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STEREOCHEMISTRY OF BENZENESULPHENYL CHLORIDE ADDITION TO A STRAINED CYCLOBUTENE

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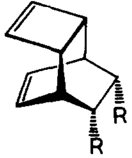
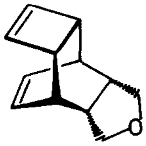
Electrophilic additions of sulphenyl chlorides to olefins have been extensively studied and are considered to be highly stereospecific trans-additions proceeding in two steps via episulphonium (thiiranium) ion intermediates.[1] Simple olefins like cyclohexene[2a] as well as strained olefins e.g.,norbornene,[2b,3] bicyclo [2.2.1] hex-2-ene[2c] and acenaphthene,[2d] with marked propensity for cis additions,[4] conform to the above mechanism and furnish exclusive trans products with arylsulphenyl chloride. In the case of norbornyl system, this two step addition via episulphonium ion intermediate has been used to arrive at significant mechanistic and stereochemical conclusions.[3] This communication reports the first nonstereospecific addition of benzenesulphenyl chloride (PhSCl) to the strained cyclobutene double bond of tricyclo $[4.2.2.0^{2,5}]$deca-3,7-diene derivatives 1 & 2, which seems to discount the involvement of the bridged episulphonium ion[1,2] in the product determining step of the reaction.

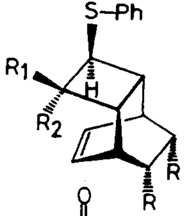


1. $R = \underset{\underset{O}{\|}}{C}-OCH_3$



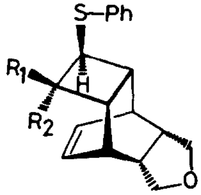
2

Addition of PhSCl to a methylene chloride solution(-20°) of diester 1 containing small amount of suspended calcium carbonate and separation (silica gel) yielded a 3:1 mixture of trans and cis adducts[5] 3 & 4 in quantitative yield. The stereochemistry of 3 & 4 has been deduced from their pmr spectra.[6] The olefinic protons at C_7 and C_8 appeared as a sharp triplet (δ6.55) in the cis-adduct 4 due to symmetrical endo substitution at C_3 and C_4 and as a diffused multiplet (δ6.46) in the trans adduct 3 due to unsymmetrical endo substitution.Furthermore, the exo proton (δ4.42) at C_3 in trans adduct 3 exhibited significant shielding due to the cis vicinal phenylthio group[3] as compared to the C_3 endo proton (δ4.9) in 4. Similarly, the addition of PhSCl to the tetracyclic ether 2 furnished a 3:1 mixture of trans and cis adducts[5] 5 & 6 in almost quantitative yield.



3. $R = \overset{\overset{O}{\|}}{C}-OCH_3, R_1=H, R_2=Cl$

4. $R = \underset{\underset{O}{\|}}{C}-OCH_3, R_1=Cl, R_2=H$



5. $R_1 = H, R_2 = Cl$

6. $R_1 = Cl, R_2 = H$

The simultaneous formation of cis and trans addition products from 1 & 2 with PhSCl can be explained through a free carbonium ion intermediate but is not compatible with the intermediacy[1] of an episulphonium ion. Further support for this contention is derived from the results[7] of addition of IN_3 and $Hg(OAc)_2$ to 1 & 2, which proceed via the corresponding three membered intermediates and furnish exclusive cis-addition products under the dominant influence of twist strain[4] factors.

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3. H.C. Brown and K.T. Liu, J. Amer. Chem. Soc., 92, 3502 (1970).
4. T.G. Traylor, Acc. Chem. Res., 2, 152 (1969).
5. Compound 3: $C_{20}H_{21}O_4SCl$; mp 119-20°; ir(KBr): 1740,1210,740 cm^{-1}; pmr($CDCl_3$): δ7.25(5H, s, phenyl), 6.46 (2H, m, olefinic), 4.42 (1H, t, H-C-Cl), 3.7 (1H, t, H-C-S-Ph), 3.56(6H, s, -$COOCH_3$). Compound 4: $C_{20}H_{21}O_4SCl$; mp 201-3°; ir(KBr): 1740,1215,755 cm^{-1}; pmr($CDCl_3$):δ7.5(5H,s,phenyl), 6.55(2H,t,olefinic), 4.9 (1H, t, H-C-Cl), 3.6(6H, s, $COOCH_3$). Compound 5: $C_{18}H_{19}OSCl$; mp 143-4°; ir(KBr): 3050, 1575, 740 cm^{-1}; pmr($CDCl_3$):δ7.18(5H, m, phenyl), 6.39(2H, m, olefinic), 4.5(1H,t,H-C-Cl), 3.2-4.1(5H, m, H-C-S-Ph & ether). Compound 6: $C_{18}H_{19}OSCl$; mp 152-3°; ir(KBr): 3060,1520,1050,745 cm^{-1}; pmr($CDCl_3$): δ 7.5(5H, s, phenyl), 6.35(2H,t, olefinic), 4.88(1H, t, H-C-Cl), 3.1-4(5H, m, H-C-S-Ph and ether).
6. For the configurational assignment of tricyclo$[4.2.2.0^{2,5}]$dec-7-enes, see, J.P. Snyder and D.G. Farnum, J. Org. Chem., 31, 1699 (1966).
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