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RING OPENING REACTIONS OF VINYL CYCLOPROPANES WITH *para* TOLUENE SULPHONYL IODIDE.

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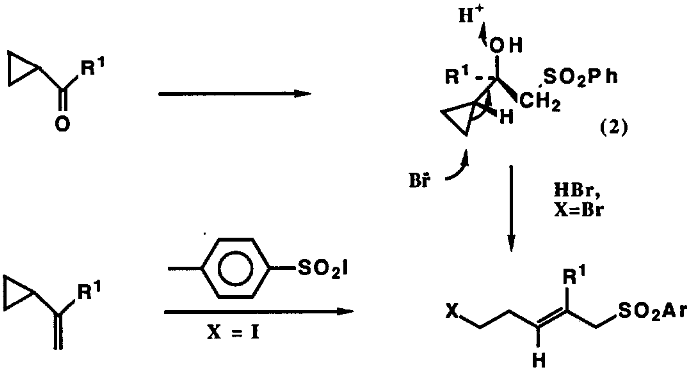
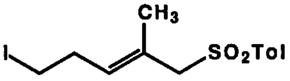
Abstract Substituted 1-iodo-5-*para* toluene sulphonyl pent-3-enes are readily prepared by regiospecific ring opening of vinyl cyclopropanes with *para* toluene sulphonyl iodide. Intramolecular carbanionic cyclisation of the cisoid isomers *via* α or γ alkylation is substrate dependent.

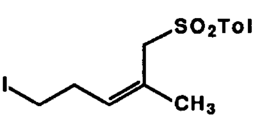
The stereoselective *trans* olefin synthesis pioneered by Julia[1] and extended by the Johnson school[2] has found extensive application in the synthesis of terpenes, insect pheromones, and polyolefin cyclisation precursors[3]. In practice, however, as illustrated (Scheme 1) for the case of the particularly useful polyfunctional sulphone synthon[4] (**1**), ring opening of the hydroxyalkyl cyclopropane (**2**) requires relatively vigorous acidic or Lewis acid conditions. Herein, we report an alternative strategy for elaboration of this functional array under mild neutral conditions by reaction of vinyl cyclopropanes (**3**) with *para* toluene sulphonyl iodide (Scheme 1). This crystalline reagent is readily prepared[5] by reaction of the sodium sodium salt of para toluene sulphinic acid with iodine.



Scheme 1



(4)

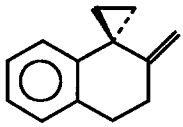
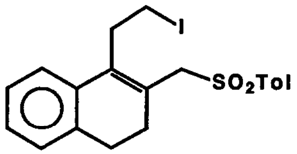
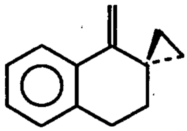
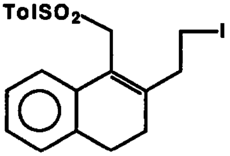
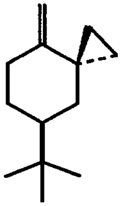
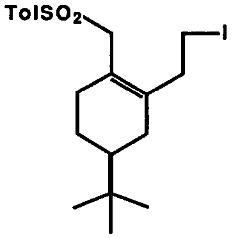
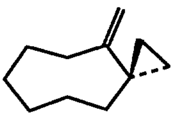
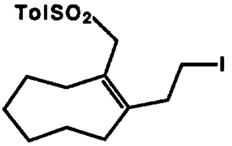


(5)

In the first instance, we chose to examine the reaction of the simple vinyl cyclopropane ($3, R^1=CH_3$). Addition of (3) to a dichloromethane solution of tosyl iodide (1.0 equiv.) containing propylene oxide as proton scavenger gave, after three hours at 40°C and chromatographic separation, the E iodo sulphone (4) (47%) and the corresponding Z isomer (5) (19%). In contrast to the classical ring opening, in which the high stereoselectivity is ascribed[1] to the adoption of the preferred conformation shown in structure (2), direct addition of the tosyl group to the olefinic terminus with concomitant generation of a neighbouring sp^2 centre is clearly less sterically demanding.[8]

It was also of interest to extend this reaction to a series of spiroannulated cyclopropane derivatives which are constrained to afford only the cisoid isomer. Compounds (6) - (9) were simply constructed by a sequence involving efficient reaction of the enolate anion with 2-chloroethyldimethylsulphonium iodide[6] and subsequent Wittig olefination.

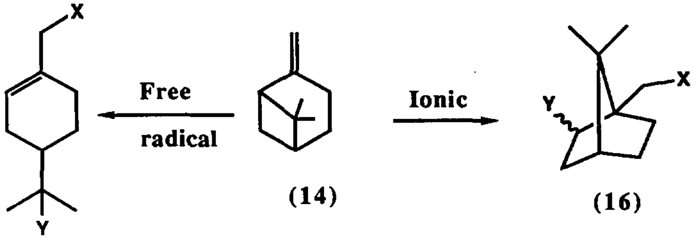
TABLE 1

VINYL CYCLOPROPANE	TOSYL IODIDE ADDUCT	% YIELD
 6	 10	78
 7	 11	95
 8	 12	59
 9	 13	52

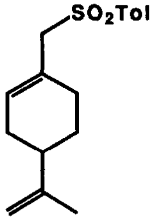
The results in this series (Table 1) demonstrate the utility of the reaction for preparation of annulated cisoid isomers, and the successful reaction of the readily polymerised "styrene" derivative (7) is particularly worthy of note.

From the mechanistic standpoint, this reaction was originally conceived as a free radical chain process featuring addition of the *para* toluene sulphonyl radical to the olefin followed by cyclopropylcarbinyl radical rearrangement[7] and capture of the resultant open chain homoallylic radical by tosyl iodide. Considerable literature precedent[8] exists for the addition of variously substituted sulphonyl halides to simple unsaturated systems by such a mechanism. In order to investigate this point, we have examined the reaction of tosyl iodide with β-pinene (**14**), since addition of a reagent X-Y in a free radical chain reaction is known to give rise to the menthane skeleton (**15**), whereas generation of an incipient carbocation by addition of an electrophile

X^+ may be followed by Wagner-Meerwein rearrangement to give bicyclo [2.2.1] derivatives (**16**). Such a vicinal alkyl shift is not anticipated in radical chemistry.[10]



(15) (14) (16)

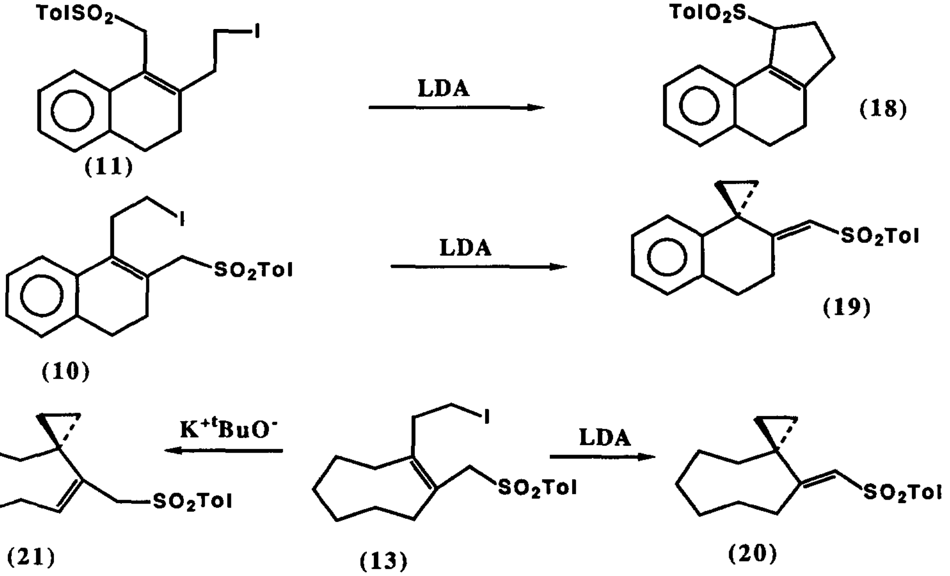


(17)

In the event, *para* toluene sulphonyl iodide may be tuned to display the characteristics of both a free radical and an ionic reagent. Reaction in dichloromethane gave both the labile tertiary iodide (**15**), (X = SO_2Tol, Y = I) (18%) and the *exo* and *endo* adducts (**16**) (X = SO_2Tol, Y = I) (20%) together with the elimination product (**17**) (11%).

Photolysis using a tungsten lamp in petroleum ether as solvent at low temperature led to faster reaction rates, although it was not possible to suppress formation of the ionic products (**16**). Contrastingly, use of polar 1,2-dimethoxyethane in the presence of hydroquinone did effectively quench the radical component of the reaction.

We have also briefly examined intramolecular carbanionic ring closure reactions of the adducts possessing the cisoid stereochemistry around the double bond. Treatment of the iodo sulphone (**11**) derived from α-tetralone with lithium diisopropylamide furnished an excellent yield (92%) of the cyclopentene derivative (**18**), thus illustrating the useful concept that a vinylcyclopropane rearrangement[11] with incorporation of functionality may be achieved in two steps without resort to the high temperatures normally required in such systems. However, similar treatment of the β-tetralone-derived adduct (**10**) led to the functionalised vinyl cyclopropane (**19**) (47%) *via* a γ alkylation sequence.



(11) (18) (10) (19) (21) (13) (20)

Although intermolecular alkylation of allylic sulphone anions occurs exclusively at the α position as expected for an inductively stabilised carbanion,[12] the formation of the γ alkylated product (**19**) cannot be simply rationalised in terms of the additional benzylic stabilisation of the anion derived from (**10**), since reaction of the cyclooctyl derivative (**13**) also afforded the spirocyclic vinylcyclopropane (**20**). Use of potassium *tert* butoxide in this latter reaction led to isolation of the thermodynamically more stable deconjugated product (**21**). On the basis of n.m.r. studies which demonstrate that the methyl group of the tolyl residue in sulphone (**11**) resonates at almost 0.6 p.p.m. towards higher field than normal, we propose that a π-stacking interaction in (**11**) allows the pendant iodoalkyl side chain to adopt a suitable conformation for closure to the five membered ring. In the absence of such a phenomenon the preferred conformation demands spatial separation of the aryl sulphone residue and the iodoalkyl group with a resultant preference for formation of the γ alkylation product.

In summary, the reaction of easily prepared *para* toluene sulphonyl iodide with readily available vinyl cyclopropanes[11] offers a mild regiospecific route to highly functionalised homoallylic iodides.

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