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PAPER

Concerning the deprotonation of the trimethylsulfonium ion by the dimethylsulfinyl anion

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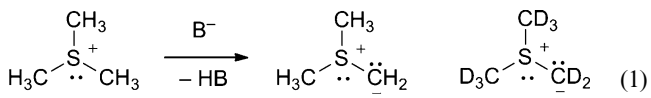
As shown by deuterium labelling experiments, the deprotonation of the trimethylsulfonium ion (**1**) by the dimsyl anion (**8**) is accompanied by extensive hydrogen exchange. This cannot be explained by an acid–base equilibrium between the trimethylsulfonium ion (**1**) and the dimsyl anion (**8**) on one side and dimethylsulfonium methylide (**2**) and DMSO on the other side, because for thermodynamic reasons this process is irreversible due to the limited life-time of **2**. Therefore, the isotopic exchange that accompanies the deprotonation is an indicator of a more complex deprotonation process. It is suggested that in a kinetically controlled reaction, a proton of **1** is transferred to the O-atom of **8** rather than to the carbanionic centre. This means that instead of DMSO, its tautomer, hydroxy-methylsulfonium methylide (**10**), is obtained in the deprotonation process. Similarly, in the acid–base interaction between DMSO and its conjugate base **8**, the formation of the DMSO tautomer **10** is kinetically favoured. The intermediate **10** produced in this way transfers a DMSO-derived proton to **1** when it intervenes in the back reaction **10** + **2** → **8** + **1**. An alternative mechanism based on methyl group exchange between **1** and **8** could be excluded by a ^{13}C-labelling experiment. The hydrogen exchange according to the suggested scenario is taking place in competition with the reaction of dimethylsulfonium methylide (**2**) with electrophilic substrates. This explains the different degrees of isotopic exchange when compounds of different electrophilicities are used to scavenge **2** from the deprotonation–hydrogen distribution equilibria.

Introduction

In aprotic, dipolar solvents the trimethylsulfonium ion (**1**) is easily deprotonated to yield dimethylsulfonium methylide (**2**), which is a versatile reagent in organic synthesis.[1,2]



(1)

1 **2** **[D$_8$]2**

In a more recent application, Kitano and Ohashi[3] reported on the nucleophilic *ortho*-methylation of *ortho*-substituted nitrobenzenes by action of **2**. Based on deuterium labelling experiments,[4] we could show that the reaction proceeds essentially according to the concept of vicarious nucleophilic substitution.[5] The reaction sequence is outlined for 2-nitroanisole (**3**) as substrate in Scheme 1.

The formation of the Meisenheimer complex (σ^H-adduct) **4** is followed by the E1-like β-elimination *via* **5** to give the elimination product **6** with the sulfur ylide **2** acting as base. The concomitantly formed trimethylsulfonium ion (**1**) protonates **6** to give the methylation product **7**.

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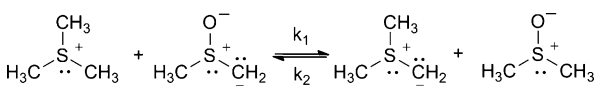
Intriguingly, we observed an almost complete deuterium depletion of the transferred methylene group of octadeuteriodimethylsulfonium methylide ([D$_8$]**2**) when the perdeuteriated sulfur ylide was prepared from [D$_9$]**1** with the dimethysulfinyl (dimsyl) carbanion (**8**) as base in DMSO.[4] By way of contrast, the dideuteriated methylene group was introduced intact into **7** when [D$_9$]**1** was deprotonated by sodium hydride in DMF.

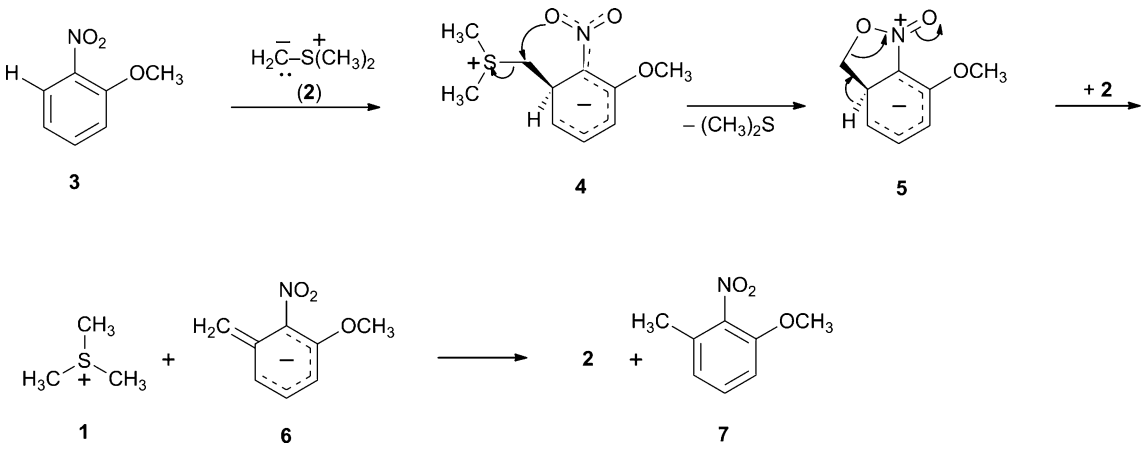
The loss of deuterium in the attempted generation of [D$_8$]**2** from [D$_9$]**1** and the dimsyl anion (**8**) cannot be explained with the establishment of the acid–base equilibrium (eqn (2)). With the pK_a values for DMSO (35)[6] and the trimethylsulfonium ion (24.5),[7,8] an equilibrium constant of $K = 10^{10.5}$ follows for this acid–base reaction. Therefore, the rate constant for the back reaction $k_2 = K^{-1}k_1 \approx 10^{-10.5}k_1$ is too small to account for a rapid hydrogen exchange within the mean life-time of a few minutes reported for the dimethylsulfonium methylide (**2**).[2]



(2)

1 **8** **2**

The hydrogen exchange accompanying the formation of **2** clearly indicates that the deprotonation of **1** with the dimsyl anion (**8**) is more complex than expressed by eqn (2). Because the deprotonation of sulfonium ions by the dimsyl anion in



Scheme 1 The nucleophilic *ortho*-methylation of 2-nitroanisole (**3**) by dimethylsulfonium methylide (**2**).[4]

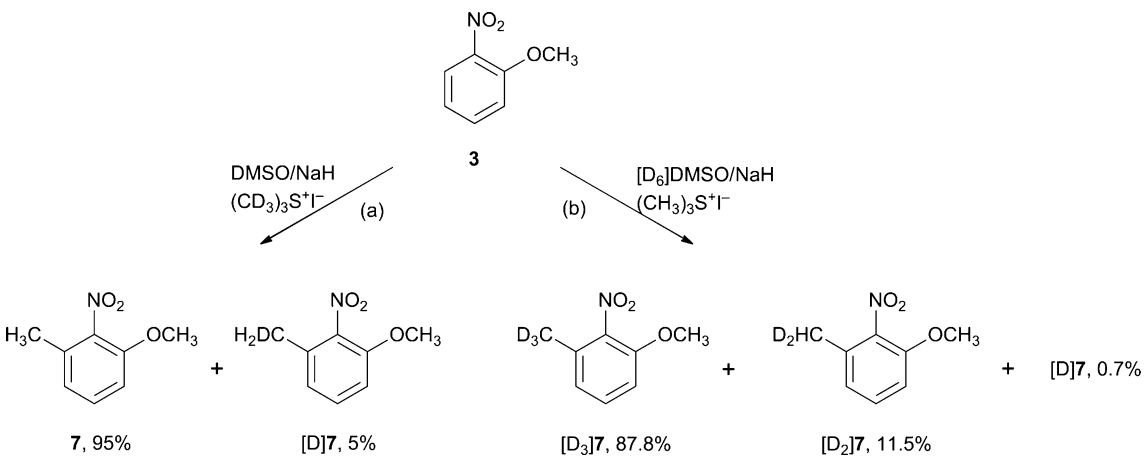
DMSO is the classical protocol for the generation of sulfur ylides,[2] it is of some interest to obtain deeper insights into this process. In the present article, the results of ^{13}C- and D-labelling experiments are presented and a mechanism is suggested to account for the unexpected hydrogen exchange that accompanies the deprotonation of the trimethylsulfonium ion (**1**) by the dimsyl anion (**8**).

Results and discussion

As explained in the introduction, only a small portion of the deuterium labelling in [D_9]**1** survived in the introduced methyl group of compound **7** when the transferring reagent **2** was prepared by deprotonation with the dimsyl anion **8** in DMSO. Mass spectrometric measurements reveal that only 5% [D_1]**7** is present. The ^1H NMR spectrum confirms that the 3-methyl group of 1-methoxy-3-methyl-2-nitrobenzene (**7**) is almost completely free of deuterium. The strong singlet for CH_3 at 2.29 ppm is accompanied by a partly overlapping triplet of very low intensity at ~2.27 ppm for CH_2D. In a complementary experiment, unlabelled **1** was deprotonated by [D_5]**8** in [D_6]DMSO and then reacted with **3**. The molecular ion peak region of the methylation product exhibits the following isotopic distribution: *m/z* 170 (100), 169 (13), 168 (0.75), which corresponds to 87.8% CD_3, 11.5% CD_2H and 0.7% CDH_2. In the ^1H NMR spectrum, a singlet signal for the 3-methyl group is absent and replaced by a complex multiplet of weak intensity composed of a quintet at δ = 2.255 ppm (CD_2H) and a triplet at 2.264 ppm (CH_2D). The above deuterium labelling experiments are summarized in Scheme 2.

The substitution of the hydrogen atoms in dimethylsulfonium methylide (**2**) by hydrogen atoms originating from DMSO was further demonstrated by addition of an equimolar amount of trimethylsulfonium iodide (**1**·I^-) to a solution of [D_5]**8** in [D_6]DMSO. After standing for 1 h, to allow the generated dimethylsulfonium methylide to decompose, ^1H NMR spectroscopy indicated an increase of the signal for the residual protons in [D_6]DMSO corresponding, within experimental error, to 9 ^1H-atoms per added trimethylsulfonium iodide (**1**·I^-) (referenced against internal dioxane) (Fig. 1). The hydrogen transfer from **1** to DMSO is coupled to the presence of dimsyl anion, because a solution of **1**·I^- in pure [D_6]DMSO is stable over several weeks.

The experimental results leave it beyond doubt that the trimethylsulfonium-derived hydrogen atoms of the sulfur ylide **2** become superseded by hydrogen atoms descending from DMSO, before the reagent **2** can introduce the *ortho*-methyl group into 2-nitroanisole according to Scheme 1.



Scheme 2 Methylation of 2-nitroanisole (**3**) with dimethylsulfonium methylide prepared from $(CD_3)_3S^+I^-$ in DMSO (a) and $(CH_3)_3S^+I^-$ in [D_6]DMSO (b).

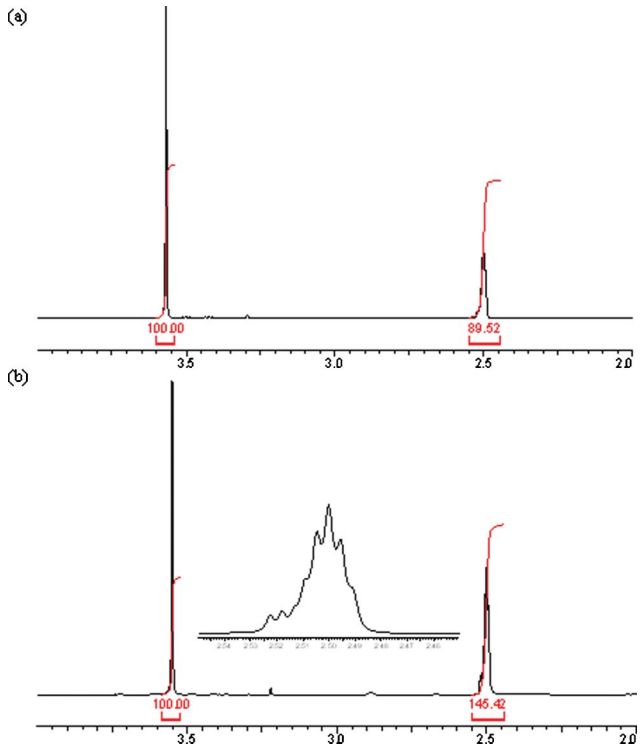
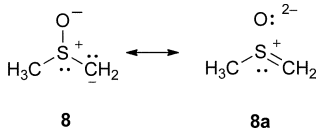


Fig. 1 (a) ^{1}H NMR spectrum of a mixture of [D$_6$]DMSO (550 µL, 7.775 mmol, $\delta = 2.50$ ppm) and dioxane (5 µL, 0.059 mmol, $\delta = 3.55$ ppm) showing the residual protons. From the intensity ratio it follows that the [D$_6$]DMSO contains 0.92 atom% ^{1}H atoms. The deuteriation degree of this [D$_6$]DMSO used was given as 99.5% by the supplier. (b) ^{1}H NMR spectrum obtained after addition of NaH (12.5 mg, 0.52 mmol) to a mixture of [D$_6$]DMSO (1.500 mL, 21.205 mmol) and dioxane (43 µL, 0.505 mmol) followed after 15 min by trimethylsulfonium iodide (**1**·I$^-$) (107 mg, 0.52 mmol corresponding to 4.68 mmol ^{1}H-atoms). All manipulations were performed under a stream of nitrogen and the spectrum was measured after 1 h to allow for decomposition of the deprotonation product **2** into ethene and dimethyl sulfide. From the intensity ratio, it follows that the signal at 2.50 ppm represents, after correction for the residual protons in [D$_6$]DMSO, 4.70 mmol ^{1}H-atoms.

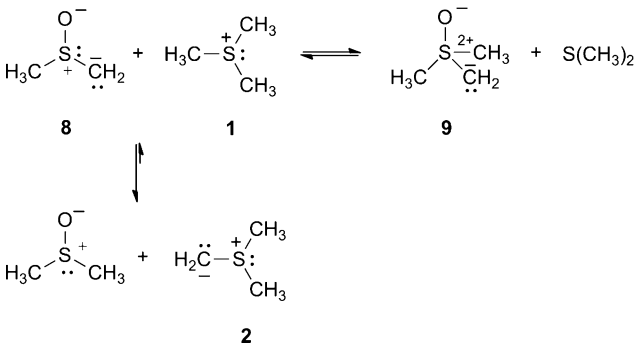
Formally, the isotopic exchange in the trimethyl sulfonium/dimsyl/DMSO system can occur by two modes. (1) The appearance of DMSO-derived hydrogen atoms in the sulfur ylide (**2**) and *vice versa* could be the result of a methyl group exchange. (2) The carbon–sulfur framework of the interacting species remains intact, but the hydrogen atoms migrate between the two species.

In the context of possibility (1), a study by Buncel and coworkers[12] on the denticity of the dimsyl anion toward 1,3,5-trinitrobenzene is of interest. Three dimsyl σ^{H}-adducts could be identified by NMR spectroscopy, which demonstrates the unique tridentate character of the dimsyl anion as an O-, S-, and C-nucleophile. The O- and S-adducts are the kinetically favoured complexes, whereas the C-adduct represents the thermodynamically preferred product. It has been concluded that the structure **8** fully represents the tridentate nature of the dimsyl anion. In terms of natural resonance theory, its weight amounts to 77.3% and some delocalization by admixture of double bond–no bond structures, amongst them **8a** contributes 8%, stabilizing the anion.[13]



8 **8a** (3)

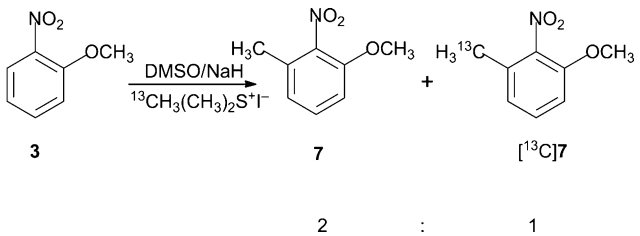
The potential nucleophilicity of the central S-atom in the dimsyl anion (**8**) could be the base for an exchange of methyl groups between the sulfonium ion **1** and the anion **8**. Initiated by an S_N2 attack on **1**, an equilibrium with the dimethyl-oxosulfonium methylide (**9**) with two equivalent methyl substituents could be established (Scheme 3). In the back reaction, a DMSO-derived methyl group can be transferred with the same probability as the return of the original methyl group. Because the dimsyl anion equilibrates with its parent DMSO, which is present in excess, this scenario could result in an almost complete exchange of the methyl groups in **1** for methyl groups originating from DMSO. Provided this equilibrium operates fast enough parallel to the practically irreversible formation of dimethylsulfonium methylide (**2**), the steps summarized in Scheme 3 could give a possible rationalization of the observed isotopic scrambling results.



8 **1** **9** **2**

Scheme 3 Methyl group exchange *vs.* deprotonation as competing parallel reactions.

To put this hypothesis to the test, [^{13}C]methyldimethylsulfonium iodide ([^{13}C]**1**·I$^-$) was prepared from dimethyl sulfide and [^{13}C]methyl iodide (99% ^{13}C) and applied to the methylation of **3**. In the ^{1}H NMR spectrum of the methylation product, the signal for the 3-methyl substituent is split into a singlet ($\delta = 2.28$ ppm) and a doublet ($^{1}J(^{13}C,H) = 129$ Hz) in the ratio 2 : 1. The NMR data and a ^{13}C-labelling degree of 32.6% derived from the mass spectrum indicate that one labelled and two unlabelled carbon atoms are utilized in the methylation of **3** (Scheme 4). Thus, the ^{13}C-labelling experiment excludes a methyl group exchange mechanism (Scheme 3) to rationalize the hydrogen exchange between dimsyl/DMSO on one side and



3 **7** [^{13}C]**7**

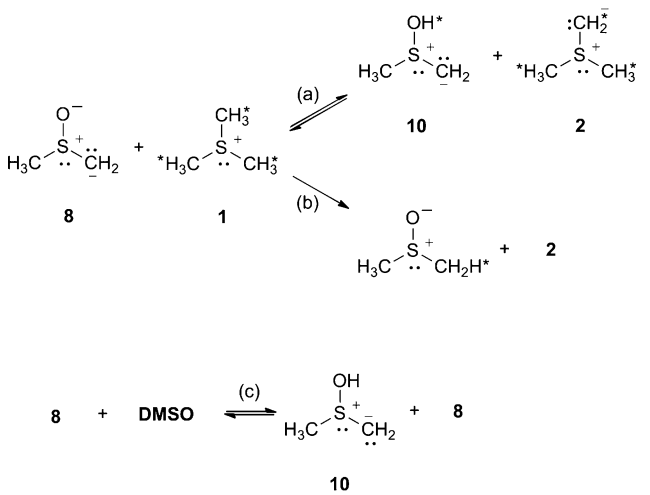
2 : 1

Scheme 4 Methylation of 2-nitroanisole with DMSO/NaH/$^{13}CH_3$-$(CH_3)_2S^+I^-$.

trimethylsulfonium/dimethylsulfonium methylide on the other side.

The remaining possibility (2) requires a hydrogen jumping process between the two interacting species coupled with a reversible deprotonation to guarantee the return to trimethylsulfonium ions with partly exchanged hydrogen atoms. When this is repeated many times the hydrogen atoms introduced by the sulfonium ion **1** and DMSO are finally statistically distributed over the deprotonation product dimethylsulfonium methylide (**2**) and the solvent DMSO.

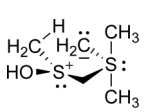
Reversibility of the deprotonation of the trimethyl sulfonium ion (**1**) should become possible when the negatively charged oxygen atom of the dimsyl anion (**8**) instead of the carbanionic center abstracts a proton from **1** (equilibrium (a) in Scheme 5).[14] In this case, in equation (2), dimethyl sulfoxide is replaced by its formal "enol" hydroxy-methylsulfonium methylide (**10**), which according to *ab initio* and DFT calculations is *ca.* 100 kJ mol^{-1} less stable than DMSO.[15] However, reversibility is not sufficient to explain the observed hydrogen exchange because in the back reaction the same proton would return to its origin. Therefore, the reversibility of the deprotonation has to be supplemented by a process allowing for hydrogen interchange.



8 + DMSO (c) 10 + 8

Scheme 5 Kinetic (a) *vs.* thermodynamic controlled (b) deprotonation of the trimethylsulfonium ion (**1**) and kinetically favoured *O*-protonation of **8** by its conjugated acid DMSO (c). The hydrogen atoms of **1** are marked as H* to indicate the difference of the hydroxy proton of **10** in equilibria (a) and (c).

In a first attempt to explain the hydrogen scrambling, we envisaged the possibility of hydrogen transfer in some sort of intermediate complex between DMSO- and trimethylsulfonium-derived species. The reversible formation of the sulfurane complex[16] **11** by nucleophilic attack of the carbanionic centre in **10** at the sulfur atom in **2** may illustrate this hypothesis. In the proper conformation, the sulfurane **11** would accomplish the structural conditions for hydrogen exchange between the two combined entities *via* a six-membered transition state.



11

However, provided that the kinetically favoured proton transfer to the O-atom of **8** is a general principle for the acid–base interaction of CH-acids and the ambident dimsyl anion (**8**), a rationalization of the H-exchange is possible which requires no additional assumption such as intermediate complex formation. Analogously to the kinetically preferred formation of **10** in the deprotonation of **1** by the dimsyl anion (**8**), the interaction between DMSO and its conjugate base **8** should also generate a stationary concentration of the DMSO tautomer **10** (equilibrium (c) in Scheme 5).

The DMSO tautomer **10** generated according to equilibrium (c) contains a hydroxy proton originating from DMSO, thus, when it intervenes in equilibrium (a), a DMSO-derived H-atom becomes incorporated into the trimethylsulfonium ion (**1**). Provided that the kinetically favoured proton transfers from **1** and DMSO, respectively, to the O-atom of **8** work fast enough against the thermodynamic sink (formation of **2** and DMSO, (b) in Scheme 5) the substitution of the hydrogen atoms in **2** by hydrogen atoms introduced with DMSO would find a feasible explanation.

At this point it may be necessary to address the possible involvement of water traces in the hydrogen exchange process.[17] The residual water in the solvents DMSO ([D$_6$]DMSO) and THF is $\ll$40 and $\ll$20 ppm, respectively. With regard to some additional water introduced by the glassware *etc.*, the H_2O concentration in the reaction mixtures should not exceed 50 ppm.

The dimsyl reagent used to deprotonate **1** is prepared by reaction of DMSO with sodium hydride. Adventitious water traces dragged in by solvents will be transformed into NaOH under these conditions. The amount of free water formed by the equilibrium (4) is $\ll$ 1% of the moisture introduced by the solvents. This follows from the equilibrium constant of (4) (~$10^{-3.7}$) and the large excess of **8** produced by the deprotonation of DMSO with NaH. The deuterium loss in the case of [D$_6$]DMSO caused by this equilibrium can be neglected because [D$_6$]DMSO is several orders of magnitude more abundant than the proton source, water.

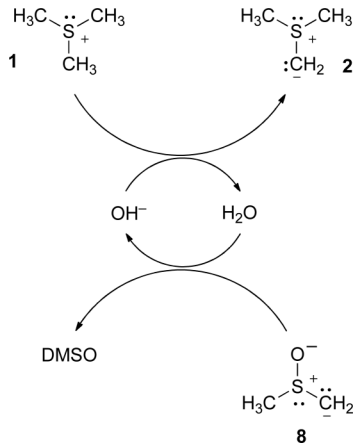
$$\text{DMSO} + \text{OH}^- \rightleftharpoons \mathbf{8} + \text{H}_2\text{O} \qquad (4)$$

After the addition of trimethylsulfonium iodide (**1**·I$^-$), the deprotonation of **1** by OH$^-$ (reaction (5)) contributes an insignificant amount to the formation of dimethylsulfonium methylide (**2**), when compared with the deprotonation of **1** by the dimsyl anion (**8**). However, reaction (5) becomes important with respect to the formation of water. The trimethylsulfonium ion (**1**) is >10 orders of magnitude more acidic than DMSO, therefore, this process overrides reaction (4) as water source.

$$\mathbf{1} + \text{OH}^- \rightleftharpoons \mathbf{2} + \text{H}_2\text{O} \qquad (5)$$

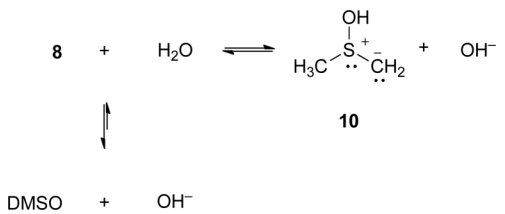
The water concentration now present in the system corresponds to the water content of solvents used, however, each H_2O molecule now contains a proton originating from the trimethylsulfonium ion (**1**). In combination with the protonation of **8** by water, this could give rise to a catalytic cycle for the transfer of one hydrogen atom from **1** into DMSO (Scheme 6), provided that this process is competitive with the deprotonation of **1** by **8**.

However, the almost complete exchange of the hydrogen atoms of **1** by hydrogen atoms of DMSO cannot be rationalized with such a catalytic cycle, because this scenario does not include a way back from **2** to **1**, which is a *condicio sine qua none* for extensive hydrogen scrambling.



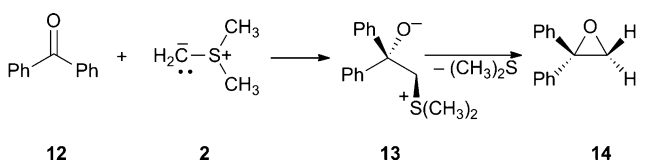
Scheme 6 Possible catalytic cycle for the transfer of a hydrogen atom from **1** to DMSO.

As discussed above, the ambident nature of the dimsyl anion (**8**) may afford the DMSO tautomer **10** as kinetic protonation product. For H_2O as Brønsted acid, this is illustrated in Scheme 7. If it is presumed that the *O*-protonation competes efficiently with the thermodynamically controlled formation of DMSO and that the DMSO tautomer **10** is consumed in the back reaction of equilibrium (a) of Scheme 5, the water traces present in the reaction mixture would initiate a sequence by which hydrogen atoms of the trimethylsulfonium ion (**1**) are transferred *via* H_2O and **10** back to **1**. Therefore, it is concluded that the involvement of water traces in the acid–base chemistry of the reaction mixture has no marked influence on the deuterium labelling results.



Scheme 7 *O*-Protonation *vs. C*-protonation of **8** by H_2O.

The mechanistic rationalizations given above describe the hydrogen exchange as a competitive process to the reaction of the sulfur ylide **2** with electrophilic substrates like **3**. This means that compounds of different electrophilicity should react with the sulfur ylide **2** to give products of varying extents of isotopic exchange. This was verified by the generation of dimethylsulfonium methylide (**2**) in [D_6]DMSO followed by addition of benzophenone (**12**) according to the Corey–Chaykowski reaction[2] (Scheme 8).



Scheme 8 Corey–Chaykowski reaction.

The deuterium incorporation into the methylene group of 2,2-diphenyloxirane (**14**) is relatively small. In the ^{1}H NMR spectrum two singlets at 3.30 ppm and 3.29 ppm in the ratio of ~1 : 0.09 are seen for CH_2 and CHD (the ^2J(H,D) coupling is too small to be resolved). This indicates the formation of ~15% monodeuteriated oxirane **14**. The mass spectrometric determination of the deuterium content is rendered difficult due to the presence of a strong $[M - H]^+$ peak in the EI spectrum of **14**, which could not be brought to disappearance by lowering the electron voltage. The partly deuteriated oxirane **14** was therefore reduced by $LiAlH_4$ into 1,1-diphenylethanol.[18] Mass spectrometric analysis of the reduction product indicates the presence of 16.0% [D_1] and 0.3% [D_2]. In the ^{1}H NMR spectrum of the reduction product, the methyl group is represented by a singlet at 1.98 ppm (CH_3) and a triplet (CH_2D), high field shifted by 0.017 ppm, in the ratio of ~3 : 0.5, which corresponds to ~20% monodeuteration. Because no base line separation could be achieved, this is in acceptable agreement with the mass spectrometric determination.

The comparison of the deuterium incorporation into the methyl group of **7** and the methylene group of **14** shows a marked difference in the progress of deuterium incorporation in the methylene transferring reagent dimethylsulfonium methylide (**2**) generated from **1** in [D_6]DMSO, when **2** is scavenged with **3** (formation of **7**) and **12** (formation of **14**), respectively. In the first case, more than 99% of the introduced methyl groups of **7** consist of CD_2X (X = D or H), whereas interception by benzophenone (**12**) results in 2,2-diphenyloxirane (**14**) with less than 20% CHD. This means that the isotopic exchange between **1** and [D_6]DMSO is more or less complete before dimethylsulfonium methylide (**2**) reacts with 2-nitroanisole (**3**) (Scheme 1). By way of contrast, the first step of the Corey–Chaykowski reaction (formation of **13**, Scheme 8) is fast enough to scavenge **2** at an early state of the H/D exchange.

Conclusions

Deprotonation of the trimethylsulfonium ion (**1**) to dimethylsulfonium methylide (**2**) by action of dimsyl anion (**8**) in DMSO is accompanied by hydrogen exchange. This follows from the paradoxical result that the nucleophilic *ortho*-methylation of 2-nitroanisole (**3**) yields essentially unlabelled **7**, when reagent **2** is generated from perdeuteriated [D_9]**1** with the dimsyl anion in DMSO, whereas the reagent **2** obtained from unlabelled **1** in [D_6]DMSO transfers more than 99% CD_2X (X = H, D) into the introduced methyl group of **7**. The acid–base reaction between the trimethylsulfonium ion (**1**) and dimsyl anion (**8**) on one side and dimethylsulfonium methylide (**2**) and DMSO on the other side cannot account for the isotopic interchange, because for thermodynamic reasons this acid–base reaction is practically irreversible in terms of the life-time of **2**.

To explain this apparent contradiction it is suggested that the potentially ambident conjugate base of DMSO abstracts a proton from **1** by its negatively charged oxygen rather than by its carbanionic center. This replaces DMSO in the acid–base reaction by its tautomer hydroxy-methylsulfonium methylide (**10**), which according to theory is ~100 kJ mol^{-1} less stable. Therefore, a reversible deprotonation–reprotonation equilibrium is established, which in combination with a hydrogen exchange process could be responsible for the observed labelling results. We suggest that the DMSO tautomer **10** is also formed by O-mediated proton transfer from DMSO to its conjugate base **8**. The tautomer **10** generated in this way transfers a DMSO-derived H-atom to the

trimethylsulfonium ion **1** when it participates in the reprotonation of dimethylsulfonium methylide (**2**). The hydrogen exchange operates in competition with the product-forming reaction of dimethylsulfonium methylide (**2**) with electrophilic substrates. Therefore, the extent of hydrogen exchange in the transferred methylene group depends on the electrophilicity of the substrates.

From the results presented in this article, it can be concluded that the hydrogen/deuterium atoms of DMSO/[D_6]DMSO can be exchangeable even in contact with much weaker Brønsted bases than the conjugate dimsyl anion **8**.

Experimental

^{1}H and ^{13}C NMR spectra were recorded with a Bruker Avance spectrometer. EI mass spectra were obtained with a TSQ-70 triple stage mass spectrometer. Commercial anhydrous DMSO and [D_6]DMSO was further dried by sonification over CaH_2 for several hours followed by vacuum distillation. The residual H_2O traces in [D_6]DMSO were determined by spiking with toluene or dioxane and the integration of the ^{1}H signals in the ^{1}H NMR spectrum. The H_2O concentrations obtained range from 20 to 40 ppm.[19] The glassware used in the experiments was thoroughly dried in a stream of nitrogen before use. [^{13}C]Methyl-dimethylsulfonium iodide ([^{13}C]**1**·I^-) was obtained from dimethyl sulfide and [^{13}C]methyl iodide (99 atom% ^{13}C) according to the procedure for the unlabelled sulfonium iodide.[2] ^{1}H NMR (400 MHz, [D_6]DMSO) δ = 2.88 ppm (d, 6H ($^3J(^{13}C,^1H)$ = 3.48 Hz and d, 3H, $^1J(^{13}C,^1H)$ = 144.66 Hz).

Reaction of [D_9]**1**·I^-/DMSO/NaH with 2-nitroanisole (3)

To a mixture of anhydrous DMSO (3.25 mL) and anhydrous THF (H_2O < 20 ppm) (1.25 mL)—to avoid freezing—sodium hydride (30 mg, 1.25 mmol) was added under a nitrogen atmosphere. After 15 min the mixture was cooled in an ice–water bath and perdeuteriated trimethylsulfonium iodide ([D_9]**1**·I^-, 255 mg, 1.25 mmol) was added in one portion under stirring. At a temperature < 10 °C, 2-nitroanisole (**3**, 100 mg, 0.65 mmol) in 1 mL DMSO was added dropwise. The reaction mixture was allowed to warm slowly to room temperature and stirring was continued for 16 h. After mixing with ice water the reaction mixture was extracted with petroleum ether (40–60 °C) (5 × 7.5 mL). The extracts were washed with brine (5 × 7.5 mL) and dried over sodium sulfate. Flash chromatography with mixtures of PE (40–60 °C) and CH_2Cl_2 furnished unreacted starting material and 1-methoxy-3-methyl-2-nitrobenzene (**7**) (yield: 40–45%, calculated for consumed starting material). For spectral data see ref. 4. The presence of 5% D in the 3-methyl group follows from a weak triplet signal at 2.27 ppm overlapping with the strong singlet signal for CH_3 at 2.29 ppm in the ^{1}H NMR spectrum and a corresponding increase of the M + 1 satellite peak in the EI spectrum.

Reaction of **1**·I^-/[D_6]DMSO/NaH with 2-nitroanisole (3)

Replacement of [D_9]**1**·I^- by unlabelled sulfonium salt **1**·I^- and DMSO by [D_6]DMSO resulted in a product consisting of 87.8% [D_3]**7**, 11.5%[D_2]**7**, and 0.7% [D]**7** as derived from the molecular ion peak region in the mass spectrum. In the ^{1}H NMR the singlet peak for the 3-CH_3 group is absent and replaced by a quintet for CD_2H at 2.255 ppm superimposed by a weak triplet for CH_2D.

Reaction of [^{13}C]methyl-dimethylsulfonium iodide [^{13}C]**1**·I^-/DMSO/NaH with 3-nitroanisole (3)

Application of [^{13}C]**1**·I^- and DMSO in the above procedure gave the product [methyl-^{13}C]**7** containing *ca.* 33% ^{13}C in the 3-CH_3 group; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 2.29 ppm consisting of a singlet and a doublet $^1J(^{13}C,^1H)$ = 129.1 Hz, s : d ratio = 2 : 1); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 16.9 ppm ($^1J(^{13}C,3\text{-}^{13}C)$ = 43.9 Hz).

Partly deuteriated (at C3) 2,2-diphenyloxirane (14)

To a mixture of [D_6]DMSO (1.5 mL) and THF (1 mL) sodium hydride (27 mg, 1.12 mMol) is added under nitrogen. After 20 min the vial was immersed in an ice–water bath (5–10 °C) and trimethylsulfonium iodide (**1**·I^-, 225 mg, 1.10 mmol) was added under stirring. This was followed by addition of benzophenone (**12**, 100 mg, 0.55 mmol) in THF (0.5 mL). Usual work-up furnished 85 mg (79%) **14**; m.p. 54–55 °C, ref. 2. m.p. 54–56 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 3.29, 3.30 (two s for CHD and CH_2, ratio ~0.18 : 2), 7.29–7.31 (m, 10H).

Reduction with $LiAlH_4$ according to ref. 18 furnished 1,1-diphenylethanol, m.p. = 79–80 °C, ref. 18. m.p. = 80–81 °C.

The ^{1}H NMR spectrum shows a singlet at 1.98 ppm (CH_3) and a triplet at 1.96 ppm (CH_2D) for the partly deuteriated methyl group (ratio ~3 : 0.5). From the molecular ion peak region of the EI mass spectrum a deuteriation degree of 16% D_1 and 0.3% D_2 was calculated.

Notes and references

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