# Synthesis and Reactions of 3,4-Bis(trimethylsilyl)furan and 2-Methyl-3,4-bis(trimethylsilyl)furan

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3,4-Bis(trimethylsilyl)furan (**2**) and 2-methyl-3,4-bis(trimethylsilyl)furan (**3**) have been synthesised and found to undergo a Diels–Alder reaction as well as a regiospecific Friedel–Crafts acylation (regioselective desilylation), regiospecific deuteriodesilylation.

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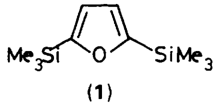
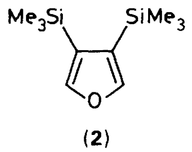
It is well known that trimethylsilyl-substituted carbocycles and heterocycles readily undergo electrophilic aromatic substitution at the *ipso* position, because of the β-effect induced by silicon.[1] In light of this fact, the use of organosilicon substituents as directing groups has become a powerful tool in organic synthetic strategies directed towards the regiospecific construction of polysubstituted arenes.[2] Whilst studying the Diels–Alder reaction between furans and strained alkynes,[3] we were interested in exploring the role of silicon as a potential directing group in the regiospecific synthesis of substituted furans. 2,5-Bis(trimethylsilyl)furan (**1**)[4] and other trimethylsilyl-substituted furans[5] have been prepared, whereas the synthesis of 3,4-bis(trimethylsilyl)furan (**2**) has never been recorded. Here we report the synthesis and reactions of (**2**) and 2-methyl-3,4-bis(trimethylsilyl)furan (**3**).

The preparation of (**2**) and (**3**) was based on the Diels–Alder reaction of oxazoles.[6] Thus, reactions of oxazoles[7] (**4**) and (**5**) with bis(trimethylsilyl)acetylene (**6**) furnished (**2**)[8] and (**3**),[8] respectively, presumably *via* the corresponding intermediates (**7**) and (**8**) (Scheme 1).

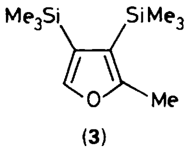
Having a reliable route to (**2**) and (**3**), we then studied their reactivities. It is of particular interest to investigate the Diels–Alder cycloaddition[9] of (**2**) as a diene. Thus, (**2**) was



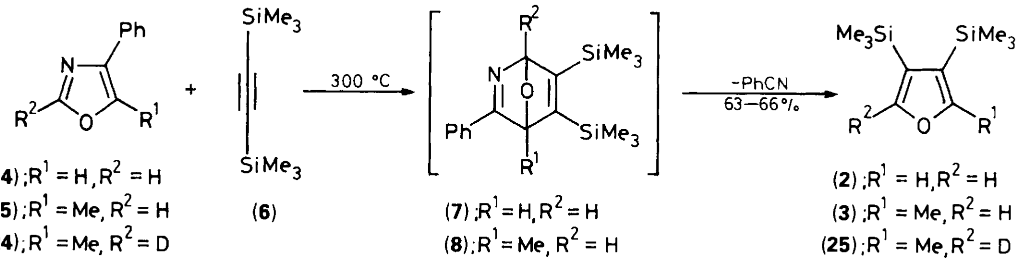
(**1**)



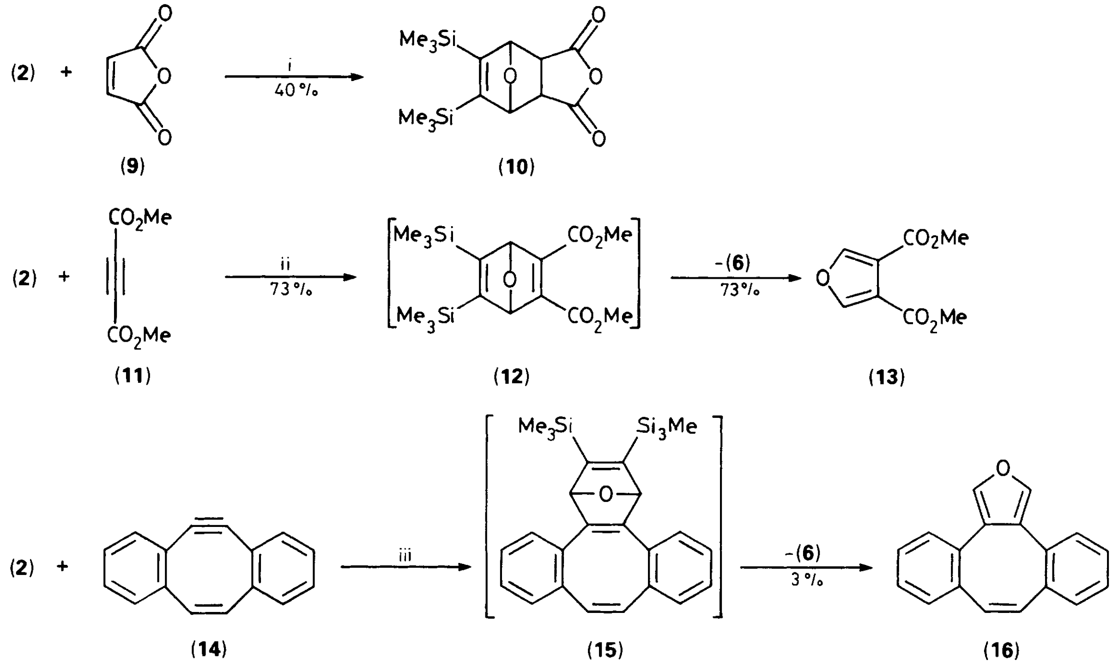
(**2**)



(**3**)



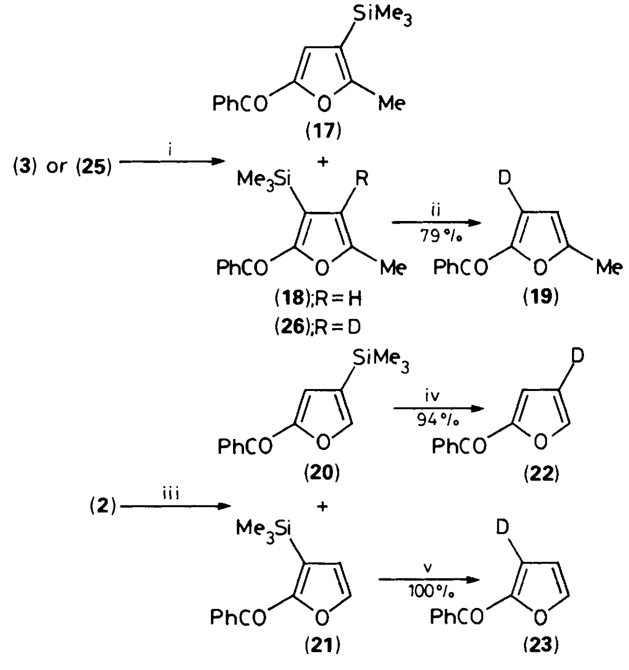
**Scheme 1**



**Scheme 2.** *Reagents and conditions*: i, room temp., 4 days; ii, 75 °C; iii, room temp., hexanes, 60 h.

allowed to react with (**9**) at room temperature to provide the expected adduct (**10**).[8] However, surprisingly, similar reactions of (**2**) with (**11**) and (**14**)[10] furnished (**13**)[11,8] and (**16**),[8] presumably through extrusion of (**6**) from the intermediates (**12**) and (**15**), respectively (Scheme 2).

In addition to Diels–Alder cycloaddion, preliminary results showed that the Friedel–Crafts acylation of (**3**) with benzoyl chloride and aluminium chloride gave a chromatographically separable 1:3 mixture of (**17**)[8] and (**18**)[8] in 56% yield (Scheme 3). The structure of (**18**) was unequivocally confirmed by a regiospecific deuteriodesilylation reaction, which yielded deuteriated compound (**19**).[8] Similarly, acylation of (**2**) gave in 40% yield a 1:1 separable mixture of (**20**)[8] and (**21**),[8] which again could be converted regiospecifically to (**22**)[8] and (**23**),[8] respectively. Steric effects obviously play an important role in preventing the *ipso* attack of the acylium ion, and therefore, not surprisingly, the acylation reaction occurs at the usual α-position.[12] In order to understand the nature of the acylation–desilylation process, we prepared deuteriated compound (**24**)[8]† in 75% yield by deprotonation of (**5**) with butyl-lithium, followed by quenching with deuterium oxide. A Diels–Alder reaction between (**24**) and (**6**) gave (**25**)[8]† in 61% yield. As expected, Friedel–Crafts acylation converted (**25**) to



**Scheme 3.** *Reagents*: i, PhCOCl, $AlCl_3$, $CH_2Cl_2$; ii, $CF_3CO_2D$, $CHCl_3$; iii, as i; iv and v, as ii.

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† All deuteriated compounds showed 45 ± 2% deuterium content, as substantiated by n.m.r. spectrometry.

**(26)**[8]† in 38% yield. The deuteriated counterpart of **(17)** was not isolated because insufficient starting material **(25)** was used in this particular transformation. From this study, it is likely that the acylation proceeds with intramolecular migration of protons.

In conclusion, we have shown that 3,4-bis(trimethylsilyl) furans are able to undergo a Diels–Alder reaction as well as regiospecific electrophilic substitution (regioselective desilylation), regiospecific deuteriodesilylation. Further work on regiospecific preparation of polysubstituted furans and deuteriated furans[13] using **(2)** and **(3)** as starting materials is in progress.

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