# 1-Formyl- and 1-Diazoalkanesulfonates

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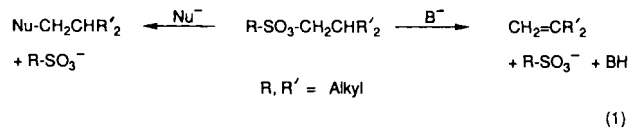
The deprotonation of the neopentyl, isobutyl and isopropyl esters of methane- and ethanesulfonic acid with *n*-butyllithium and subsequent reaction with ethyl formate afforded the corresponding 1-formylalkanesulfonates in 77–90% yield. 1-(Methoxymethylene)alkanesulfonates could be obtained by additional treatment with dimethyl sulfate and base, as examplified in the case of neopentyl 1-formylethanesulfonate. Furthermore, the formylated sulfonates were converted into the stable 1-diazoalkanesulfonates in 28–65% yield employing arylsulfonyl azides as diazo group transfer reagents. The chemical behaviour of the novel 1-diazoalkanesulfonates resembles that of 1-diazoalkanephosphonates, e. g., deprotection to the 1-diazoalkanesulfonate anion resulted in rapid denitrogenation. The thermolysis of isobutyl 1-diazoethanesulfonate in an inert solvent afforded isobutyl vinylsulfonate as the major product.

**1-Formyl- und 1-Diazoalkansulfonate**

Durch Deprotonierung der Neopentyl-, Isobutyl- und Isopropylester der Methan- und Ethansulfonsäure mit *n*-Butyllithium und nachfolgende Reaktion mit Ameisensäure-ethylester wurden die entsprechenden 1-Formylalkansulfonsäureester in 77–90% Ausbeute erhalten. Am Beispiel des 1-Formylethansulfonsäure-neopentylesters wurde gezeigt, daß durch weitere Umsetzung mit Dimethylsulfat und Base 1-(Methoxymethylen)alkansulfonsäureester zugänglich sind. Die 1-Formylalkansulfonsäureester konnten mit Arylsulfonylaziden durch entformylierende Diazogruppenübertragung in 28–65% Ausbeute zu den stabilen 1-Diazoalkansulfonsäureestern umgesetzt werden. Die chemischen Eigenschaften dieser neuen Diazoverbindungen gleichen denen der 1-Diazoalkanphosphonsäureester, so führt z. B. die Entschützung zum Sulfonatanion zur spontanen Stickstoffabspaltung. Die Thermolyse des 1-Diazoethansulfonsäure-isobutylesters in inertem Lösungsmittel ergab Vinylsulfonsäure-isobutylester als Hauptprodukt.

Diazo compounds have proven extremely valuable not only from a mechanistic point of view, but also in terms of synthetic application. 1,3-Dipolar cycloadditions[1] and thermal or photochemical denitrogenation with subsequent reaction/rearrangement of the carbenes formed[2] are among the most prominent transformations. Methods for the preparation of various types of α-diazocarbonyl compounds are well-established[3], and their role as key intermediates in numerous complex syntheses demonstrates their snythetic potential.

Comparatively little is known concerning the preparation and properties of the analogous acyl diazo compounds derived from sulfur or phosphorus, e. g. α-diazophosphonates[3] and α-diazosulfones[3,4]. To the best of our knowledge, no preparative approach to the sulfur analogues of α-diazocarboxylates, i. e. 1-diazoalkanesulfonates, appears to have been reported in the literature. Unlike transformations of sulfones or carboxylates, all manipulations on sulfonates must take into account the pronounced electrophilicity of the carbon atom bound to the sulfonate oxygen. At first sight, the reaction with bases or nucleophiles should preferentially lead to the corresponding sulfonate anion [eq. (1)].




(1)

It has been known for some time, however, that alkyl alkanesulfonates can cleanly be alkylated without cleavage employing alkyl halides and lithium alkyl bases at low temperature[5]. With this in mind it appeared reasonable to assume that the analogous *formylation* of alkyl alkanesulfonates may provide alkyl 1-*formyl*alkanesulfonates. The latter ones could then be converted into the desired alkyl 1-diazoalkanesulfonates employing arylsulfonyl azides as diazo transfer reagents[3]. Finally, treatment with nucleophiles such as sodium thiophenolate should afford the corresponding 1-diazoalkanesulfonate anions.

In fact, deprotonation of the alkyl alkanesulfonates **1a–e** (Scheme 1) with *n*-butyllithium at −90°C and subsequent reaction with ethyl formate afforded the alkyl 1-formylalkanesulfonates **2a–e** (Scheme 1, cf. Experimental for yields and analytical data).

Whereas compounds **2b,d,e** could be obtained analytically pure by kugelrohr distillation, the derivatives **2a,c** of methanesulfonic acid underwent extensive decomposition upon attempted distillation. Analysis was carried out on their 2,4-dinitrophenylhydrazones, and the crude, stable lithium enolates of the sulfonates **2a,c** were used for further reactions. Isobutyl 2-methylthioethanesulfonate (**5**) was prepared as shown in eq. (2) and also subjected to the formylation procedure. However, only mixtures of starting material and isobutyl methyl sulfide, but no formylated product could be identified ($^1$H NMR) after workup.

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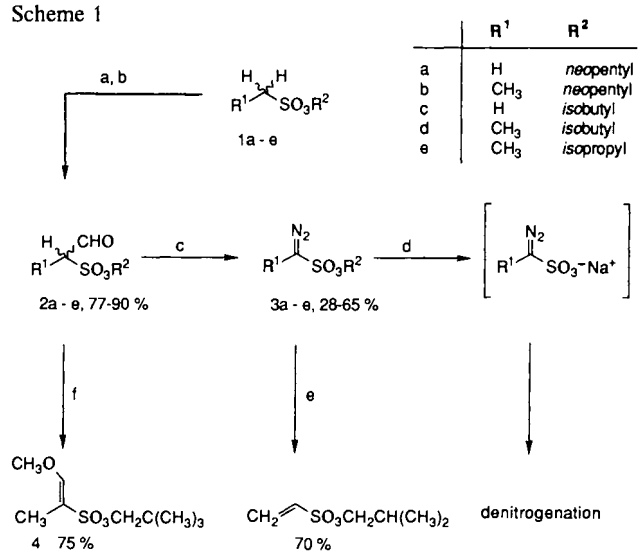
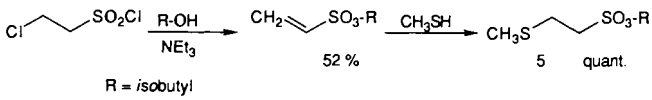
Scheme 1

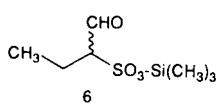



(2)

Alkylation of the 1-formylalkanesulfonate **2b** with potassium *tert*-butoxide and dimethyl sulfate gave the 1-(methoxymethylene)alkanesulfonate **4** (Scheme 1). The stereochemistry of the C=C double bond could not be derived unambigously from the spectral data (cf. Experimental). However, the analogous methylation of α-formylsulfones was shown to yield the methyl enol ethers in the *E* configuration[6]. Therefore, compound **4** (Scheme 1) may also be assumed to have *E* configuration around the C=C double bond.

The reaction of the formylated sulfonates **2a–e** with arylsulfonyl azide (Scheme 1) could be carried out in two ways. The isolated 1-formylalkanesulfonates **2b, d, e** and the crude lithium enolates of **2a, c** were treated with 4-carboxybenzenesulfonyl azide[7] under phase-transfer conditions (method A), or tosyl azide was added directly to the reaction mixtures resulting from the formylation of the alkanesulfonates **1a–e** (method B). Standard workup and chromatography on silica gel afforded the pure 1-diazoalkanesulfonates **3a–e** (cf. Experimental for yields and analytical data).



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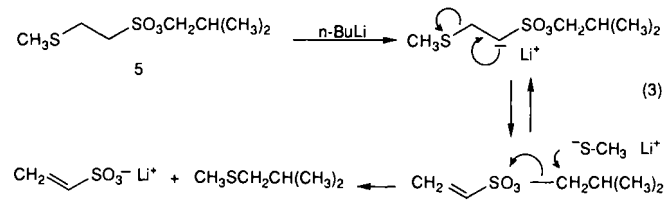
Attempts to apply the diazo group transfer reaction (Scheme 1) to the known[3] silyl ester **6** failed. IR analysis of the reaction mixtures did not indicate the formation of a diazo compound under any of the reaction conditions tried.

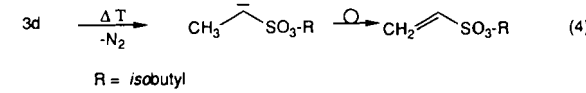
The 1-diazoalkanesulfonates **3c–e** could smoothly be cleaved with sodium thiophenolate or sodium methoxide at ambient temperature (Scheme 1). $^1$H NMR monitoring of the reaction clearly showed the formation of the corresponding thiophenyl or methyl ether, respectively. Unfortunately, the cleavage reaction was spontaneously followed by denitrogenation of the sulfonate anions formed, yielding complex product mixtures.

Unlike the 1-diazoalkanesulfonate anions, the alkyl 1-diazoalkanesulfonates **3a–e** are thermally relatively stable. For example, the half-lives of the diazo compounds **3a** and **3d** at 80°C in 1,1,2,2-tetrachloroethane or toluene were estimated at 41 min and 16 min, respectively ($^1$H NMR). In the case of **3d**, $^1$H NMR monitoring revealed that isobutyl vinylsulfonate was formed as the major product (ca. 70%, Scheme 1).

The synthetic approach to alkyl 1-formylalkanesulfonates presented here appears to be broadly applicable. Clearly, some general limitations of reactions involving carbanionic intermediates must be considered. For example, nucleofugal substituents in the β-position are not tolerated. In the case of 2-methylthioethanesulfonate [**5**, eq. (2)], elimination of methanethiolate and subsequent deprotection of the vinylsulfonate most likely account for the failure of the formylation procedure [eq. (3)].




The conversion of the alkyl 1-formylalkanesulfonates **2a–e** into the alkyl 1-diazoalkanesulfonates **3a–e** could be achieved in synthetically useful yields (Scheme 1). As mentioned earlier, the pronounced electrophilicity of alkyl sulfonates must be taken into account as a potential source of side reactions under the basic conditions of the diazo transfer reaction. It appears that the steric hindrance imposed by both the neopentyl (**2a, b**, Scheme 1) and the isobutyl group (**2c, d**, Scheme 1) sufficiently moderates this undesireable reactivity. The comparatively low yield of isopropyl 1-diazoethanesulfonate (**3e**) most likely reflects the higher reactivity of isopropyl sulfonates towards nucleophilic attack and illustrates the limitations of our method. Clearly, the trimethylsilyl sulfonate **6**[8] – a potentially strong electrophile[9] – does not match the requirements discussed above.




(4)

The thermal stability of alkyl 1-diazoalkanesulfonates follows the general pattern observed for other diazo compounds. For example, alkyl substitution at the 1-position results in decreased stability towards thermal denitrogenation[10] (e.g. **3a** vs. **3d**, cf. Experimental). As in the case of 1-diazoalkanephosphonates, the presence of the electron-withdrawing ester functionality is essential for reasonable ther-

mal stability[11]. Generation of the corresponding anions results in spontaneous loss of nitrogen (Scheme 1)[11]. The thermal reactivity of isobutyl 1-diazoethanesulfonate (**3d**, Scheme 1) is best explained assuming initial loss of nitrogen and subsequent 1,2-H shift in the carbene intermediate [eq. (4)].

Financial support from the *Fonds der Chemischen Industrie* is gratefully acknowledged. We wish to express our gratitude towards Dr. *G. Dürner* and his staff for HPLC support.

## Experimental

*General:* Melting points are uncorrected. – Elemental analyses were either carried out in-house with a Heraeus CHN Rapid elemental analyzer or by Analytische Laboratorien Malissa and Reuter, Engelskirchen, West Germany. – IR spectra were recorded with a Perkin-Elmer 257 instrument. – $^1$H NMR spectra were measured at 270 MHz with a Bruker WH-270 spectrometer or at 300 MHz with a Bruker AM-300 spectrometer, δ(TMS) = 0 ppm. – UV/VIS spectra were taken with a Cary 15 instrument. – Waters equipment was used for analytical and semipreparative HPLC separations.

*Alkyl Alkanesulfonates* **1a–e**: The procedure described for the sulfonates **1a,b**[5] was adapted for the preparation of compounds **1c–e**.

**1a**: 86% (78%)[5b] after kugelrohr distillation at 59°C/0.5 Torr. – IR (film): $\tilde{\nu}$ = 2960 cm$^{-1}$ (CH), 1350 (SO), 1170 (SO). – $^1$H NMR ($CDCl_3$): δ = 0.98 (s, 9H, C–$CH_3$), 2.98 (3H, $CH_3$), 3.82 (s, 2H, $CH_2$–C).

$C_6H_{14}O_3S$ (166.2) Calcd. C 43.35 H 8.49
Found[5b] C 43.53 H 8.58

**1b**: 81% (90%)[5b] after kugelrohr distillation at 62°C/0.3 Torr. – IR (film): $\tilde{\nu}$ = 2960 cm$^{-1}$ (CH), 1345 (SO), 1175 (SO). – $^1$H NMR ($CDCl_3$): δ = 1.00 (s, 9H, C–$CH_3$), 1.43 (t, *J* = 7.4 Hz, 3H, $CH_2$–$CH_3$), 3.14 (q, *J* = 7.4 Hz, 2H, $CH_2$–$CH_3$), 3.87 (s, 2H, $CH_2$–C).

$C_7H_{16}O_3S$ (180.3) Calcd. C 46.69 H 8.95
Found[5b] C 46.57 H 9.12

**1c**: 74% after kugelrohr distillation at 49°C/0.25 Torr. – IR (film): $\tilde{\nu}$ = 2960 cm$^{-1}$ (CH), 1350 (SO), 1170 (SO). – $^1$H NMR ($CDCl_3$): δ = 0.99 (d, *J* = 6.7 Hz, 6H, CH–$CH_3$), 2.05 (sept, *J* = 6.7 Hz, 1H, $CH$–$CH_3$), 3.01 (s, 3H, $CH_3$), 3.98 (d, *J* = 6.6 Hz, 2H, $CH_2$–CH).

$C_5H_{12}O_3S$ (152.2) Calcd. C 39.46 H 7.95
Found C 39.22 H 7.78

**1d**: 82% after kugelrohr distillation at 81°C/0.25 Torr. – IR (film): $\tilde{\nu}$ = 2960 cm$^{-1}$ (CH), 1345 (SO), 1160 (SO). – $^1$H NMR ($CDCl_3$): δ = 0.99 (d, *J* = 6.7 Hz, 6H, CH–$CH_3$), 1.43 (t, *J* = 7.4 Hz, 3H, $CH_2$–$CH_3$), 2.04 (sept, *J* = 6.7 Hz, 1H, $CH$–$CH_3$), 3.14 (q, *J* = 7.4 Hz, 2H, $CH_3$–$CH_2$), 3.99 (d, *J* = 6.5 Hz, 2H, $CH_2$–CH).

$C_6H_{14}O_3S$ (166.2) Calcd. C 43.35 H 8.49
Found C 43.21 H 8.32

**1e**: 85% after kugelrohr distillation at 85°C/0.2 Torr. – IR (film): $\tilde{\nu}$ = 2985 cm$^{-1}$ (CH), 1345 (SO), 1170 (SO). – $^1$H NMR ($CDCl_3$): δ = 1.41 (t, *J* = 7.4 Hz, 3H, $CH_3$–$CH_2$), 1.42 (d, *J* = 6.2 Hz, 6H, CH–$CH_3$), 3.10 (q, *J* = 7.4 Hz, 2H, $CH_3$–$CH_2$), 4.94 (sept, *J* = 6.2 Hz, 1H, $CH$–$CH_3$).

$C_5H_{12}O_3S$ (152.2) Calcd. C 39.46 H 7.95
Found C 39.23 H 7.81

*Isobutyl Vinylsulfonate:* With exclusion of moisture, a solution of 15.6 g (95.8 mmol) of 2-chloroethanesulfonyl chloride and 6.52 g (88.0 mmol) of 2-methylpropanol in 30 ml of absol. dichloromethane was placed into a three-necked, round-bottomed 100-ml flask, equipped with an addition funnel, thermometer, and a magnetic stirring bar. The flask was cooled with ice and 15.2 g (192 mmol) of pyridine were added with rapid stirring at such a rate that the temperature of the reaction mixture did not exceed 10°C. After completion of the addition, the precipitate was removed by filtration and washed with dichloromethane. The filtrate was washed with 2 M hydrochloric acid (3 × 50 ml), dried over anhydrous magnesium sulfate, and evaporated. The residual yellow oil was purified by kugelrohr distillation at 56°C, 0.1 Torr, affording 8.17 g (57%) of a colorless oil.

**CAUTION:** Alkyl vinylsulfonates are known to be severe skin irritants.

IR (film): $\tilde{\nu}$ = 2970 cm$^{-1}$ (CH), 1615 (C=C), 1470 (CH), 1340 (SO), 1170 (SO). – $^1$H NMR ($CDCl_3$): δ = 0.94 (d, *J* = 6.7 Hz, 6H, CH–$CH_3$), 2.00 (sept, *J* = 6.7 Hz, 1H, $CH$–$CH_3$), 3.86 (d, *J* = 6.3 Hz, 2H, $CH_2$–CH), 6.11 (d, $J_{2\text{-H}trans,1\text{-H}}$ = 9.6 Hz, 1H, 2-$H_{trans}$), 6.40 (d, $J_{2\text{-H}cis,1\text{-H}}$ = 16.6 Hz, 1H, 2-$H_{cis}$), 6.52 (dd, $J_{1\text{-H},2\text{-H}cis}$ = 16.6 Hz, $J_{1\text{-H},2\text{-H}trans}$ = 9.7 Hz, 1H, 1-H).

$C_6H_{12}O_3S$ (164.2) Calcd. C 43.88 H 7.37
Found C 43.71 H 7.26

*Isobutyl 2-Methylthioethanesulfonate* (**5**): A 10-ml round-bottomed flask was flushed with nitrogen, cooled to −30°C, and 320 mg (6.65 mmol) of methanethiol was condensed in. A solution of 1.08 g (6.58 mmol) of isobutyl vinylsulfonate in 2 ml of chloroform was added, followed by ca. 50 mg of triethylamine. The flask was stoppered, and the reaction mixture kept at ca. 20°C for 15 h. The solvent was then removed in vacuo and the residual colorless liquid was submitted to kugelrohr distillation at 150°C, 0.05 Torr, affording 1.39 g (100%) of **5** as a colorless oil. – IR (film): $\tilde{\nu}$ = 2965 cm$^{-1}$ (CH), 1465 (CH), 1350 (SO), 1160 (SO). – $^1$H NMR ($CDCl_3$): δ = 0.99 (d, *J* = 6.9 Hz, 6H, CH–$CH_3$), 2.04 (sept, *J* = 6.8 Hz, 1H, $CH$–$CH_3$), 2.16 (s, 3H, $CH_3S$), 2.88–2.93 (m, 2H, 2-H), 3.34–3.39 (m, 2H, 1-H), 4.01 (d, *J* = 6.5 Hz, 2H, $CH_2$–CH).

$C_7H_{16}O_3S_2$ (212.3) Calcd. C 39.60 H 7.59
Found C 39.49 H 7.50

*Alkyl 1-Formylalkanesulfonates* **2a–e**: A flame-dried three-necked 50-ml flask, equipped with a septum and a magnetic stirring bar, was charged under nitrogen with a solution of 5.55 mmol of alkyl alkanesulfonate **1a–e** in 10 ml of absol. THF. The flask was cooled to −90°C, and 3.85 ml of a 1.6 M solution of *n*-butyllithium in hexane (6.16 mmol) were injected with stirring. After 15 min at −90°C, 830 mg (11.2 mmol) of dry ethyl formate was added. The reaction mixture was allowed to warm up to −30°C within 60 min. The cooling bath was removed and the flask was warmed to ca. 20°C within 30 min. In the cases of the alkyl 1-formylalkanesulfonates **2a,c**, the solvent was pumped off, and the residual solid lithium enolates (90% yield in both cases) were used without further purification for the derivatization to the 2,4-dinitrophenylhydrazones or for the diazo transfer reaction (vide infra). In the cases of the alkyl 1-formylalkanesulfonates **2b,d** or **e**, 50 ml of 2 M hydrochloric acid was added, and the mixture was extracted with chloroform (3 × 50 ml). The combined organic phases were dried over anhydrous magnesium sulfate and evaporated. The residual yellow oils were subjected to kugelrohr distillation, affording the alkyl 1-formylalkanesulfonates **2b,d,e** as colorless oils.

**2b**: 82% after kugelrohr distillation at 120°C/0.2 Torr. – IR (film): $\tilde{\nu}$ = 2960 cm$^{-1}$ (CH), 1735 (CO), 1475 (CH), 1350 (SO), 1170

(SO). – $^1$H NMR ($CDCl_3$): δ = 0.98 (s, 9H, C–$CH_3$), 1.60 (d, $J$ = 6.9 Hz, 3H, $CH_3$), 3.95 (s, 2H, $CH_2$–C), 4.04 (dq, $J_{CH,CH_3}$ = 6.9 Hz, $J_{CH,CHO}$ = 1.3 Hz, 1H, CH), 9.81 (d, $J$ = 1.3 Hz, 1H, CHO).

$C_8H_{16}O_4S$ (208.3) Calcd. C 46.14 H 7.74
Found C 46.06 H 7.59

**2d**: 77% after kugelrohr distillation at 145°C/0.1 Torr. – IR (film): $\tilde{\nu}$ = 2970 $cm^{-1}$ (CH), 1735 (CO), 1470 (CH), 1350 (SO), 1170 (SO). – $^1$H NMR ($CDCl_3$): δ = 0.98 (d, $J$ = 6.8 Hz, 6H, CH–$CH_3$), 1.59 (d, $J$ = 6.9 Hz, 3H, $CH_3$–CH), 2.05 (sept, $J$ = 6.4 Hz, 1H, CH–$CH_3$), 4.03 (dq, $J_{CH,CH_3}$ = 7.1 Hz, $J_{CH,CHO}$ = 1.6 Hz, 1H, CH–CHO), 4.08 (d, $J$ = 6.5 Hz, 2H, $CH_2$–CH), 9.79 (d, $J$ = 1.5 Hz, 1H, CHO).

$C_7H_{14}O_4S$ (194.3) Calcd. C 43.28 H 7.26
Found C 43.15 H 7.19

**2e**: 80% after kugelrohr distillation at 120°C/0.01 Torr. – IR (film): $\tilde{\nu}$ = 2990 $cm^{-1}$ (CH), 1735 (CO), 1455 (CH), 1340 (SO), 1175 (SO). – $^1$H NMR ($CDCl_3$): δ = 1.44 (d, $J$ = 6.2 Hz, 6H, CH–$CH_3$) 1.57 (d, $J$ = 7.0 Hz, 3H, $CH_3$–CH), 3.98 (dq, $J_{CH,CH_3}$ = 7.0 Hz, $J_{CH,CHO}$ = 1.3 Hz, 1H, $CH_3$–CH), 5.05 (sept, $J$ = 6.2 Hz, 1H, CH–$CH_3$), 9.78 (d, $J$ = 1.2 Hz, 1H, CHO).

$C_6H_{12}O_4S$ (180.2) Calcd. C 39.99 H 6.71
Found C 39.75 H 6.77

*2,4-Dinitrophenylhydrazones (2,4-DNPHs) of Neopentyl-* (**2a**) *and Isobutyl Formylmethanesulfonate* (**2c**): Samples (0.555 mmol) of the crude lithium enolates of the alkyl 1-formylalkanesulfonates **2a,c** were prepared as described above and dissolved in 10 ml of methanol. A solution of 198 mg (1.00 mmol) of 2,4-dinitrophenylhydrazine in 5 ml of methanol was added, followed by 2 ml of concd. sulfuric acid. The yellow precipitation was removed by filtration and recrystallized from methanol.

*2,4-DNPH of* **2a**: m.p. 121.5°C. – IR (KBr): $\tilde{\nu}$ = 3285 $cm^{-1}$ (NH), 2975 (CH), 1615 (C=N), 1325 (SO), 1170 (SO). – $^1$H NMR ($CDCl_3$): δ = 1.00 (s, 9H, C–$CH_3$), 3.98 (s, 2H, $CH_2$–C), 4.23 (d, $J$ = 5.9 Hz, 2H, $CH_2$–CH=), 7.56 (t, $J$ = 5.9 Hz, 1H, $CH_2$–CH=), 7.93–9.13 (m, 3H, aryl-H), 11.31 (s, 1H, NH).

$C_{13}H_{18}N_4O_7S$ (374.4) Calcd. C 41.71 H 4.85 N 14.96
Found C 41.61 H 4.71 N 14.88

*2,4-DNPH of* **2c**: m.p. 108.5°C. – IR (KBr): $\tilde{\nu}$ = 3300 $cm^{-1}$ (NH), 2980 (CH), 1615 (C=N), 1335 (SO), 1170 (SO). – $^1$H NMR ($CDCl_3$): δ = 0.99 (d, $J$ = 6.7 Hz, 6H, CH–$CH_3$), 2.07 (sept, $J$ = 6.7 Hz, 1H, CH–$CH_3$), 4.10 (d, $J$ = 6.6 Hz, 2H, $CH_2$–CH), 4.21 (d, $J$ = 5.9 Hz, 2H, $CH_2$–CH=), 7.52 (t, $J$ = 5.9 Hz, 1H, $CH_2$–CH=), 7.93–9.14 (m, 3H, aryl-H), 11.30 (s, 1H, NH).

$C_{12}H_{16}N_4O_7S$ (360.3) Calcd. C 40.00 H 4.47 N 15.55
Found C 40.07 H 4.56 N 15.56

*Attempted Formylation of Isobutyl 2-Methylthioethanesulfonate* (**5**): Application of the procedure described above to isobutyl 2-methylthioethanesulfonate (**5**) resulted in mixtures of unchanged sulfonate **5** and isobutyl methyl sulfide[12] ($^1$H NMR), accounting for ca. 80% (mol-%) of the starting material.

*Neopentyl 1-Methoxy-1-propene-2-sulfonate* (**4**): A flame-dried 25-ml round bottomed flask, equipped with an addition funnel and a magnetic stirring bar was charged under nitrogen with a solution of 1.08 g (9.60 mmol) of potassium *tert*-butoxide in 5 ml of absol. THF. A solution of 2.00 g (9.61 mmol) of neopentyl 1-formylethanesulfonate (**2b**) in 5 ml of absol. THF was added dropwise with stirring at ca. 20°C. After completion of the addition, stirring at ca. 20°C was continued for another 10 min. The solvent was removed in vacuo, the remaining colorless solid was suspended in 10 ml of absol. acetonitrile, and 1.21 g (9.60 mmol) of dimethyl sulfate was added. The mixture was stirred at ca. 20°C for 15 h, filtered, and evaporated. The oily residue was purified by kugelrohr distillation at 75°C, 0.02 Torr, affording 1.60 g (75%) of a colorless oil which crystallized upon cooling to 4°C (m.p. 39°C). – IR (KBr): $\tilde{\nu}$ = 2970 $cm^{-1}$ (CH), 1660 (C=C), 1460 (CH), 1340 (SO), 1190 (SO). – $^1$H NMR ($CDCl_3$): δ = 0.98 (s, 9H, C–$CH_3$), 1.86 (d, $J$ = 1.2 Hz, 3H, 3-H), 3.63 (s, 2H, $CH_2$–C), 3.88 (s, 3H, $OCH_3$), 7.15 (q, $J$ = 1.2 Hz, 1H, 1-H).

$C_9H_{18}O_4S$ (222.3) Calcd. C 48.63 H 8.16
Found C 48.51 H 8.13

*Alkyl 1-Diazoalkanesulfonates* **3a–e**. – *Method A:* A 50-ml round-bottomed flask was flushed with nitrogen and charged with a solution of 4.80 mmol of alkyl 1-formylalkanesulfonate **2b,d** or **e** in 25 ml of dichloromethane; 25 ml of 2 M aqueous ammonia was added, followed by 5.45 g (27.0 mmol) of 4-carboxybenzenesulfonyl azide[7]. The reaction mixture was rapidly stirred with exclusion of light at ca. 20°C for 20 h. The organic layer was separated, and the aqueous phase was extracted with chloroform (3 × 20 ml). The combined organic phases were dried with anhydrous magnesium sulfate and evaporated. The remaining yellow oil was chromatographed on silica gel (adsorbent/substrate, 100:1, eluting with hexane/ether, 2:1), affording the pure alkyl 1-diazoalkanesulfonates **3b,d** or **e** as clear yellow oils. In the cases of the alkyl 1-formylalkanesulfonates **2a,c**, the crude solid lithium enolates (4.80 mmol) were added to the two-phase system described above. The reaction mixture was worked up as described for **3b,d,e**.

*Method B:* The alkyl alkanesulfonates **1a–e** were formylated as described above. After warming up to ca. 20°C, 1.09 g (5.55 mmol) of tosyl azide was added, and stirring was continued for 20 h. The solvent was pumped off, and the semi-solid residue was stirred with 20 ml of ether under exclusion of moisture. The white solid was filtered off and briefly washed with ether. The filtrate was evaporated, and the residual yellow oil was chromatographed on silica gel (absorbent/substrate, 100:1, eluting with hexane/ether, 2:1), affording the pure alkyl 1-diazoalkanesulfonates **3a–e** as clear yellow oils.

In all cases, analytical samples were additionally purified by semi-preparative HPLC on Nucleosil 50–10, eluting with hexane/ethyl acetate, 10:1.

**3a**: 28% (method A), method B did not afford significant quantities of the diazo compound. – IR (film): $\tilde{\nu}$ = 2960 $cm^{-1}$ (CH), 2110 ($N_2$), 1475 (CH), 1365 (SO), 1160 (SO). – UV (hexane): $\lambda_{max}$ (lg ε) = 225 nm (4.023), 396 (1.000). – $^1$H NMR ($CDCl_3$): δ = 1.00 (s, 9H, C–$CH_3$), 3.84 (s, 2H, $CH_2$–C), 5.24 (s, 1H, CH=$N_2$).

$C_6H_{12}N_2O_3S$ (192.2) Calcd. C 37.49 H 6.29 N 14.57
Found C 37.62 H 6.19 N 14.31

**3b**: 65% (method A), 33% (method B). – IR (film): $\tilde{\nu}$ = 2970 $cm^{-1}$ (CH), 2095 ($N_2$), 1470 (CH), 1365 (SO), 1165 (SO). – UV (hexane): $\lambda_{max}$ (lg ε) = 230 nm (4.001), 424 (1.041). – $^1$H NMR ($CDCl_3$): δ = 1.00 (s, 9H, C–$CH_3$), 2.10 (s, 3H, $CH_3$), 3.79 (s, 2H, $CH_2$–C).

$C_7H_{14}N_2O_3S$ (206.3) Calcd. C 40.76 H 6.84 N 13.58
Found C 41.02 H 6.86 N 13.62

**3c**: 28% (method A), method B did not afford significant quantities of the diazo compound. – IR (film): $\tilde{\nu}$ = 2980 $cm^{-1}$ (CH), 2110 ($N_2$), 1480 (CH), 1360 (SO), 1190 (SO). – UV (hexane): $\lambda_{max}$ (lg ε) = 225 nm (4.014), 392 (1.079). – $^1$H NMR ($CDCl_3$): δ = 1.00 (d, $J$ = 6.7 Hz, 6H, $CH_3$), 2.05 (sept, $J$ = 6.7 Hz, 1H, CH–$CH_3$), 3.96 (d, $J$ = 6.5 Hz, 2H, $CH_2$–CH), 5.30 (s, 1H, CH=$N_2$).

$C_5H_{10}N_2O_3S$ (178.2) Calcd. C 33.70 H 5.65 N 15.72
Found C 33.91 H 5.59 N 15.57

**3d**: 35% (method A), 45% (method B). – IR (film): $\tilde{\nu}$ = 2970 $cm^{-1}$ (CH), 2090 ($N_2$), 1470 (CH), 1360 (SO), 1185 (SO). – UV (hexane): $\lambda_{max}$ (lg ε) = 230 nm (3.986), 425 (1.041). – $^1H$ NMR ($CDCl_3$): δ = 1.00 (d, $J$ = 6.7 Hz, 6H, $CH-CH_3$), 2.05 (sept, $J$ = 6.7 Hz, 1H, $CH-CH_3$), 2.10 (s, 3H, $CH_3$), 3.91 (d, $J$ = 6.5 Hz, 2H, $CH_2-CH$).

$C_6H_{12}N_2O_3S$ (192.2) Calcd. C 37.49 H 6.29 N 14.57
Found C 37.70 H 6.24 N 14.32

**3e** (decomposed upon attempted HPLC purification): 13% (method A), 30% (method B). – IR (film): $\tilde{\nu}$ = 2985 $cm^{-1}$ (CH), 2090 ($N_2$), 1475 (CH), 1355 (SO), 1175 (SO). – UV (hexane): $\lambda_{max}$ (lg ε) = 230 nm (ca. 3.94), 424 (ca. 1.11). – $^1H$ NMR ($CDCl_3$): δ = 1.42 (d, $J$ = 6.3 Hz, 6H, $CH-CH_3$), 2.09 (s, 3H, $CH_3$), 4.80 (sept, $J$ = 6.3 Hz, 1H, $CH-CH_3$).

*Attempted Diazotation of Trimethylsilyl 1-Formylpropanesulfonate* (**6**): Trimethylsilyl 1-formylpropanesulfonate[8] (**6**) was treated with equimolar amounts of tosyl azide and base (potassium *tert*-butoxide, triethylamine, or sodium hydride) in absol. THF or was subjected to the diazotation procedure described above (method A). IR monitoring of the reactions did not indicate the formation of a diazo compound.

*Reaction of the Alkyl 1-Diazoalkanesulfonates* **3c–e** *with Sodium Thiophenolate or Sodium Methoxide:* A solution of ca. 0.3 mmol of the alkyl 1-diazoalkanesulfonate **3c,d** or **e** in 0.5 ml $CD_3OD$ was placed into an NMR tube. Equimolar amounts of sodium thiophenolate or sodium [$D_3$]methoxide were dissolved in 0.3 ml of $CD_3OD$. Upon mixing, the yellow solutions turned colorless with concomitant evolution of gas within a few minutes. $^1H$-NMR monitoring revealed the formation of isobutyl and isopropyl methyl or thiophenyl ether, respectively. The characteristic signals of the 1-diazoalkanesulfonate moieties had completely vanished, complex product mixtures were formed.

*Thermolysis of Alkyl 1-Diazoalkanesulfonates* **3a,d**: Ca. 0.2 mmol of the alkyl 1-diazoalkanesulfonate was dissolved in 1 ml of degassed [$D_8$]toluene or [$D_2$]-1,1,2,2-tetrachloroethane and placed into an NMR tube. $^1H$ NMR spectra were taken at 80°C, and the decay of the starting material was monitored by multiple integrations, using the solvent signals as internal standard. First-order analysis, of the concentration vs. time profiles gave the rate constants and half-lives listed below (accuracy ca. ±10%).

| Compound | Solvent | $T$ [°C] | $k$ [$s^{-1}$] | $t_{1/2}$ [min] |
|---|---|---|---|---|
| **3d** | [$D_8$]toluene | 80 | $7.2 \times 10^{-4}$ | 16 |
| **3d** | [$D_2$]-1,1,2,2-tetrachloroethane | 80 | $8.4 \times 10^{-4}$ | 14 |
| **3a** | [$D_8$]toluene | 80 | $2.4 \times 10^{-4}$ | 48 |

When isobutyl 1-diazoethanesulfonate (**3d**) was thermolyzed in [$D_2$]-1,1,2,2-tetrachloroethane, isobutyl vinylsulfonate could be identified ($^1H$ NMR) as the major product (ca. 70%).

CAS Registry Numbers

**1a**: 16427-42-2 / **1b**: 25056-29-5 / **1c**: 16156-53-9 / **1d**: 120263-36-7 / **1e**: 14245-62-6 / **2a**: 120263-40-3 / **2a** (2,4-DNPH): 120263-38-9 / **2b**: 120263-41-4 / **2c**: 120263-42-5 / **2c** (2,4-DNPH): 120263-39-0 / **2d**: 120263-43-6 / **2e**: 120263-44-7 / **3a**: 120263-45-8 / **3b**: 120263-46-9 / **3c**: 120263-47-0 / **3d**: 120263-48-1 / **3e**: 120263-49-2 / **4**: 120263-50-5 / **5**: 120263-37-8 / **6**: 72458-50-5 / isobutyl vinylsulfonate: 13654-95-0 / 2-chloroethanesulfonyl chloride: 1622-32-8 / 4-carboxybenzenesulfonyl azide: 17202-49-2 / trimethylsilyl chlorosulfonate: 4353-77-9 / (*E*)-trimethylsilyl 1-butenyl ether: 19980-23-5 / (*Z*)-trimethylsilyl 1-butenyl ether: 19980-22-4

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[8] [8a] K. Hofmann, G. Simchen, *Synthesis* **1979**, 699. – [8b] K. Hofmann, G. Simchen, *Liebigs Ann. Chem.* **1984**, 39. – [8c] *Note:* Trimethylsilyl 1-formylpropanesulfonate (**6**) was obtained in analytically pure form in 80% yield by addition of 1 eq. of trimethylsilyl chlorosulfonate[13] to a solution of *E*/*Z*-trimethylsilyl 1-butenyl ether[14] in 1,2-dichloroethane at ca. 20°C and subsequent rapid kugelrohr distillation at 100°C/0.01 Torr, ca. 50 mg of potassium hydrogen carbonate being added prior to the distillation. In our hands, this preparation proved superior to the one reported[8a,b].
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