Notes

Synthesis of γ-Oxo Sulfones via Palladium- and Platinum-Catalyzed Hydrosulfination

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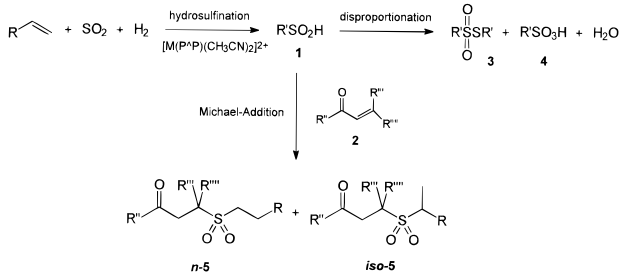
The Michael addition of sulfinic acids (**1**) with α,β-unsaturated carbonyl compounds (**2**) to give γ-oxo sulfones (**5**) is a well-established reaction.[1] Due to the instability of aliphatic sulfinic acids however, difficulties occur. Especially the lower aliphatic sulfinic acids readily undergo disproportionation to thiosulfonic acid esters (**3**), sulfonic acids (**4**), and water even at room temperature. Thus, preparation of the corresponding Michael adducts (**5**) requires very special conditions. Usually this implies time-consuming syntheses of alkanesulfinic acids and often involves the use of the appropriate sulfinate salts, which in turn require an acidic reaction medium for the Michael addition.[2]

Here we report a simple route to γ-oxo sulfones with aliphatic substituents by making use of the hydrosulfination reaction which we have described recently.[3]

In analogy to hydroformylation, alkenes react with SO_2 and H_2 to give sulfinic acids as intermediates which are not stable under the reaction conditions and undergo the foregoing disproportionation. However, they can be trapped in situ by simply adding α,β-unsaturated carbonyl compounds to the reaction mixture; this leads to γ-oxo sulfones in good yields as illustrated in Scheme 1.

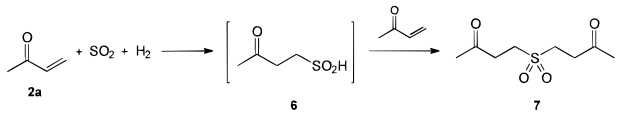
Scheme 1



Cationic palladium(II) or platinum(II) complexes with chelating diphosphines as ligands serve as catalysts.

The Michael acceptors, being functionalized alkenes themselves, can also be hydrosulfinated. For example, methyl vinyl ketone (**2a**) first forms the ketosulfinic acid **6**, which then adds in a second step to another substrate molecule (serving as S-nucleophile) to yield the diketo sulfone **7** as shown in Scheme 2. No disproportionation products of **6** can be detected.

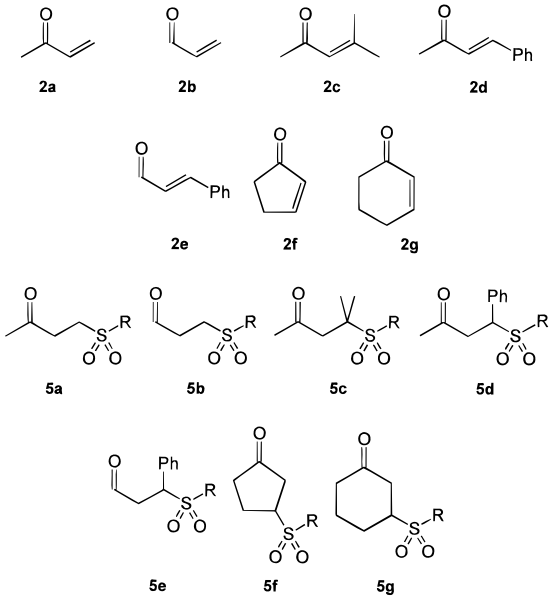
Scheme 2



If another unfunctionalized alkene like propene is present, the Michael acceptor will not be hydrosulfinated, due to its lower reactivity. Under identical reaction conditions, methyl vinyl ketone is hydrosulfinated in the absence of an olefin in 18 h in poor turnover numbers (TON) of 70, whereas pure propene is hydrosulfinated in 15 h with TON of 870.

It is also noteworthy that mesityl oxide and 2,3-dimethylbut-2-ene by themselves cannot be hydrosulfinated. This is explainable by steric hinderance: According to the proposed mechanism,[3b] coordination of the alkene to the catalyst complex followed by insertion is essential. The alkenes mentioned are too bulky to undergo these reaction steps. However, mesityl oxide turns out to be small enough to react very well as a Michael acceptor with sulfinic acids.

The α,β-unsaturated carbonyl compounds **2a**−**g** have been successfully used as "trapping agents" in hydrosulfination of propene according to Scheme 1, and the results are listed in Table 1.



As shown in Table 1, best results are obtained with mesityl oxide (**2c**), cyclopent-2-en-1-one (**2f**), and cyclohex-2-en-1-one (**2g**) as trapping agents. After the standard reaction time, the yield is quantitative. Thus, experiments with a shorter reaction time (3 and 4 h,

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Table 1. Palladium-Catalyzed Synthesis of γ-Oxo Sulfones from Propene, Sulfur Dioxide, and Hydrogen in the Presence of an α,β-Unsaturated Carbonyl Compound[a]

acc/prd	*n*(cat.) (mmol)	*m*(C_3H_6) (g)	*m*(SO_2) (g)	*m*(acc) (g)	*t* (h)	*m*(prd) (g)	TON	yield (%)
2a/5a	0.132	3.7	3.6	4.0	16.5	5.0	210	50
2b/5b	0.140	4.0	4.6	4.0	18	5.7	250	50
2c/5c	0.132	3.0	3.2	4.0	16.5	8.5	310	100
2c/5c	0.097	2.8	4.1	5.7	3	3.7	190	31
2d/5d	0.105	3.1	4.8	8.8	15	4.0	150	27
2e/5e	0.094	4.1	2.1	4.0	17	4.6	200	65
2f/5f[b]	0.106	3.6	2.8	5.4	15.5	8.4	420	100
2f/5f[b]	0.100	3.8	2.9	5.4	4	4.3	230	51
2g/5g[b]	0.097	2.9	2.7	6.0	15	8.6	430	100
2g/5g[b]	0.099	2.7	2.9	6.0	4	4.6	220	49

[a] Acc, acceptor; prd, product; cat., (dppp)Pd$(CH_3CN)_2^{2+}$; dppp, 1,3-bis(diphenylphosphino)propane; T = 80 °C; solvent, CH_2Cl_2; $p(SO_2)$ = 2 bar; $p(C_3H_6)$ = 8 bar; $p(H_2)$ = 25 bar; yield with regard to the substrate in lowest concentration, determined by GC, uncorrected. [b] Yield determined by NMR as product decomposes during GC analysis.

Table 2. Platinum-Catalyzed Synthesis of γ-Oxo Sulfones from Propene, Sulfur Dioxide, and Hydrogen in the Presence of an α,β-Unsaturated Carbonyl Compound[a]

acc/prd	ligand	*n*(cat.) (mmol)	*m*(C_3H_6) (g)	*m*(SO_2) (g)	*m*(acc) (g)	*m*(prd) (g)	TON	yield (%)
2c/5c	dppp	0.153	5.9	4.3	6.0	2.3	70	20
2c/5c	dppb	0.153	5.9	3.6	6.0	2.3	70	20
2c/5c	dippp	0.148	5.5	4.4	6.0	2.7	90	20
2f/5f	dippp	0.148	4.1	3.8	5.3	2.9	100	25
2g/5g	dippp	0.150	4.2	3.5	5.8	2.7	90	25

[a] Acc, acceptor; prd, product; cat., (P∧P)Pt$(CH_3CN)_2^{2+}$; T = 120 °C; t = 17 h; solvent, CH_2Cl_2; $p(SO_2)$ = 2 bar; $p(C_3H_6)$ = 8 bar; $p(H_2)$ = 26 bar; yield with regard to the substrate in lowest concentration, determined by GC, uncorrected; dppp, 1,3-bis(diphenylphosphino)-propane; dppb, 1,4-bis(diphenylphosphino)butane; dippp, 1,3-bis(diisopropylphosphino)propane.

Table 3. *n*-:*iso*-Selectivity in Hydrosulfination[a]

M	ligand	R	*n*	*T* (°C)	*n*:*iso*[b]
Pd	dppp	Ph	3	80	6:1
Pd	dppb	Ph	4	80	6:1
Pd	dippp	*i*-Pr	3	80	8:1
Pd	dtbpe	*t*-Bu	2	80	12:1
Pt	dppe	Ph	2	120	10:1
Pt	dppp	Ph	3	120	13:1
Pt	dppb	Ph	4	120	14:1
Pt	dippp	*i*-Pr	3	120	72:1

[a] Catalyst, $[(R_2P(CH_2)_nPR_2)M(CH_3CN)_2]^{2+}$; acceptor, mesityl oxide (**2c**); T = 120 °C; t = 16−18 h; solvent, CH_2Cl_2; $p(SO_2)$ = 2 bar; $p(C_3H_6)$ = 8 bar; $p(H_2)$ = 26 bar; dppe, 1,2-bis(diphenylphosphino)ethane; dppp, 1,3-bis(diphenylphosphino)propane; dppb, 1,4-bis(diphenylphosphino)butane; dippp, 1,3-bis(diisopropylphosphino)propane; dtbpe, 1,2-bis(di-*tert*-butylphosphino)ethane. [b] Determined by GC analysis.

respectively) were carried out, leading to TON of 190, 230, and 220, respectively.

In the experiments presented here, propene was employed as the standard alkene. In general, higher alkenes like 1-butene or 1-hexene can be used, also.

Besides palladium, platinum also shows catalytic activity. The results in Table 2 show that in spite of a higher reaction temperature significantly lower TON are achieved.

An inherent advantage of the Pt systems over Pd systems can be seen in a higher *n*-:*iso*-selectivity, indicative for a ligand/metal-controlled organometallic coordination mechanism. The maximum ratio of linear to branched product is 12:1 in the case of Pd catalysts.[4] With Pt a ratio of up to 72:1 can be achieved, corresponding to an amount of more than 98% of linear product (see Table 3).

Experimental Section

General Methods. Solvents were purified, dried, and saturated with argon by standard methods. Other chemicals were used as purchased. Reactions were carried out under an argon atmosphere using common Schlenk technique.

Pd catalysts were prepared according to the method of Herwig.[3b]

Pt catalysts were generated in adaption of Yamamoto's method.[5] To a suspension of 0.15 mmol of $[(COD)PtCl_2]$[6] in 0.5 mL of CH_2Cl_2 was added an equimolar amount of diphosphine in 1.5 mL of CH_2Cl_2. After the mixture was stirred for 1 h, 2 equiv of $AgBF_4$ in 1 mL of CH_3CN was added. The precipitated AgCl was filtered off after 30 min, and the resulting clear solution was immediately used for catalytic experiments.

Catalytic experiments were carried out in 150 mL hastelloy autoclaves equipped with a glass beaker and a magnetical stirrer. After introduction of the catalyst solution and the Michael acceptor, CH_2Cl_2 was added to a total volume of 30 mL. SO_2 (2 bar), propene (8 bar), and H_2 (25 bar) were added successively. The autoclave was placed into an oil bath already heated to reaction temperature. After the reaction time, the autoclave was cooled rapidly by means of an ice bath and a stream of cold air. The pressure was released slowly, and after the autoclave was opened, the solvent was evaporated in vacuo at room temperature.

The resulting mixture of *n*- and *iso*-γ-oxo sulfones was analyzed by NMR and GC (assignment of *n*- and *iso*-product confirmed by GC−MS). Recrystallization from ether or CH_2Cl_2/pentane increased the amount of the linear product. Thus, the NMR data given only refer to the *n*-isomer.

4-(Propylsulfonyl)-2-butanone (5a). ^{1}H-NMR (300 MHz, $CDCl_3$): δ 1.09 (t, 3H, J = 7 Hz), 1.89 (sext, 2H), 2.25 (s, 3H), 2.89 (t, 2H, J = 8 Hz), 3.02 (t, 2H, J = 7 Hz), 3.25 (t, 2H, J = 7 Hz). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 13.1, 15.9, 29.9, 35.1, 46.8, 55.4, 204.9. IR (KBr) ν(CO) 1716, ν(SO_2) 1259, 1130 cm^{-1}. Anal. Calcd for $C_7H_{14}O_3S$: C, 47.17; H, 7.92. Found: C, 46.71; H, 7.58.

3-(Propylsulfonyl)-1-propanal (5b). ^{1}H-NMR (300 MHz, $CDCl_3$): δ 1.10 (t, 3H, J = 7 Hz), 1.90 (sext, 2H, J = 7 Hz), 2.99 (t, 2H, J = 8 Hz), 3.09 (t, 2H, J = 7 Hz), 3.28 (t, 2H, J = 7 Hz), 9.38 (s, 1H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 13.1, 15.4, 15.9, 35.6, 45.3, 53.8, 55.4, 197.3.

4-(Propylsulfonyl)-4-methyl-2-pentanone (5c). ^{1}H-NMR (300 MHz, $CDCl_3$): δ 1.12 (tr, J = 7.4 Hz, 3H), 1.54 (s, 6H), 1.94 (m, 2H), 2.22 (s, 3H), 2.93 (tr, J = 8.1 Hz, 2H), 2.94 (s, 2H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 13.4, 14.5, 20.2, 32.1, 45.3, 47.3, 61.4, 204.9. IR (KBr): ν(CO) 1724, ν(SO_2) 1286, 1103 cm^{-1}. Anal. Calcd for $C_9H_{18}O_3S$: C, 52.40; H, 8.79. Found: C, 51.58; H, 8.90.

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4-(Propylsulfonyl)-4-phenyl-2-butanone (5d). ^{1}H-NMR (300 MHz, $CDCl_3$): δ 0.96 (t, J = 7 Hz, 3H), 1.78 (sext, J = 8 Hz, 2H), 2.16 (s, 3H), 2.66 (t, J = 8 Hz, 2H), 3.23 (dd, J_1 = 9 Hz, J_2 = 18 Hz), 3.54 (dd, J_1 = 4 Hz, J_2 = 18 Hz, 1H), 4.70 (dd, J_1 = 9 Hz, J_2 = 4 Hz, 1H), 7.2−7.5 (m, 5H), 9.63 (br s, 1H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 13.1, 15.4, 30.4, 41.3, 52.2, 63.0, 129.1, 129.2, 129.4, 133.3, 203.4. IR (KBr): ν(CO) 1716, $\nu(SO_2)$ 1281, 1130 cm^{-1}. Anal. Calcd for $C_{13}H_{18}O_3S$: C, 61.39; H, 7.13. Found: C, 61.54; H, 7.12.

3-(Propylsulfonyl)-3-phenylpropanal (5e). ^{1}H-NMR (300 MHz, $CDCl_3$): δ 1.68 (m, 2H), 2.60 (m, 2H), 3.16 (ddd, J_1 = 1 Hz, J_2 = 9 Hz, J_3 = 18 Hz, 1H), 3.49 (ddd, J_1 = 1 Hz, J_2 = 9 Hz, J_3 = 18 Hz, 1H), 4.67 (dd, J_1 = 9 Hz, J_2 = 18 Hz, 2H), 7.2−7.6 (m, 5H), 9.63 (br s, 1H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 13.4, 15.4, 41.7, 52.0, 61.8, 129.3, 129.4, 197.0). IR (KBr): ν(CO) 1719, $\nu(SO_2)$ 1283, 1132 cm^{-1}. Anal. Calcd for $C_{12}H_{16}O_3S$: C, 59.97; H, 6.71. Found: C, 60.22; H, 6.71.

3-(Propylsulfonyl)cyclopentanone (5f). ^{1}H-NMR (300 MHz, $CDCl_3$): δ 1.03 (tr, J = 7 Hz, 3H), 1.79−1.87 (m, 2H), 2.2−2.7 (m, 8 H), 2.9−2.93 (m, 2H), 3.6−3.7 (m, 1H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 13.3, 15.5, 22.5, 37.0, 38.1, 53.2, 57.4, 212.9. IR (KBr): ν(CO) 1749, $\nu(SO_2)$ 1280, 1123 cm^{-1}. Anal. Calcd for $C_8H_{14}O_3S$: C, 50.50; H, 7.42. Found: C, 50.42; H, 7.53.

3-(Propylsulfonyl)cyclohexanone (5g). ^{1}H-NMR (300 MHz, $CDCl_3$): δ 1.01 (tr, J = 7 Hz, 3H), 1.6−2.05 (m, 7H), 2.15−2.25 (m, 5H), 2.6−2.8 (m, 1H), 2.85−3.0 (m, 1H), 3.2−3.35 (m, 1H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 13.3, 15.4, 23.2, 23.6, 40.0, 40.6, 52.1, 59.5, 206.6. IR (KBr): ν(CO) 1713, $\nu(SO_2)$ 1270, 1119 cm^{-1}. Anal. Calcd for $C_9H_{16}O_3S$: C, 52.91; H, 7.89. Found: C, 52.93; H, 7.87.

Bis(3-oxobutyl)sulfone (7). ^{1}H-NMR according to Kerber and Starnick.[7] ^{13}C-NMR (75 MHz, $CDCl_3$): δ 29.9, 35.3, 47.8, 203.9. IR (KBr): ν(CO) 1713, $\nu(SO_2)$ 1239, 1136 cm^{-1}.

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