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REGIOSELECTIVE HYDROXYSULPHENYLATION OF DERIVATIVES OF ALLYLIC ALCOHOLS AND AMINES

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Abstract Reaction of manganic acetate with diphenyldisulphide in dichloromethane-trifluoroacetic acid in the presence of allylic esters or amides of allylamine gives trifluoroacetoxysulphides and hence by ready hydrolysis vicinal hydroxysulphides. The regiochemical outcome can be controlled by selection of either an acetyl- or trifluoroacetyl derivative.

Hydroxysulphenylation of alkenes using lead (IV) tetra-acetate to oxidize organic disulphides in dichloromethane-trifluoroacetic acid to give trifluoroacetoxysulphide intermediates and then by hydrolysis vicinal hydroxysulphides was first developed by Trost et al.[1] We have used[2] a number of inorganic oxidants including manganese (III) acetate to functionalise simple alkenes. We now report in this and the following[3] communication two extensions of the Trost procedure for hydroxysulphenylation based on our use of manganic acetate. In the following paper we report the functionalisation of unsaturated nitriles, a procedure which permits the efficient synthesis of functionalised lactones. In this paper we describe the functionalisation of allylic esters and amides of allylamine. The outstanding feature of these additions is the good regiochemical control in which choice of an acetyl- or a trifluoroacetyl derivative determines the regiochemical outcome.

From the appropriate alcohol or amine, esters and amides were prepared by reaction with acetic anhydride or trifluoroacetic anhydride. Esters and amides were reacted with diphenyldisulphide (or in one case di-n-propyldisulphide) and manganese (III) acetate in dichloromethane-trifluoroacetic acid. After complete reaction (typically initiated at 0°C and then allowed to warm to room temperature and stand for 4h) an aqueous work up and extraction afforded diols from trifluoroacetate esters, monoacetates from acetate esters and hydroxyamides from amides. The monoacetates were readily hydrolysed to the appropriate diols. All products shown in the Table were isolated by chromatography and are either known compounds or were fully characterised (i.r. ^{1}H and ^{13}C n.m.r. and microanalysis of their 4-nitrobenzoate esters).

Addition of diphenyldisulphide to allyl acetate (Table entry 1) occurs with the opposite regiochemistry to that observed with allyl trifluoroacetate (entry 2). In the case of addition to allyl acetate the reaction pathway is indicated by isolation of the two monoacetates. Their formation implies that the acetate group by neighbouring group participation controls the regiochemistry in addition to allyl acetate. Such a neighbouring group participation has been observed in other electrophilic additions to allylic esters. Although in early bromination studies[4] with allyl acetate no neighbouring group participation was observed, with allyl benzoate both in bromination[5] and other oxidative additions[6] evidence for ester participation was obtained. Recently the ester functionality in allylic

TABLE Hydroxysulphenylation of Allylic Compounds

Entry	Alkene	Disulphide	Products Yield (%)[a]	
1	CH_2CHCH_2OAc	PhSSPh	$PhSCH_2CHOHCH_2OAc$	(71)
			$PhSCH_2CHOAcCH_2OH$	(11)
2	CH_2CHCH_2OX	PhSSPh	$HOCH_2CHSPhCH_2OH$	(98)
3[b]	CH_2CHCH_2OAc	nPrSSnPr	$nPrSCH_2CHOHCH_2OH$	(64)
			$HOCH_2CHSnPrCH_2OH$	(13)
4	CH_2CHCH_2OX	nPrSSnPr	$HOCH_2CHSnPrCH_2OH$	(84)
5	CH_2CHCH_2NHAc	PhSSPh	$PhSCH_2CHOHCH_2NHAc$	(87)
6	CH_2CHCH_2NHX	PhSSPh	$PhSCH_2CHOHCH_2NHX$	(19)
			$HOCH_2CHSPhCH_2NHX$	(68)
7[c]	$CH_2CHCHMeOAc$	PhSSPh	$PhSCH_2CHOHCHMeOH$	(65)
8[d]	$CH_2CHCHMeOX$	PhSSPh	$HOCH_2CHSPhCHMeOH$	(98)
9[e]	$CH_2CHCHPhOX$	PhSSPh	$HOCH_2CHSPhCHPhOH$	(76)
10	$MeCHCHCH_2OX$	PhSSPh	$MeCHOHCHSPhCH_2OH$	(99)
11	CH_2CEtCH_2OX	PhSSPh	$HOCH_2CEtSPhCH_2OH$	(9)
			$PhSCH_2CEtOHCH_2OH$	(90)
12	$CH_2CHCH_2CH_2OAc$	PhSSPh	$PhSCH_2CHOHCH_2CH_2OAc$	(69)
13	$CH_2CHCH_2CH_2OX$	PhSSPh	$PhSCH_2CHOHCH_2CH_2OH$	(40)
			$HOCH_2CHSPhCH_2CH_2OH$	(45)
14	$CH_2CH(CH_2)_3OX$	PhSSPh	$PhSCH_2CHOH(CH_2)_3OH$	(77)

X = $COCF_3$

a Yields are based on isolated products after chromatographic separation;

b Products separated after hydrolysis of intermediate monoacetates;

c Inseparable mixture of diols characterised as ketals (see text). Ratio (7):(8) ~1:3;

d Separable mixture of diols characterised as ketals (see text). Ratio (1):(2) ~2:1;

e Only one diastereoisomer obtained (see text).

acetates[7] has been used to control stereochemistry in epoxidations. In addition to aceta esters of homoallylic alcohols,[8] product studies similarly establish neighbouring group participation in iodination reactions.

Our observation of Markovnikov addition to N-propenylacetamide (entry 5) also accords wit the limited literature precedents. N-Allylacetamides afford 2-oxazolines both on acid catalysed cyclisation[9] and on iodination.[10] Again neighbouring group participation has b recently described in the amidoselenation[11] of derivatives of homoallylic amines, and in addition[12,13] of tellurium tetrachloride to N-allylamides. Hence the regiochemical outco of additions to acetate esters (entries 1, 3, 7 and 12) and to the acetamide (entry 5) ha good literature precedent.

In marked contrast there is no precedent for the use of a trifluoroacetyl group to control the regiochemistry of addition to allylic- and homoallylic compounds. We find that by comparison with additions to allyl acetate use of a trifluoroacetate as in allyl trifluoroacetate completely reverses the regiochemistry in addition of diphenyldisulphide (entry 2) and di-n-propyldisulphide (entry 4). Again in additions to esters of but-3-en-2-ol, whilst the Markovnikov terminal sulphides are obtained from the acetate (entry 7), the anti-Markovnikov non-terminal sulphides are obtained from the trifluoroacetate (entry 8). In these additions (entries 7 and 8) diastereoisomers are obtained. In the case of the separable diols (1) and (2) from the trifluoroacetate, conversion to the respective ketals (3) and (4) permitted structural assignments[14] to be made. Similarly the 1,2-diols (5) and (6) from the acetate were converted to the ketals (7) and (8) permitting assignments[15] to be made. Addition to crotyl trifluoroacetate (entry 10) is also completely regioselective and again gives a mixture of diastereoisomers. The products (1) and (2) are obtained in a different ratio from that observed in addition to but-3-en-2-ol. In contrast to these additions lacking stereoselectivity the 1,3-diol (9) is obtained (entry 9) with both complete regio- and stereoselectivity. Formation of the single diol (9) was confirmed by conversion to the single ketal (10).[16]

In the above additions to the trifluoroacetate esters, the regiochemical outcome is attributed to inductive effects. In accordance with this view the effect is diminished in a trifluoroacetamide. Hence from allyl trifluoroacetamide (entry 6) although anti-Markovnikov addition is markedly favoured the Markovnikov addition becomes a significant minor pathway. In entry 11 the effect of an extra alkyl substituent is observed. It has a major influence on the regiochemical outcome as the anti-Markovnikov pathway (the favoured pathway if the inductive effect of the trifluoroacetoxy group is strong) becomes the minor route. In the cases of a homoallylic trifluoroacetate ester (entry 13) and a case (entry 14) where the trifluoroacetate group is further removed from the double bond the diminished effect of the trifluoroacetate group is observed.

From these results we conclude that the trifluoroacetoxy group when present in allyl esters or in an allyl trifluoroacetamide has a sufficiently powerful control of regiochemistry in hydroxysulphenylation to permit the desired regiochemistry to be selected by choice of the appropriate ester or amide functionality. We believe that this control is not unique to hydroxysulphenylation but is likely to be found in other electrophilic additions to allyl derivatives.

Acknowledgement

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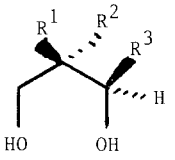
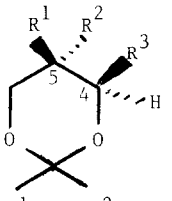
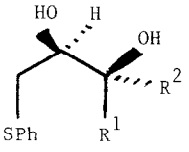


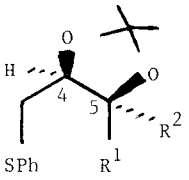
(1) R^1=H; R^2=SPh; R^3=Me
(2) R^1=SPh; R^2=H; R^3=Me
(9) R^1=H; R^2=SPh; R^3=Ph



(3) R^1=H; R^2=SPh; R^3=Me
(4) R^1=SPh; R^2=H; R^3=Me
(10) R^1=H; R^2=SPh; R^3=Ph



(5) R^1=Me; R^2=H
(6) R^1=H; R^2=Me



(7) R^1=Me; R^2=H
(8) R^1=H; R^2=Me

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14. J_{4ax5ax}= 11 Hz in (3). J_{4ax5eq}<3 Hz in (4).
15. δ4.21 p.p.m. for H-4. and δ4.32 for H-5 in (7); and δ3.74 for H-4, and δ3.93 for H-5 in (8).
16. J_{4ax5ax} = 11 Hz in (10).

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