Benzylic C–H Functionalisation by [Et₃SiH + KO'Bu] leads to Radical Rearrangements in o-tolyl Aryl Ethers, Amines and Sulfides

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Dedicated to Professor Bernd Giese on the occasion of his 80th birthday.

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Abstract: Reaction of Et₃SiH + KO'Bu with diaryl ethers, sulfides and amines that feature an ortho alkyl group leads to rearrangement products. The rearrangements arise from formation of benzylic radicals, likely formed through hydrogen atom abstraction by triethylsilyl radicals. The rearrangements involve cyclisation of the benzylic 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'Bu.

Introduction

In 2013, Grubbs et al. reported[1] that heating Et₃SiH with KO'Bu afforded a novel reagent which has since been shown to carry out a whole 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 thiophenes 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 10[7] and converts primary and secondary amines, e.g. 11 to their silylated derivatives 12[9,10] in this case, 12. The analogous silane, Et₂SiH₂ (and less efficiently, Et₃SiH) in combination with KO'Bu, converts styrenes, e.g. 13 to their hydrosilylated derivatives, in this case, 14[8].

It appears that many different types of reactive species may be produced from heating Et₃SiH with KO'Bu, and the nature of the reactive species present in this mixture is really not fully understood. Houk, Stoltz et al. detected[5] TEMPO-SiEt₃, 15, following addition of TEMPO, which provides evidence for triethylysilyl radicals 16, and Jeon et al. have proposed K + [Et₃Si(H)₂O'Bu] - 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\[5\] 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 Et3SiH/KO’Bu reaction conditions (3 eq. of both reagents at 130°C for 18 h) in the absence of solvent, rearranged product 20 (78%) was isolated (Scheme 3). Control thermal reactions (i) with KO’Bu but with no Et3SiH, (ii) with Et3SiH but with no KO’Bu and (iii) with neither reagent (a purely thermal rearrangement is known at 320°C\[12\]) returned only starting material, which confirmed that the combination of Et3SiH and KO’Bu was essential for the transformation.

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 reorganises 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).

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

Varying the nature of the silane showed that trimethylsilanes as well as methyldiphenylsilane and phenyldimethylsilane worked comparably well (Table 3).

On the other hand, triphenylsilane was much less effective and triisopropylsilane gave no conversion at all, suggesting that substantial stabilisation of the silyl radical in triphenylsilyl radical, or substantial steric

Scheme 2. Recent transformations by Et3SiH + KO’Bu.

Scheme 3. Truce-Smiles rearrangement of radical 21.
hindrance around silicon, in the triisopropyl radical, adversely affected the rearrangement. Interestingly, the reagent that Jeon et al. found to work most effectively in their hydrosilylation reactions,[b] diethylsilane, Et₂SiH₂, was much less effective in this transformation (Entry 7).

In a study of the influence of different bases on the reaction, KO'Bu was effective for the aryl migration of substrate 19 to phenol 20 (Entry 1, Table 4). Switching to NaO'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'Bu (Entry 4). A control experiment (absence of Et₂SiH) 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 di-phenyl 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 CH₂ benzylc position in 30 is easier than from the CH₃ 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 proplyphenyl 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%).

Substrate 27 provided useful information on the routes to activation for rearrangement. It does not feature an easily abstractable benzylc H-atom, as C–H bonds to sp²-carbons are so strong, but the terminal sp²-methyl group C–H bonds in cinnamyl compound

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

| Entry | Temperature, T (°C) | 20 (%) | 19 (%) |
|-------|---------------------|--------|--------|
| 1[a]  | 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.

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

| Entry | Reaction Time | 20 (%) | 19 (%) |
|-------|---------------|--------|--------|
| 1[a]  | 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.

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

| Entry | Silane | 20 (%) | 19 (%) |
|-------|--------|--------|--------|
| 1[a]  | Et₂SiH | 78     | 0      |
| 2     | Ph₂SiH | 35     | 38     |
| 3     | Ph₂MeSiH | 73   | 0      |
| 4     | PhMe₂SiH | 77   | 0      |
| 5     | (Pr)₂SiH | 0    | 100    |
| 6     | *Pr₂SiH | 74     | 0      |
| 7     | Et₂SiH₂ | 43     | 27     |

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

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

| Entry | Base   | 20 (%) | 19 (%) |
|-------|--------|--------|--------|
| 1[a]  | KO'Bu  | 78     | 0      |
| 2     | NaO'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.
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.

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

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**Scheme 4.** Probing the scope of the rearrangement.

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

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

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.

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.

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

![Scheme 7. Rearrangements in THF as solvent, compared to solvent-free conditions.](image)

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

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

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

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 KOtBu 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 KOtBu 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.

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

Scheme 8. Rearrangement of diarylamines.

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

| Entry | Silane | Radical Initiator | T (°C) | 20 (%) | 19 (%) |
|-------|--------|-------------------|--------|--------|--------|
| 1     | Et3SiH | BPO               | 130    | 0      | 81     |
| 2     | Et3SiH | DTBP              | 130    | 0      | 77     |
| 3     | Et3SiH | 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-tert-butyl peroxide; AIBN = 2,2′-azobisobutyronitrile; TTMSS = tris(trimethylsilyl)silane.
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 \textsuperscript{t}Bu + Et\textsubscript{3}SiH. 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.\textsuperscript{[19]} Therefore, 1-(bromomethyl)-2-phenoxybenzene 64 was reacted with TTMSS (trist trimethylsilylsilane) in the presence of AIBN (Scheme 9). 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.

**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 mol\textsuperscript{−1}. Fuller computational details are available in the SI file, which show that this 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 mol\textsuperscript{−1}, while the cyclisation to the 6-membered ring intermediate has a barrier of 22.8 kcal mol\textsuperscript{−1}. Conversion of 66 to 68 represents the rate determining step in to conversion to 69.

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 product 69 from anion 66.

Conclusion

In summary, reaction of Et₃SiH+KO’Bu 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. Et₃SiH and KO’Bu.[11]

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