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THE ROLE OF ELECTRONIC FACTORS IN REAGENTS IN CONTROLLING THE STEREOCHEMISTRY OF ARYLSULFENYL CHLORIDES ADDITION

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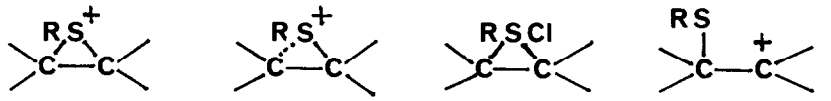
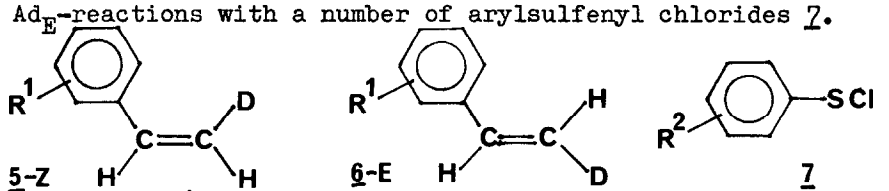
Abstract. For a series of substituted arylsulfenyl chlorides the stereochemistry of Ad_E-reactions with a series of substituted Z- and E-ß-deuterostyrenes has been elucidated. Non-stereospecific reaction was observed only for the pair 2,4-dinitrobenzenesulfenyl chloride-p-methoxystyrene; for all the other reactants the reaction proceeded in a strictly stereospecific manner.

Addition of sulfenyl halides to acyclic alkenes almost uniformly proceeds as a trans-stereospecific reaction[1,2] and this fact is usually interpreted as the result of the initial formation of bridged ionic or covalent intermediates 1 - 3[3]. The non-stereospecific reaction course has been observed only for the addition of 2,4-dinitrobenzenesulfenyl chloride (2,4-DNBSC) to Z-anethol and related compounds.[4] Such a stereochemistry has been ascribed primarily to the effect of the strong steric interaction of the vicinal groups favoring the preferential formation of the open cationoid intermediate 4. This suggestion is believed to be substantiated by the observed exclusive trans-stereospecific course for 2,4-DNBSC addition to E-anethol.[4] However with the substrates like ß-methylstyrenes it is actually impossible to draw the reliable conclusions about the relative importance of steric and electronic effects on the stereochemistry of Ad_E-reactions.



1 2 3 4

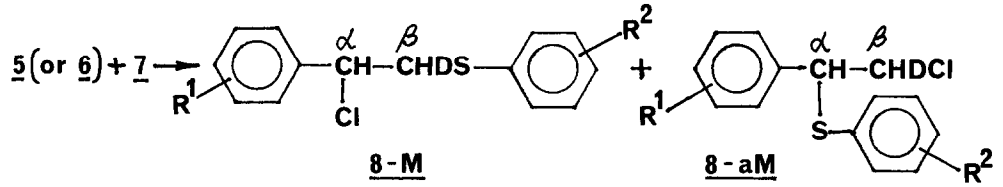
To circumvent these complications we have chosen as model compounds for the stereochemical studies a series of substituted Z- and E-ß-deuterostyrenes, 5 and 6 respectively[5] and investigated the stereochemistry of their Ad_E-reactions with a number of arylsulfenyl chlorides 7.



R^1 = 4-OCH_3, 4-CH_3, H, 3-NO_2
R^2 = 4-OCH_3, 4-CH_3, 4-NO_2, 2,4-$(NO_2)_2$

The reaction procedure runs as follows: to a solution of 0.55 mmoles of 7 in 0.3 ml of deuterated solvent ($CDCl_3$ or CD_3COOD) placed in an NMR tube a solution of 0.5 mmoles of 5 or 6 in 0.3 ml of the same solvent was added at the indicated temperature while the mixture was stirred with a flow of dry argon. PMR spectra (Brüker WM-250) were immediately recorded.

In all cases the reaction proceeded rapidly and produced quantitative yields of the respective ß-chlorosulfides 8. The latter consisted of a mixture of Markovnikov (M) and anti-Markovnikov (aM) isomers, their ratio being dependent upon the nature of the substituent R^1 in the styrene substrate (4 : 1 for R^1 = 3 - NO_2; ⩾ 25 : 1 for R^1 = 4-Me or 4-OMe).



The stereochemistry of the reaction was determined by the comparison of the PMR pattern for the $-\overset{\alpha}{C}HCl-\overset{\beta}{C}HDS-$fragment of 8 (M) with that of the $-\overset{\alpha}{C}HCl-\overset{\beta}{C}H_2S-$fragment of the corresponding undeuterated styrenes. In the latter cases these protons appear as an ABX-system with a pair of AB quartets at C_β and an X quartet at C_α centered within the ranges 3.42-3.73 and 4.82-5.09 ppm respectively (δ, $CDCl_3$). Hence for the completely stereospecific reaction of 7 with the deuterated styrenes 5 or 6 the PMR spectrum of the deuterated product 8 (M) should reveal the presence of high field and low field doublets reflecting the presence of a single diastereotopic proton at C_β and a proton at C_α (AX or BX system). The extent of non-stereospecificity could be easily evaluated by the ratio of the integration intensities of H_A and H_B signals with H_X taken as an internal standart. The signal assignment were additionally checked with the use of double resonance $\{^1H, ^1H\}$.

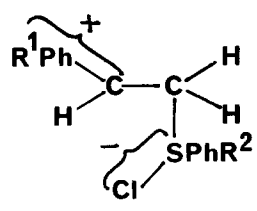
Vicinal spin-spin coupling constants for M-adducts 8 formed from E-styrenes 6 lay in the range 8.3-9.3 Hz (J_{AX}), those for M-adducts 8 from Z-styrenes 5 (J_{BX}) - in the range 5.8-6.7 Hz. In accordance with literature data for related compounds[6,7], the erythro-configuration has been assigned to the first set of compounds and threo- to the second. A similar approach was used to ascertain the stereochemistry of 8 (aM) adducts.

With the use of the aforementioned technique we have observed the followibg stereochemical patterns for the reaction under study: (1) the addition of 7 (R^2 = 4-Me or 4-NO_2) to 5 or 6 (R^1 = 3-NO_2, H or 4-Me) in $CDCl_3$ or CD_3COOD at 25°C as well as the reaction of 7 (=2,4-DNBSC) with 5 or 6 (R^1=Me) in CD_3COOD at 25°C produced as the single products threo- or erythro-isomers of 8 (M) respectively; (2) the addition of 7 (R^2=4-Me or 4-OMe) to 5 or 6 (R^1=4-OMe) in $CDCl_3$ or CD_3COOD at 25°C produced a 1:1

erythro-threo-mixture of 8, its composition being independent of the stereochemistry of the styrene used; (3) the interaction of the same reactants at -50°C (in $CDCl_3$) resulted in the formation of the pure threo-isomer 8 from 5 and the erythro isomer 8 from 6, their fast equilibration being observed with an increase in temperature (a 1:1 mixture is formed after 20 min at 25°C); (4) the addition of 7 (R^2 = 4-NO_2) to 5 or 6 (R^1=OMe) in $CDCl_3$ or CD_3COOD at + 25°C[8] formed reproducibly 19:1 or 1:19 mixtures of threo-erythro isomers of 8 respectively, their ratio being changed very slowly at +25°C (complete equilibration occurs only after 24 hours at +25°C); (5) the interaction of 7 (=2,4-DNBSC) with 5 or 6 (R^1=4-OMe) in $CDCl_3$ at +25°C[8] produced 7:3 or 3:7 mixtures of threo-erythro 8 respectively and these ratios did not change after prolonged (at least for 1 week) storage of the samples at +25°C.

The following generalization could be drawn from these data: (i) Ad_E reactions of ArSCl 7 bearing electron donating (R^2 = 4-OMe, 4-Me or H) or electron withdrawing (R^2 = 4-NO_2 or 7 = 2,4-DNBSC) substituents with ß-deuterated styrenes 5 and 6 proceeds with complete stereospecificity for all the substituents (R^1) in the styrene moiety except R^1=OCH_3; (ii) in case of 5 and 6 containing a strong electron releasing substituent R^1=OCH_3 a slight decrease in the stereospecificity is observed for the addition of 7 containing a single strong acceptor group (R^2 = 4-NO_2) and almost complete non-stereospecificity occurs when the reagent contains two nitro groups (7 = 2,4-DNBSC).

Thus one is forced to the conclusion that the case (i) is indicative of the formation of the bridged intermediate at the product-determining step, while in the case (ii) the process is channeled (at least partially) via the formation of an non-cyclic intermediate. We suggest for the latter the alternative structures of a zwitter-ion 9 or an intimate ion-pair 10.



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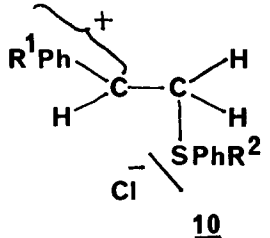

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The effective stabilization of the open intermediate vs. the bridged one is undoubtedly provided for by purely electronic effects due to the presence of the strong donor substituent (R^1 = 4-OCH_3) in the alkene residue and the strong acceptor group in the electrophile (7 = 2,4-DNBSC); the involvement of any steric effect in this case seems to be very unprobable. Hence one may also suggest that the observed non-stereospecificity of the 2,4-DNBSC addition to Z-anethol[4] must be considered as a natural result of the operating electronic effects and does not necessarily imply the involvement

of steric interactions in the intermediate (vide supra). On the contrary the stereospecificity of the 2,4-DNBSC addition to E-anethol seems to be rather puzzling and it is difficult to explain this result at the present.

For the arylsulfenylation of styrenes we have earlier presented kinetical data showing the existence of two alternative mechanisms for the rate-determining step of this process.[9] The stereochemical results outlined above clearly indicate a similar possibility for the product determining step. The implications of these data taken together with the recent results of isotope effect studies[10] will be discussed in a full paper.

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