α-Sulfonyl Ethers; Part XII[1]. Methyl Sulfonylformates from 1-Methoxyvinyl Sulfones

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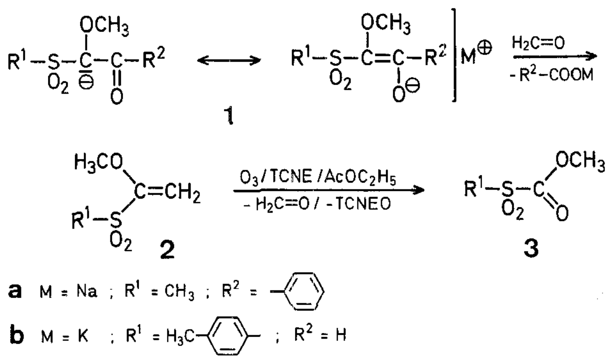
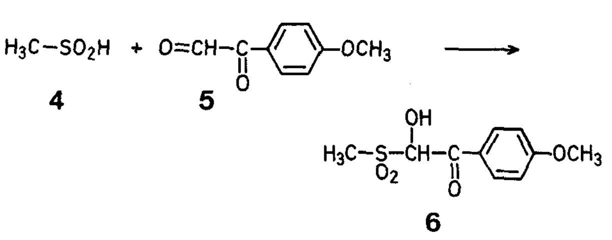
In a preceeding paper[2] we reported the ozonolysis of 1-methoxyvinyl sulfones (**2**). Compounds **2** were synthesised by carbonyl olefination of formaldehyde with the sodium salt of α-methoxyphenacyl methyl sulfone[3] (**1a**) in the case of the aliphatic **2a**, and by a simplified method from the potassium enolates of α-arylsulfonyl-methoxyacetaldehydes[1] (**1b,c**) in the case of the aromatic sulfones **2b,c**. Ozonolysis of compounds **2** gave rise to a new class of compounds having an alkoxycarbonyl group attached to a sulfonyl group. These compounds (**3**), which are in fact carbonic acid derivatives (dimethyl- and *S*-aryl *O*-methyl thiocarbonate *S,S*-dioxides) but may also be regarded as methoxycarbonyl methyl(aryl) sulfones, will be named here, for reasons of simplicity but less correctly, methyl sulfonylformates. The first compounds reported[4] to contain an authentic —SO_2—CO— unit were the "sulfonylcarbamates" (aminocarbonyl sulfones, sulfonylformamides). An earlier assumption[5] that alkyl carbonochloridates (alkyl chloroformates) react with sodium arenesulfinates to give minor amounts of alkyl sulfonylformates was found to be wrong; ^{1}H-N.M.R. control gave no characteristic signals of **3** (**b**). A recent publication[6] which reports the successful oxidation of thiocarbonates to the corresponding *S*- oxides and *S,S*-dioxides (**3**) with 3-chlorobenzoperoxoic acid prompted us tu publish our present results.



The ozonolysis[7] was carried out in ethyl acetate in the presence of tetracyanoethylene[8] (TCNE); the products **3** were purified by distillation (**3a**), recrystallization (**3c**), or short-path distillation followed by recrystallization (**3b**), and thus obtained in reasonable yields.

The methyl sulfonylformates **3** are colorless products which are very sensitive to moisture. A few solvolysis experiments were carried out with **3a**. Upon addition of an equimolar amount of methanol to a solution of **3a** in chloroform, the characteristic ^{1}H-N.M.R. signals of **3a** and of methanol ($\delta_{OCH_3} = 3.5$ ppm) disappear gradually while the characteristic signals of dimethyl carbonate ($\delta_{OCH_3} = 3.83$ ppm) and methanesulfinic acid ($\delta_{CH_3} = 2.7$ ppm) appear. Stirring of **3a** in water affords a solution of methanesulfinic acid (**4**) with evolution of carbon dioxide. The formation of **4** from the methanolysis of **3a** was proven by trapping **4** with 4-methoxyphenylglyoxal (**5**) to give α-hydroxy-4-methoxyphenacyl methyl sulfone[9] (**6**).



1-Methoxyvinyl Methyl Sulfone (2a):
This compound is prepared according to Ref.[3].

4-Methyl- (2b) and 4-Chlorophenyl 1-Methoxyvinyl Sulfone (2c): The potassium enolate of the α-arylsulfonyl-methoxyacetaldehyde[1] (**1b,c**; 0.02 mol) is dissolved in dry dimethyl sulfoxide (20 ml) with gentle warming. Dry trioxane (0.6 g, 0.02 mol) is added, the mixture is stirred for 15 min, and then poured into ice water. The crystalline sulfone **2** is isolated by suction and recrystallized from methanol.

Sulfone **2b**; yield: 2.5 g (59%); m.p. 97°[2].

Sulfone **2c**; yield: 3 g (65%); m.p. 91°.

$C_9H_9ClO_3S$	calc.	C 46.45	H 3.90
(232.7)	found	46.5	3.87

I.R. (KBr): ν_{max} = 1640 (C=C), 1330, 1152 (SO_2) cm^{-1}.

^{1}H-N.M.R. ($CDCl_3$/TMS): δ = 3.67 (s, OCH_3); 4.80, 5.55 ppm (J_{AB} = 4 Hz, CH_2).

Ozonolysis of Sulfones 2 to Methyl Sulfonylformates (3):
The sulfone **2** (0.1 mol) and tetracyanoethylene (10.24 g, 0.08 mol) are dissolved in dry ethyl acetate (400 ml). The solution is treated with ozone/oxygen (~1.5 mmol ozone/min at ~60 l gas/h) at 10–20° (cooling with ice bath) under usual conditions. After absorption of an equimolar amount of ozone, the reaction is complete when ozone passes unchanged through the reaction mixture. Ethyl acetate is distilled off, and the residue is treated with dry chloroform, and undissolved tetracyanooxirane removed by filtration. The solvent is evaporated in vacuo to leave the crude product **3** which is immediately purified as described below.

Methyl Methylsulfonylformate (**3a**): The product is purified by fractional distillation in vacuo; yield: 60%; b.p. 55°/0.0005 torr. The contamination of **3a** by tetracyanoethylene and tetracyanooxirane cannot be removed by distillation.

$C_3H_6O_4S$ (138.1).

I.R. (neat): ν_{max} = 1768 (C=O); 1338, 1134 cm^{-1} (SO_2).

^{1}H-N.M.R. ($CDCl_3$/TMS): δ = 3.19 (CH_3); 4.12 ppm (OCH_3).

Methyl 4-Methylphenylsulfonylformate (**3b**): The product (yield: 60%) is purified by short-path distillation (76°/0.004 torr) and then further purified by recrystallization from dry ethyl acetate/petroleum ether (1:1); yield: 25%; m.p. 35°.

$C_9H_{10}O_4S$	calc.	C 50.47	H 4.71
(214.2)	found	50.5	4.92

I.R. (neat): ν_{max} = 1765 (C=O); 1335, 1140 cm^{-1} (SO_2).

^{1}H-N.M.R. ($CDCl_3$/TMS): δ = 2.47 (CH_3); 3.95 ppm (OCH_3).

Methyl 4-Chlorophenylsulfonylformate (**3c**): The product is recrystallized from dry ethyl acetate/petroleum ether (1:1); yield: 43%; m.p. 95–96°. [In the pure product, no peroxidic compounds could be detected though only 80% of the calculated amount of tetracyanoethylene had been added to the reaction mixture; the tetracyanoethylene had not even been completely consumed in the reaction.]

$C_8H_7ClO_4S$	calc.	C 40.94	H 3.01
(234.7)	found	40.8	2.98

I.R. (KBr): ν_{max} = 1767 (C=O); 1340, 1140 cm^{-1} (SO_2).

^{1}H-N.M.R. ($CDCl_3$/TMS): δ = 4.00 ppm (OCH_3).

M.S. (*m/e*) of **3a–c**; characteristic fragments:

	3a	**3b**	**3c**
R—SO_2COOCH_3	138: –[a]	214: +	234/236: –[a]
R—SO_2CH_3	94: +	170: +	190/192: +
R—SO_2	79: +	155: +	175/177: +
R—SO	63: +	139: +	159/161: +
H_3C—CO—O—	59: +	59: +	59: +

[a] $M^{\oplus}$ cannot be observed.

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[7] **Warning!** To avoid contamination of the products by tetracyanoethylene and tetracyanooxirane, one ozonolysis experiment was carried out in absolute acetone as solvent on a 0.1 mol scale [acetone was chosen because the ozonide from isobutene which possesses an acetone unit in the molecule has been described as a rather stable compound with b.p. 42–42.5°/140 torr: R. Criegee, G. Blust, H. Zinke, *Chem. Ber.* **87**, 766 (1954)]. However, after 1/10 of the calculated ozonization time, a *violent explosion* occurred without prior noticeable rise of the reaction temperature.

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