Ethynyl *p*-Tolyl Sulphone as an Acetylene Equivalent in Diels–Alder Reactions

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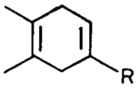
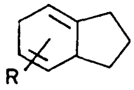
Summary Ethynyl *p*-tolyl sulphone undergoes addition to a number of conjugated dienes and the resulting adducts can be reduced to the corresponding cyclohexa-1,4-dienes using sodium amalgam.

THE low Diels–Alder reactivity of acetylene towards conjugated dienes, coupled with the synthetic usefulness of cyclohexa-1,4-dienes, has led to the development of a number of dienophilic acetylene equivalents.[1] Almost all examples are compounds of the type XCH=CHY, and in practice difficulties arise owing to low dienophile reactivity, to problems in elimination of XY from the adduct, or to lack of regioselectivity in the elimination step where Y=H. An alternative approach is to utilise a compound of the type XC≡CH where X activates the triple bond towards dienes, and is subsequently replaceable by H. We now report that aryl ethynyl sulphones can be employed in this way.

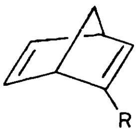
Thus, ethynyl *p*-tolyl sulphone[2] underwent addition to a number of conjugated dienes to give the adducts in the Table. For (**1**), (**3**), and (**5**) the adducts were obtained in nearly quantitative yield, while the *trans*, *trans*-1,4-diphenylbuta-1,3-diene adduct (**7**) and anthracene adduct (**9**) were obtained in 58 and 54% yield respectively.



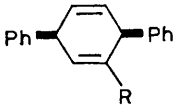
(1) R = Ts
(2) R = H



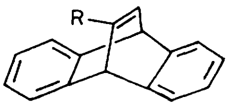
(3) R = Ts
(4) R = H



(5) R = Ts
(6) R = H



(7) R = Ts
(8) R = H



(9) R = Ts
(10) R = H

Ts = p-$MeC_6H_4SO_2$

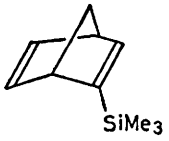
TABLE. Reduction of adducts from ethynyl *p*-tolyl sulphone with sodium amalgam.

Adduct	Reduction conditions	Product (yield)
(**1**)	MeOH–$NaH_2PO_4.2H_2O$–18 °C[a]	(**2**) (49%)
(**3**)	MeOH–$NaH_2PO_4.2H_2O$–18 °C[b]	(**4**) (47%)
(**5**)	MeOH–$NaH_2PO_4.2H_2O$–18 °C[b]	(**6**) (27%)
(**7**)	MeOH–$NaH_2PO_4.2H_2O$–reflux[c]	(**8**) (56%)
(**9**)	MeOH–THF(1 : 1)–Na_2HPO_4–18 °C[d]	(**10**) (35%)

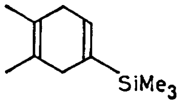
[a] 5% Na–Hg, 6 mol. equiv.; [b] 6% Na–Hg, 6 mol. equiv; [c] 1% Na–Hg, 7 mol. equiv.; [d] 6% Na–Hg, 2 mol. equiv. (THF= tetrahydrofuran).

It is known that αβ-unsaturated sulphones can be reduced to olefins.[3] We find that reduction of the adducts with sodium amalgam under the conditions shown (Table) gave the corresponding cyclohexa-1,4-dienes in moderate yield. Na_2HPO_4, previously used as buffer in Na/Hg reduction of substituted sulphones,[4] did not prevent base-catalysed isomerisation in the case of (**7**) and we used $NaH_2PO_4.2H_2O$ which proved more effective. The major side products accompanying the cyclohexadienes were the sulphone derived by reduction of the conjugated double bond, and the further reductive cleavage product from this. Previous attempts to prepare the dihydroindane (**4**) had failed.[5]

In a similar way, the adducts from *p*-tolyl trimethylsilylethynyl sulphone[2] with cyclopentadiene and 2,3-dimethylbutadiene were reduced with Na/Hg/MeOH–NaH_2PO_4 to (**11**) and (**12**) in yields of 88 and 93% respectively. These are formal Diels–Alder adducts of trimethylsilylacetylene, itself a poor dienophile.[6]



(11)



(12)

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