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SILICON IN ORGANIC SYNTHESIS. 12. trans-1-BENZENESULFONYL-2-(TRIMETHYLSILYL)ETHYLENE, A DIELS-ALDER DIENOPHILE EQUIVALENT OF ACETYLENE AND MONOSUBSTITUTED ACETYLENES[1]

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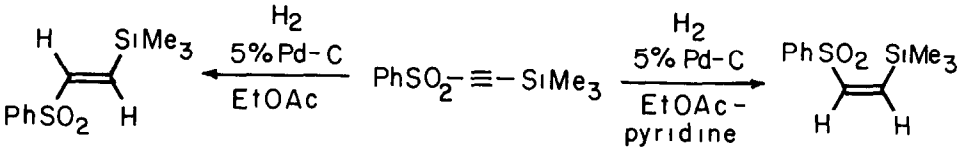
Summary: trans-1-Benzenesulfonyl-2-(trimethylsilyl)ethylene and its 1,2-d_2 derivative enter into Diels-Alder cycloaddition to give products which are smoothly eliminated with fluoride ion. Alkylation of the α-sulfonyl carbanion can precede elimination, such that synthetic equivalents for HC≡CH, HC≡CD, DC≡CD, RC≡CH, and RC≡CD are now available.

The low dienophilic reactivity and explosive nature of acetylene under pressure is well known, thus a HC≡CH synthon is required if general access to 1,4-cyclohexadienes is to be gained by cycloaddition chemistry. Indeed, a number of acetylene equivalents have been developed over the years. Among these, phenyl vinyl sulfoxide (1)[2] and ethynyl p-tolyl sulfone (2)[3] appear to offer the greatest efficiency. However, whereas 1 is dependent upon elevated

$PhSOCH=CH_2$ (1) $\qquad$ $p\text{-}CH_3C_6H_4SO_2C\equiv CH$ (2)

temperatures to introduce the double bond (benzenesulfinic acid expulsion), 2 requires a strong reducing agent (sodium amalgam) to effect arylsulfonyl bond cleavage. Furthermore, neither procedure offers the option to serve also as a protocol for introducing RC≡CH Diels-Alder equivalents. We now report that trans-1-benzenesulfonyl-2-(trimethylsilyl)ethylene (3) is a reagent which not only is amenable to the exercise of such options, but allows as well for introduction of the double bond under exceptionally mild conditions.

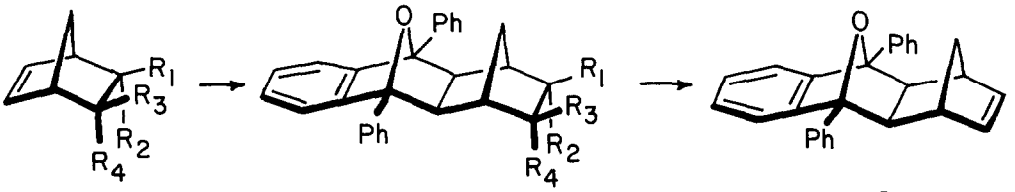
Dienophile 3 is accessible by Calas' procedure which involves free radical addition of



3 $\qquad$ 5 $\qquad$ 4

benzenesulfonyl chloride to trimethylvinylsilane and subsequent dehydrochlorination with triethylamine.[4] Alternatively, we have found that 3 and its cis isomer (4) can be individually prepared in high yield from the readily available[5] common acetylenic precursor 5 by hydrogenation at 50 psi. Notably, 4 undergoes efficient catalyzed isomerization to the E isomer in the absence of pyridine. When a benzene solution of 3 and excess cyclopentadiene

was allowed to stand at 20°C for 3.5 days, there was produced a separable 2:1 mixture (89%) of 6a and 6b.[6] The stereochemistries of these adducts were deduced on the basis of their ^{1}H NMR spectra, the structurally enforced dihedral angle relationships giving rise to diagnostic coupling constants.[7] The significantly lower reactivity of 4 was evident from the length of time (2.5 weeks) required to attain a 30% yield of 6c.[8] In addition to converting 6a-c directly to norbornadiene, the initial adducts were first treated with 1,3-diphenylisobenzofuran to deliver the polycyclic systems 7a-c (yields >85%).[9] Olefination of these substances to the bridged ether 8[10] was achieved analogously ($Bu_4N^+F^-$; THF solution, reflux 3.5 hrs, 91-100%).[11] The observation that all three stereoisomers of 7 undergo the conversion to 8 signifies that the loss of Me_3Si- and



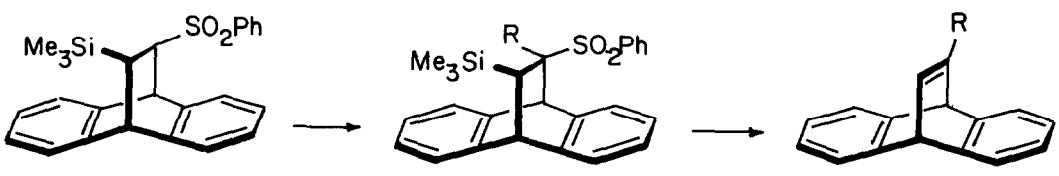
6 7 8

a, R_1 = $SiMe_3$, R_2 = H, R_3 = H, R_4 = SO_2Ph b, R_1 = H, R_2 = $SiMe_3$, R_3 = SO_2Ph, R_4 = H c, R_1 = H, R_2 = $SiMe_3$, R_3 = H, R_4 = SO_2Ph

$PhSO_2$- has no geometric restrictions. This is not to say that there is no stereochemical dependence, since prior equilibration of the phenylsulfonyl substituent in the presence of fluoride ion remains a distinct possibility. It can be seen that the conversions of cyclopentadiene to 7 and 8 comprise new examples of domino Diels-Alder cycloadditions.[12]

The formation of adduct 9[13] proceeded smoothly (98% isolated) when a toluene solution of 3 and anthracene was heated in a sealed tube at 160°C for 7 days. As before, cis isomer 4 proved less satisfactory for our purposes, condensation with anthracene for 2 weeks affording only low yields (35%) of 9. No cis product was found. The reactivity of 9 toward $Bu_4N^+F^-$ is significantly higher than that of 7, conversion to dibenzobarrelene (84%) being complete within 1 hr.

Treatment of 9 with 2.5-3 equiv of n-butyllithium in THF resulted in conversion to the α-sulfonyl carbanion. Quenching with water returned exclusively 9, thereby indicating that protonation of the anionic intermediate is kinetically preferred from the more highly substituted face of the ethano bridge with complete retention of configuration. Substitution

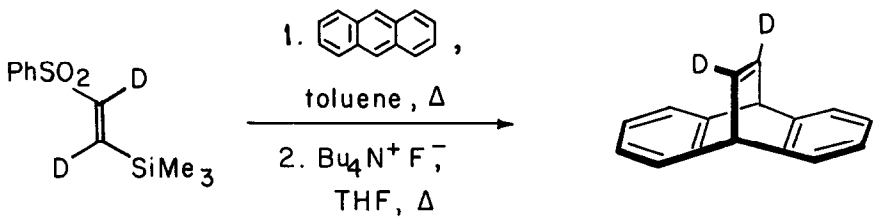


9 10 11

a, R = D ; b, R = CH_3 ; c, R = $CH_2CH=C(CH_3)_2$

of D_2O for water led to a single monodeuterio silyl sulfone whose configuration is assigned as 10a by analogy. Also, the chemical shifts of its Me_3Si- singlet and the residual ethano bridge proton remain essentially identical to those of the starting material. Methyl and prenyl substitutents as in 10b and 10c were similarly introduced. When heated in THF with $Bu_4N^+F^-$ for 1 hr, 10a-c were transformed into the previously unknown monosubstituted dibenzobarrelenes 11a-c in overall yields from 9 of 60, 58, and 63%.

The deuteration of 5 was also investigated. Adaptation of those conditions which earlier gave 3 now furnished the isotopically labeled silyl sulfone 12. Diels-Alder additio of 12 to anthracene and elimination proceeded without measurable washout of deuterium α to sulfonyl and provided 13.



12 13

In summary, trans-1-benzenesulfonyl-2-(trimethylsilyl)ethylene (3) is a conveniently prepared reagent which can serve as a useful acetylene and acetylene-d_2 (from 12) equivalent in Diels-Alder reactions. Although the dienophilic reactivity of 3 is no better than that of 1 and 2 and probably somewhat lower, this silyl sulfone does deliver adducts which are very smoothly eliminated by fluoride ion under relatively mild conditions. Additionally, 3 brings broader scope to this area of chemistry by virtue of alkylation options available to its adducts.[14]

References and Notes

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(6) All new compounds described herein gave correct elemental analyses and/or accurate mass data. All ^{1}H NMR and IR spectra are also in accord with the assigned structures.

(7) 6a: Mp 49-50°C; ^{1}H NMR (δ, CCl_4) 7.95-7.45 (m, 5H), 6.30 (dd, J= 5 and 3Hz, 1H), 5.87 (dd, J= 5 and 3Hz, 1H), 3.47 (dd, J= 6 and 3Hz, >CHSO$_2$-), 2.90 (br s, bridgeheads H's), 1.40-1.03 (m, H_7syn and anti, >CHSiξ), and 0.13 (s, 9H). 6b: Mp 110-110.5°C; ^{1}H NMR (δ, CCl_4) 8.0-7.4 (m, 5H), 6.17 (dd, J= 6 and 2.5 Hz, 1H), 5.90 (dd, J= 6 and 3Hz, 1H), 3.07 (m, 1H), 2.93 (m, 1H), 2.76 (d, J= 6Hz, >CHSO$_2$-), 1.97 (d, J= 9Hz, H_7anti), 1.73 (dd, J = 6 and 3Hz, >CHSiξ), 1.4 (d, J= 9Hz, H_7syn), and 0.0 (s, 9H).

(8) 6c: Mp 114-115°C; ^{1}H NMR (δ, CCl_4) 8.05-7.35 (m, 5H), 6.24 (dd, J= 5 and 3Hz, 1H), 5.75 (dd, J= 5 and 3Hz, 1H), 2.96 (m, bridgehead and >CHSO$_2$-), 2.67 (m, bridgehead), 1.93 (d, J = 9Hz, H_7anti), 1.27 (d, J= 9Hz, H_7syn), 0.97 (dd, J= 9 and 2Hz, >CHSiξ), and 0.30 (s, 9H

(9) 7a, mp 238-239°C; 7b, mp 127-129°C; 7c, mp 255-256°C dec.

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(13) Mp 113-114°C; ^{1}H NMR (δ, CCl_3/$CDCl_3$) 7.8-7.0 (m, 13H), 4.63 (d, J= 3Hz, 1H), 4.37 (d, J= 2Hz, 1H), 3.58 (dd, J= 9 and 3Hz, >CHSO$_2$-), 1.73 (dd, J= 9 and 2Hz, >CH-Siξ), and -0.07 (s, 9H).

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