Kurzmitteilungen: Regioselective Hydroxysulphenylation of Butadiene Using Different Metal Ions

Regioselektive Hydroxysulphenylierung von Butadien mit Hilfe verschiedener Metallionen

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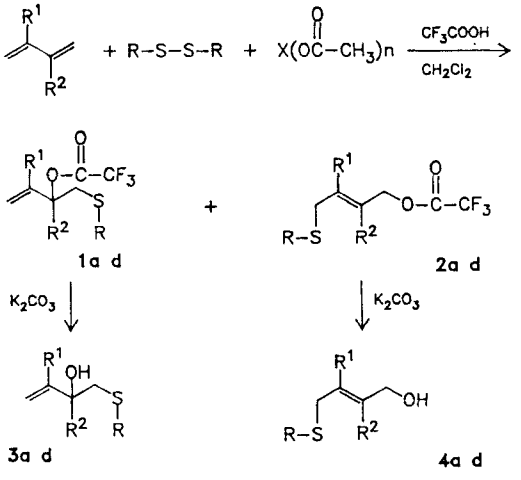
Reaction of Pb(IV)- or Mn(III)-acetates with diphenyl disulphide, ditolyl disulphide or dipropyl disulphide in the presence of butadiene or 2,3-dimethylbutadiene affords the crude trifluoroacetoxysulphides **1** and/or **2** which on basic hydrolysis readily afford the corresponding hydroxysulphides **3** and/or **4**. Under kinetic control it is possible to isolate the 1,2-adducts **3a-d** using Pb(IV)-acetate. Also, the thermodynamically more stable 1,4-adducts **4a-d** can be obtained by using Mn(III)-acetate. Cu(II)- or Fe(II)-acetates fail to undergo the trifluoroacetoxysulphenylation reaction.

The importance of vicinal oxygen and sulphur substitution stems from the great flexibility for structural elaboration[1]. Our attention has been paid to the methodology for introduction of nitrogen or oxygen functional groups to olefins accompanied by the addition of aryl or alkyl sulphur moiety[2-7]. This methodology has been utilized in regioselective synthesis of hydroxysulphides of allylic alcohols[2,3], trifluoroacetoxysulphenylation of unsaturated nitriles[4,5], and as new routes to heterocycles[6,7].

In continuation of our previous work, we now report the hydroxysulphenylation of conjugated dienes.

Trifluoroacetoxysulphenylation of butadiene using diphenyl disulphide, di-*p*-tolyl disulphide or dipropyl disulphide was affected in dichloromethane/trifluoroacetic acid (15:1) with $Pb(OAc)_4$ or $Mn(OAc)_3$ as the added oxidant. Mixtures of the hydroxylsulphides **3a-d** and **4a-d** derived from the 1,2- and 1,4-addition products **1a-d** and **2a-d** could be isolated under a basic work up (Scheme).



n = 4 when X = Pd
n = 3 when X = Mn

Comp. No.	R	R^1	R^2
3a, 4a	Phenyl	H	H
3b, 4b	Propyl	H	H
3c, 4c	4-Tolyl	H	H
3d, 4d	Phenyl	CH_3	CH_3

Table 1: Hydroxysulphenylation of butadiene under various conditions

Oxidant	disulphide	time h	temp. °C	1,2-adduct	Yield (%)	1,4-adduct	(%)
Pb IV	diphenyl	2	0	**3a**	(21)	**4a**	(28)
Pb IV	diphenyl	2	10	**3a**	(10)	**4a**	(15)
Pb IV	diphenyl	2	-20	**3a**	(35)	**4a**	(16)
Pb IV	diphenyl	2	-40	**3a**	(50)	**4a**	(-)
Pb IV	diphenyl	3	-40	**3a**	(52)	**4a**	(-)
Pb IV	di-p-tolyl	3	-40	**3b**	(54)	**4b**	(-)
Pb IV	dipropyl	3	-40	**3c**	(49)	**4c**	(-)
Mn III	diphenyl	4	0	**3a**	(13)	**4a**	(39)
Mn III	diphenyl	6	0	**3a**	(12)	**4a**	(37)
Mn III	diphenyl	6	10	**3a**	(-)	**4a**	(48)
Mn III	di-p-tolyl	6	10	**3b**	(-)	**4b**	(51)
Cu II	diphenyl	24	25	no addition			
Cu II	diphenyl	48	25	no addition			
Fe II	diphenyl	48	25	no addition			

  0365-6233/91/0707-0461 $ 3.50 + .25/0

The hydroxysulphides **3a-d** and **4a-d** were readily separated by chromatography and satisfactory analytical data were obtained. Reaction conditions were briefly examined using butadiene as starting material, different disulphide and metal ions at different temperature (Table 1).

As shown in Table 1, Pb(IV)-acetate was revealed to be a better oxidant to afford 1,2-addition product under kinetic control. The thermodynamically more stable 1,4-addition product can be obtained using Mn(III)-acetate. Also the 1,2-adducts **3a, b** readily rearrange to the thermodynamically more stable 1,4-adducts **4a, b** *via* an episulphonium ion intermediate in acidic medium. It is well established from the recent work[8,9] of *Warren's* group that under acidic conditions phenylthio migration permits a number of useful transformations *via* an episulphonium ion intermediate.

Similarly hydroxysulphenylation of 2,3-dimethylbutadiene underwent the same pathway of butadiene to give either **3d** or **4d**.

All attempts to undergo the trifluoroacetoxysulphenylation reaction of butadiene with diphenyl disulphide using Cu(II)- or Fe(II)-acetates failed even for 48 h.

Experimental Part

^{1}H- and ^{13}C-NMR spectra: Bruker 360 AM; $CDCl_3$; TMS as internal standard.- IR spectra: Beckman IR-4210.- Mass spectra: AE spectrometer.

General procedure for hydroxysulphenylation of 1,3-dienes with $Pb(OAc)_4$

$Pb(OAc)_4$ (1.58 g, 3.7 mmol) was added to dichloromethane (100 ml) at -40°C containing trifluoroacetic acid (7 ml). The disulphide (3.7 mmol) followed by the 1,3-diene (7.5 mmol) was added and the mixture was stirred at -40°C for 3 h. An initial turquoise colour faded to yellow, which continued to fade. After the reaction time, the mixture was poured into water (100 ml) and extracted with ether (3 x 100 ml). The org. phase was washed with aqueous $KHCO_3$ (3 x 50 ml) and then water (3 x 50 ml), dried over $MgSO_4$, filtered and most of the solvent was evaporated *in vacuo*. The crude trifluoroacetoxysulphide in the minimum quantity of ether (15 ml) was added to aqueous K_2CO_3 (30 ml, 20% solution). The mixture was stirred at room temp. for 24 h. Addition of water (10 ml) was followed by extraction with more ether (3 x 50 ml). The combined ethereal extracts were washed with more water (3 x 50 ml), dried over $MgSO_4$, filtered and most of the solvent was evaporated under reduced pressure to give the crude hydroxysulphides. Products were purified by chromatography over silica gel.

1-Phenylthio-3-buten-2-ol (**3a**)

348 mg, 52%, colourless oil. Found: M^+: m/z = 180.0588. $C_{10}H_{12}OS$ requires 180.0594.- ^{1}H-NMR: δ (ppm) = 2.88 (1H; s(br), -OH), 2.96 (1H; dd, J = 14; 8 Hz) and 3.13 (1H; dd, J = 14; 5 Hz) (-CH_2S-), 4.19 (1H; m, -CHO-), 5.16 (2H; d, J = 15 Hz, =CH_2), 5.85 (1H; m, =CH-), 7.10-7.45 (5H; m, aromatic).- ^{13}C-NMR: δ (ppm) = 41.79 (-CH_2S), 70.65 (-CH-O-), 116.40 (=CH_2), 126.64, 129.07, 130.16, 135.41, and 138.69 (aromatic C).- IR: $\tilde{\nu}$ (max) ($CHCl_3$): 3450 and 1590 cm^{-1}.

1-Propylthio-3-buten-2-ol (**3b**)

262 mg, 49%, colourless oil. Found: M^+: m/z = 146.0590. $C_7H_{14}OS$ requires 146.0595.- ^{1}H-NMR: δ (ppm) = 0.99 (3H; t, J = 7 Hz, -CH_3), 1.62 (2H; m, -CH_2), 2.53 (2H; t, J = 7 Hz, -CH_2S), 2.59 (1H; dd, J = 14; 8 Hz) and 2.67 (1H; dd, J = 14; 5 Hz, -CH_2S), 3.20 (1H; s(br), -OH), 4.10 (1H; m, -CH-O-), 5.15 (2H; d, J = 14 Hz, -CH_2) and 5.79 (1H; m, =CH-).- ^{13}C-NMR: δ (ppm) = 13.19 (-CH_3), 22.96 (-CH_2), 34.65 and 38.35 (-CH_2S), 69.50 (-CH.O-), 115.60 and 125.50 (olefinic C).- IR: $\tilde{\nu}$ (max) ($CHCl_3$): 3460 cm^{-1}.

1-(4-Tolylthio)-3-buten-2-ol (**3c**)

388 mg, 54%, colourless oil. Found: M^+: m/z = 194.0573. $C_{11}H_{14}OS$ requires 194.0585.- ^{1}H-NMR: δ (ppm) = 2.29 (3H; s, -CH_3), 3.02 (2H; m, -CH_2S), 3.45 (1H; s, -OH), 4.15 (1H; m, -CH-O-), 5.19 (2H; d, J = 15 Hz, =CH_2), 5.89 (1H; m, =CH-), 7.04-7.35 (4H; m, aromatic).- ^{13}C-NMR: δ (ppm) = 20.85 (-CH_3), 41.85 (-CH_2S-), 70.69 (-CH-O-), 116.09 (=CH_2), 126.90, 130.02, 130.21, 131.02, and 137.49 (olefinic and aromatic C).- IR: $\tilde{\nu}$ (max) ($CHCl_3$): 3450 and 1600 cm^{-1}.

2,3-Dimethyl-1-phenylthio-3-buten-2-ol (**3d**)

373 mg, 48%, colourless oil.- Found: M^+: m/z = 208.0580. $C_{12}H_{16}PS$ requires 208.0575.- ^{1}H-NMR: δ (ppm) = 1.39 (3H; s, -CH_3), 1.75 (3H; s, -CH_3), 2.72 (1H; s, -OH), 3.08 (1H; d, J = 6 Hz) and 3.33 (1H; d, J = 14 Hz, -CH_2S-), 4.87 (1H; m) and 5.10 (1H; d, J = 14 Hz, =CH_2), 7.12-7.41 (5H; m, aromatic).- ^{13}C-NMR: δ (ppm) = 19.61 (-CH_3), 27.21 (-CH_3), 46.90 (-CH_2S), 74.96 (-C-O), 111.50 (=CH_2), 126.50, 129.09, 130.04, 137.12, and 149.20 (olefinic and aromatic C).- IR: $\tilde{\nu}$ (max) ($CHCl_3$): 3450 and 1600 cm^{-1}.

General procedure for hydroxysulphenylation with Mn(III)-acetate

The appropriate disulphide (3.7 mmol) was added at 10°C to a stirred solution of $Mn(OAc)_3$-dihydrate (1.48 g, 5.5 mmol) in dichloromethane (100 ml) containing trifluoroacetic acid (7 ml). The unsaturated compound (7.5 mmol) was added and the solution was stirred for 6 h. The initial orange colour faded to give a colourless solution. The mixture was poured into water (100 ml). After ether extraction (3 x 100 ml), the org. phase was worked up as before and purification by column chromatography afforded the product.

4-Phenylthio-2-buten-1-ol (**4a**)

321 mg, 48%, colourless oil.- Found: M^+: m/z = 180.0560. $C_{10}H_{12}OS$ requires 180.0594.- ^{1}H-NMR: δ (ppm) = 2.70 (1H; s, -OH), 3.53 (2H; d, J = 7 Hz, -CH_2S-), 4.00 (2H; d, J = 7 Hz, -CH_2-O-), 5.72 (2H; m, -CH=CH-), 7.08-7.38 (5H; m, aromatic).- ^{13}C-NMR: δ (ppm) = 35.81 (-CH_2S-), 62.51 (-CH_2-O-), 126.20, 126.68, 128.74, 129.83, 132.53, and 140.12 (olefinic and aromatic C).- IR: $\tilde{\nu}$ (max) ($CHCl_3$): 3450 and 1590 cm^{-1}.

4-Propylthio-2-buten-1-ol (**4b**)

241 mg, 45%, colourless oil.- Found: M^+: m/z = 146.0605. $C_7H_{14}OS$ requires 146.0595.- ^{1}H-NMR: δ (ppm) = 1.0 (3H; t, J = 7 Hz, -CH_3), 1.63 (2H; m, -CH_2), 2.65 (2H; d, J = 8 Hz, -CH_2S-), 3.35 (2H; d, J = 6 Hz, -CH_2S-), 3.45 (1H; s(br), -OH), 3.89 (2H; d, J = 7 Hz, -CH_2O-), 5.65 (2H; m, -CH=CH-).- ^{13}C-NMR: δ (ppm) = 13.25 (-CH_3), 21.44 (-CH_2), 34.76 and 35.05 (-CH_2S-), 62.19 (-CH_2-O-), 125.05 and 126.30 (olefinic C).- IR: $\tilde{\nu}$ (max) ($CHCl_3$): 3450 cm^{-1}.

4-(4-Tolylthio)-2-buten-1-ol (**4c**)

366 mg, 51%, colourless oil.- Found: M^+: m/z = 194.0600. $C_{11}H_{14}OS$ requires 194.0585.- ^{1}H-NMR: δ (ppm) = 2.31 (3H; s, -CH_3), 3.55 (2H; d, J = 7 Hz, -CH_2S-), 3.60 (1H; s, -OH), 4.05 (2H; d, J = 7 Hz, -CH_2O), 5.75 (2H; m, -CH=CH-), 7.20-7.46 (4H; m, aromatic).- ^{13}C-NMR: δ (ppm) = 20.90 (-CH_3), 35.90 (-CH_2S-), 62.59 (-CH_2-O-), 126.35, 126.79, 130.10, 130.27, 131.09, and 137.50 (olefinic and aromatic C).- IR: $\tilde{\nu}$ (max) ($CHCl_3$): 3450 and 1590 cm^{-1}.

2,3-Dimethyl-4-phenylthio-2-buten-1-ol (**4d**)

348 mg, 45%, colourless oil. Found: M^+: m/z = 208.0564. $C_{12}H_{16}OS$ requires 208.0575.- ^{1}H-NMR: δ (ppm) = 1.75 (3H; s, $-CH_3$), 1.79 (3H; s, $-CH_3$), 2.70 (1H; s, -OH), 3.45 (2H; s, $-CH_2S-$), 4.05 (2H; s, $-CH_2O-$), 7.12-7.41 (5H, m, aromatic).- ^{13}C-NMR: δ (ppm) = 20.51, 22.01 ($-CH_3$), 36.01 ($-CH_2S-$), 62.60 ($-CH_2O-$), 126.20, 126.85, 128.80, 129.35, 132.17, and 139.95 (olefinic and aromatic C).- IR: $\tilde{\nu}$(max) ($CHCl_3$): 3450 and 1600 cm^{-1}.

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