A Simple and Versatile Acetylene Equivalent in Diels-Alder Reactions

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Allyl phenyl sulphone and cinnamyl *p*-tolyl sulphone underwent cycloaddition with tetraphenylcyclopentadienone, indanocyclone, 1,3-diphenylisobenzofuran, and tetraphenylcyclopentadiene to give the adducts with elimination of methyl phenyl sulphone and methyl *p*-tolyl sulphone respectively.

The sluggish reactivity of acetylene in [4 + 2] cycloaddition, and the safety hazards involved in handling it at elevated temperature and pressure, prompted us to search for a new reliable acetylene equivalent in Diels–Alder reactions. The present approach deals with the use of β , γ -unsaturated sulphones, *viz.* allyl phenyl and cinnamyl *p*-tolyl sulphone, as acetylene equivalents rather than vinyl sulphoxides¹ and ethynylic sulphones.²

In a typical experiment, allyl phenyl sulphone (1.2 equiv.) was heated with tetraphenylcyclopentadienone (1.1. equiv.) in PEG (polyethyleneglycol) 200 at 180 °C under nitrogen for 15 min; chromatographic separation on silica gel with petrolbenzene (3:1) as eluant afforded 1,2,3,4-tetraphenylbenzene (62%). Similarly reaction of 2,8-dioxo-1,3-diphenyl-2,8-dihydrocyclopent[*a*]indene (indanocyclone) with allyl phenyl sulphone gave 1,4-diphenylfluoren-9-one (74%). The intermediate adduct could not be isolated in these reactions, probably because the cycloaddition is sluggish whereas elimination of methyl phenyl sulphone occurs rapidly. Reaction of the cyclones with cinnamyl p-tolyl sulphone gave pentaphenylbenzene and 1,3,4-triphenylfluoren-9-one respectively. However allyl phenyl sulphone is more reactive than cinnamyl sulphone. Thus these reactions find utility in a one-step synthesis of tetra- and penta-substituted aromatics. The problems of the claimed low reactivity of vinyl sulphoxides and the thermal cycloreversion which is speculated to occur, together with the unfavourable elimination of phenylsulphinic acid, were overcome by the use of allyl phenyl sulphone as acetylene equivalent.

In order to study the mechanism of the elimination of



methyl phenyl sulphone, the reaction of allyl phenyl sulphone with tetraphenylcyclopentadiene was studied. The intermediate adduct could not be isolated and the reaction afforded 1,2,3,4-tetraphenylnorborna-2,5-diene. However careful investigation of the cycloaddition of tetraphenylcyclopentadiene with cinnamyl *p*-tolyl sulphone reveals that the bicyclic intermediate (1) has a favourable geometry for *cis*-elimination. The ¹H n.m.r. spectrum of this intermediate displayed a

Table 1. Cycloaddition of allyl phenyl and cinnamyl p-tolyl sulphone.

\mathbb{R}^1		R ²	R ³	R⁴	х	% Yield of (2) or (3)
Ph		Ph	н	Ph	CO	62
Ph		Ph	Н	$p-MeC_6H_4$	CO	60
Ph		Ph	Ph	$p-MeC_6H_4$	CO	51
	Α		Н	Ph	CO	74
	Α		Н	$p-MeC_6H_4$	CO	71
	Α		Ph	$p-MeC_6H_4$	CO	57
Ph		Ph	Н	Ph	CH_2	48
Ph		Ph	Н	$p-MeC_6H_4$	CH_2	47
Ph		Ph	Ph	$p-MeC_6H_4$	CH_2	38
	В		Н	Ph	0	41
	В		Ph	p-MeC ₆ H ₄	0	36

two-proton doublet at δ 4.14 showing coupling with the adjacent *exo* proton at C-5. C-6-H was a doublet of doublets at δ 3.01 (J 5.7 and 2.8 Hz) indicating coupling with the *exo* proton at C-5 and further appreciable W coupling with the *anti* proton on C-7. Further, C-5-H appeared at δ 1.79 as a multiplet, C-7-H₂ at δ 3.28 and 2.41 as doublets, and *p*-MeC₆H₄SO₂ at δ 2.10 as a singlet. Based on the ¹H n.m.r. splitting pattern observed for the intermediate (1), we conclude that the C-5-H is *exo* and C-6-H *endo*. Hence the pyrolytic elimination of methyl *p*-tolyl sulphone proceeds through a cyclic six-membered transition state.

Cycloaddition of allyl phenyl sulphone and cinnamyl p-tolyl sulphone with 1,3-diphenylisobenzofuran gives a fair yield of 1,4-diphenyl- and 1,2,4-triphenyl-1,4-epoxy-1,4-dihydronaphthalene respectively. Results are given in Table 1.

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References

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