to the pyridine ring, or with selective electron transfer to the electron-deficient pyridine ring in **47** and **48**, followed by fragmentation. In these reactions, the rearrangement product **55** (17%) or **56** (21%) was also seen from substrates **47** and **48**, respectively. When these substrates were treated with the reagent in THF as solvent, the yields of the rearrangement product increased and of the fragmentation product decreased.

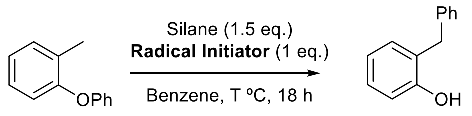
To compare the effect of other linking atoms to the oxygen of diaryl ethers, sulfur-linked substrate **49** was explored, and gave the rearrangement product **57** (43%) under solvent-free conditions and the same product (55%) when conducted in THF as solvent.



Scheme 8. Rearrangement of diarylamines.

As these reactions generally afforded greater yields of rearrangement product when conducted in THF as solvent, the next substrates, i.e. N-linked substrates, **58** and **59**, were tested only under the THF conditions (Scheme 8). These nitrogen-linked substrates gave very different results than the diphenyl ether substrates. Firstly, urea **59** afforded methylacridine **60** (13%) as the sole isolated product under our standard conditions. In this case, the benzyl radical **62** (Scheme 8) underwent formation of the 6-membered ring in **63** as opposed to the 5-*exo-trig* reaction to the spiro-intermediate of a Smiles rearrangement. Radical **63** could then be converted to dihydroacridine **61** by deprotonation followed by electron transfer.[20] As dihydroacridines are easily converted to acridines in air, this explains the additional isolation of **60** (13%) following purification. In the reaction of **59**, it was not clear at what stage the N–(C=O) bond in the urea had cleaved. Early cleavage by nucleophilic reaction by KO^{t}Bu would leave a nitrogen anion that might then undergo hydrogen atom abstraction from the benzylic position, leading to rearrangement. To explore whether this was a possibility, substrate **58** was subjected to the rearrangement reaction, but using an extra equivalent of KO^{t}Bu to deprotonate the amine N-H. This substrate was efficiently converted to the dihydroacridine **61** (57%) together with the acridine **60** (12%). With the formation of a new 6-membered ring, the regiochemistry of the rearrangement for nitrogen-linked substrates was clearly different than for their oxygen-linked counterparts, and the reasons for this will be discussed later in the paper, in conjunction with computational results.

Table 6. Probing substrate **19** with silyl radicals generated from radical initiators with silane.



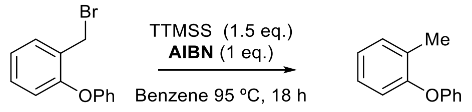
19 **20**

Entry	Silane	Radical Initiator	T (°C)	**20** (%)[a]	**19** (%)[a]
1	Et_3SiH	BPO	130	0	81
2	Et_3SiH	DTBP	130	0	77
3	Et_3SiH	AIBN	95	0	85
4	TTMSS	BPO	130	0	92
5	TTMSS	DTBP	130	0	99
6	TTMSS	AIBN	95	0	86

[a]% yield determined by internal standard (1,3,5-trimethoxybenzene); BPO = benzoyl peroxide; DTBP = di-*t*-butyl peroxide; AIBN = 2,2'-azobisisobutyronitrile; TTMSS = tris(trimethylsilyl)silane.

At this stage, our view was that the mechanism of the rearrangement of all of the relevant substrates involved an initial H-atom abstraction from the substrate by triethylsilyl radicals to give the benzyl radicals as intermediates. We were keen to compare these results with approaches where the same benzyl radical intermediates could be generated in a more conventional manner, using a silane with a thermal radical initiator. Accordingly, we took both triethylsilane and tris(trimethylsilyl)silane and our simplest substrate **19** and treated them, in parallel experiments, with azoisobutyronitrile (AIBN), dibenzoyl peroxide (BPO) and di-*tert*-butylperoxide (DTBP) to see if the same rearrangement could be triggered (entries 1-6, Table 6). However, no rearrangement product **20** was seen in any of the six experiments. The Si-H bond of triethylsilane is quite strong, while TTMSS was developed as a silane that is more susceptible to Si-H bond cleavage.[21] If benzyl radicals are formed under these conditions from **19**, then the kinetics of the Smiles rearrangement must be a lot slower than the kinetics of quenching of the radical by silane. Whereas the experiments in Table 6 feature high concentrations of silanes as quenching agents, this is likely to be very different from the cases studied in this paper with KO^{t}Bu + Et_3SiH. When these two reagents are heated together, it is known that hydrogen gas is liberated into the headspace of the reaction vessel, and this can arise, for example, from conversion of **17** to **18**. In these reactions, therefore, the concentration of abstractable Si-H hydrogens available to a transient radical at any instant, may be much lower.

Halogen atom abstraction by silyl radicals is a more normal method of creating radicals on substrates. [19] Therefore, 1-(bromomethyl)-2-phenoxybenzene **64** was reacted with TTMSS (tristrimethylsilylsilane) in the presence of AIBN. No rearranged product **20** was observed, but debrominated compound **19** (61 %) was formed. This means that the benzylic radical undergoes hydrogen atom abstraction from TTMSS faster than aryl migration under these conditions



64 **19** (61%)

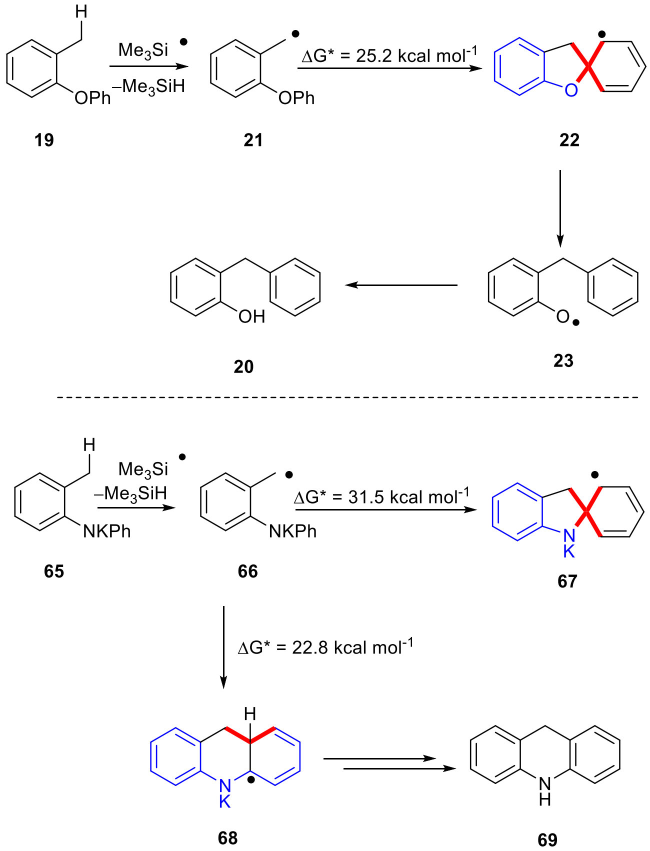
[a]% yield determined by internal standard (1,3,5-trimethoxybenzene).

Scheme 9. Reaction of bromide **64** with TTMSS.

Computational results.

The above results contrast the regiochemistry of rearrangements seen with diaryl ethers and diarylamines. In the case of diaryl ethers, and also for the sulfide case **49**, the benzyl radical cyclises to form a 5-membered ring in a spirobicyclic system, which then expels an aryloxyl or arylthiyl radical to give a Smiles rearrangement. Cyclisation to form 5-membered rings is the expected outcome from such radical cyclisations. However, formation of a benzyl radical in the corresponding diarylamine cases results in cyclisation to form a 6-membered ring, which is unusual.

We rationalise this by looking at Scheme 10, which also incorporates the headline results of our DFT calculations. In the calculations, trimethylsilane was used in place of tiethylsilane for reasons of computational economy. Trimethylsilyl radical abstracts a hydrogen atom from substrate **19** to form **21**. Radical **21** undergoes cyclisation to spiro-intermediate **22** with a very accessible barrier of 25.2 kcal mole^{-1}. Fuller computational details are available in the SI file, which show that that step is the rate determining step in the conversion of **19→20**. By comparison, the corresponding diarylamine, *o*-tolylphenylamine is likely to be in its deprotonated form, *i.e.* it is likely to exist as its potassium salt, **65**. Hydrogen atom abstraction provides radical **66**. The kinetic barrier to cyclisation to from the spiro intermediate is now a much higher 31.5 kcal mole^{-1}, while the cyclisation to the 6-membered ring intermediate has a barrier of 22.8 kcal mole^{-1}. Conversion of **66** to **68** represents the rate determining step in to conversion to **69**.



Scheme 10. Energy barriers for rearrangement of benzyl radicals

Intuitively, the difference can be rationalised, by considering the extent of resonance delocalisation of a heteroatom lone pair over an aryl ring. In **21**, an oxygen lone pair can delocalise over both aryl rings. If this radical cyclises to spiro-intermediate **22**, the delocalisation of the oxygen lone pair is now confined to just one aromatic ring (delocalisation area shown in blue), so there is an energy sacrifice in getting to the spiro-intermediate. This sacrifice will be greater for a nitrogen lone pair than for an oxygen (or sulfur) lone pair because a nitrogen lone pair is more available to undergo resonance delocalisation. For a nitrogen anion, *e.g*. **66**, the penalty for loss of delocalisation by the N-'lone pair' over one of the aryl rings will be more extreme than for neutral nitrogen, but for neutral or anionic nitrogen, the loss of resonance energy will be greater than for oxygen. The loss of resonance energy in these intermediates will be partially reflected in the transition state leading to the spiro-intermediates. By contrast, cyclisation **66**→**68** provides much greater delocalisation of the charge and spin (delocalisation area shown in blue), and again this is likely reflected in the transition state **66**→**68**. This is in line with the efficient formation of products **60** and **61** from anion **66**.

Conclusion

In summary, reaction of Et_3SiH + KO^tBu on diaryl ethers, sulfides and amines with an *ortho* alkyl group leads to rearrangement products. The rearrangements arise from formation of benzyl radicals through hydrogen atom abstraction, likely by triethylsilyl radicals. The rearrangements involve cyclisation of the benzyl radical onto the partner arene, which is the rate determining step. In the case of diaryl ethers, Truce-Smiles rearrangements are observed, arising from radical cyclisations to form 5-membered rings, but for diarylamines, cyclisations to form dihydroacridines are observed. This preference for N-linked substrates is borne out by very recent reductive rearrangements of N-aryl indoles in the presence of the same reagents, *i.e*. Et_3SiH and KO^tBu.[11]

Dedication

This paper is dedicated to Professor Bernd Giese on the occasion of his 80th birthday.

Acknowledgements

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