

## Concerning the Denticity of the Dimethylsulfinyl Anion in Meisenheimer Complexation

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**Abstract:** The denticity (O-, S-, and C-nucleophilic reactivity) of the dimethylsulfinyl carbanion ("dimsyl") toward 1,3,5-trinitrobenzene (TNB) has been studied by NMR spectroscopy, and structures of adducts have been assigned. Three dimsyl adducts are observed for the first time and have been ascribed to the O-adduct **15**, the S-adduct **16**, and the C-adduct **17**. The kinetic (**15** > **16** > **17**) and thermodynamic preference (**17** > **16** > **15**) for the reactivity of dimsyl toward TNB is compared to the known O- and C-reactivity of enolate anions and the O- and S-reactivity of dimethyl sulfoxide. Thus, dimsyl apparently represents a unique system in which three adjacent atoms having unshared electron pairs can utilize these in covalent bond formation.

### Introduction

Since the seminal paper by Corey and Chaykovsky<sup>1</sup> in 1962 reporting the first preparation of the dimethylsulfinyl carbanion (hereafter "dimsyl") in dimethyl sulfoxide (DMSO) solution, this remarkable reagent has been utilized in innumerable synthetic and mechanistic studies. Corey and Chaykovsky reported several examples of the "potency" of the dimsyl/DMSO system, notably in carbonyl addition as a C-nucleophile and in proton transfer toward enolizable ketones. Through equilibration with triphenylmethane, the CH<sub>3</sub>SOCH<sub>2</sub><sup>-</sup> basicity of 1 order of magnitude greater than Ph<sub>3</sub>C<sup>-</sup> was established.<sup>1</sup> Corey and Chaykovsky's further observation that base-catalyzed reactions occur at greatly enhanced rates in DMSO as solvent has become amply proven through the highly quoted and utilized pK<sub>a</sub> scale of carbon acids in DMSO, which has been established in the interim by Bordwell<sup>2</sup> and other workers.<sup>3</sup> Through the use of the dimsyl/DMSO reagent, over 1000 R-H pK<sub>a</sub> (DMSO) entries have now been recorded.

A number of studies have utilized the potassium *tert*-butoxide/DMSO system as also being a powerful basic/nucleophilic reagent. In the reaction of 1-iodo-2,2-dimethyl-3-phenylpropane with *t*-BuOK in DMSO, substitution of the halogen by dimsyl anion acting as a C-centered nucleophile competes with substitution by *t*-BuO<sup>-</sup>.<sup>4</sup> The observation of substitution products

derived, in part, from the dimsyl anion is in accord with pK<sub>a</sub> (*t*-BuOH) = 32.2 in DMSO.<sup>2</sup> Interestingly, a small concentration of dimsyl is also generated in DMSO-rich KOH/H<sub>2</sub>O/CH<sub>3</sub>SOCH<sub>3</sub> solution, as demonstrated through H/D exchange, eq 1, producing ultimately CD<sub>3</sub>SOCD<sub>3</sub>.<sup>5</sup>



There has been no report, to our knowledge, of a reaction involving the dimsyl/DMSO, *t*-BuOK/DMSO, or KOH/DMSO systems at a carbon center, in which dimsyl acts as an ambident O- or S-nucleophile rather than as a C-nucleophile.<sup>6</sup> This is surprising given that its parent, DMSO, is known to be alkylated on oxygen and on sulfur.<sup>7</sup> We now report the first such instance, in the case of the interaction of electron-deficient aromatics with bases. As illustrated by eq 2, such reactions entail the formation of anionic (Meisenheimer type) intermediates, or  $\sigma$ -adducts, on route to the S<sub>N</sub>Ar products when X is a potential leaving group.<sup>8</sup> Meisenheimer complexes have been isolated, fully characterized, and subjected to numerous structure-reactivity studies,<sup>8</sup> including for synthetic applications. Importantly, DMSO is typically the solvent of choice in such studies; thus, the question as to the identity of the nucleophile in the basic-DMSO systems arises here as well.

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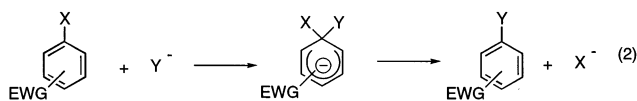
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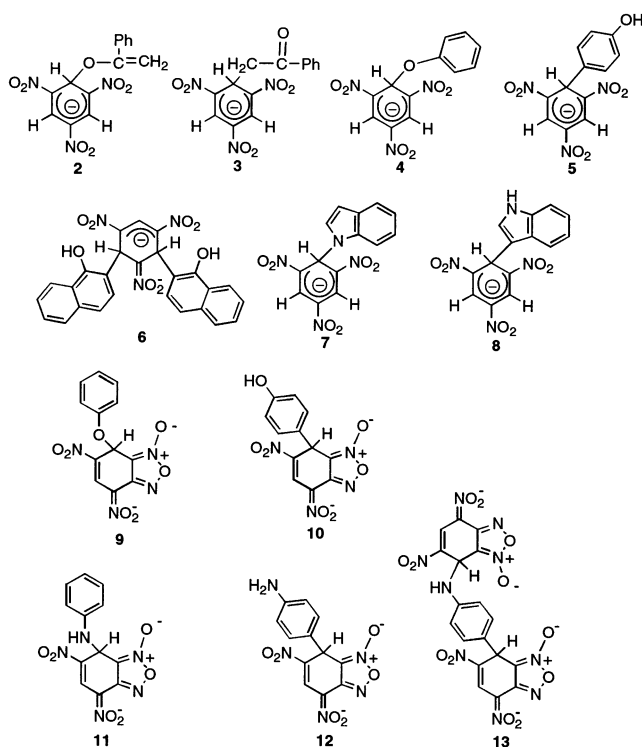
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Of special interest in the present context are  $\sigma$ -adducts derived from electron-deficient nitroaromatics and ambident anions.<sup>9</sup> Using 1,3,5-trinitrobenzene (TNB, **1**) as the standard reference electrophile, adducts **2** and **3** are obtained in the reaction of acetophenone enolate,<sup>10</sup> while **4** and **5** are derived from phenoxide as an O- and C-nucleophile, respectively;<sup>11</sup> in the case of naphthoxide, the 2:1 adduct **6** is obtained.<sup>12</sup> The  $\pi$ -excessive five-membered ring heterocyclic anions pyrrolide, indolide, and imidazolide react with TNB to give initially N-bonded adducts which subsequently undergo conversion to the C-adducts, **7** and **8** being illustrative examples.<sup>13</sup> Going on to the superelectrophilic 4,6-dinitrobenzofuroxan (DNBF),<sup>14</sup> **9** and **10** are derived from adventitious phenoxide,<sup>15</sup> and **11–13** from aniline as N- and C-nucleophile.<sup>16</sup> Note that the less electrophilic TNB reacts with aniline only as a N-nucleophile.<sup>17</sup> Thus, while bidentate Meisenheimer complexation behavior has been described ranging from O- versus C-nucleophilic reactivity with enolates and phenoxide to N- and C-reactivity with pyrrolide and indolide anions, the potential tridentate O-, S-, and C-reactivity of a species such as dimsyl anion has hitherto not been scrutinized. The present article examines the denticity of the dimethylsulfinyl (“dimsyl”) carbanion toward TNB.

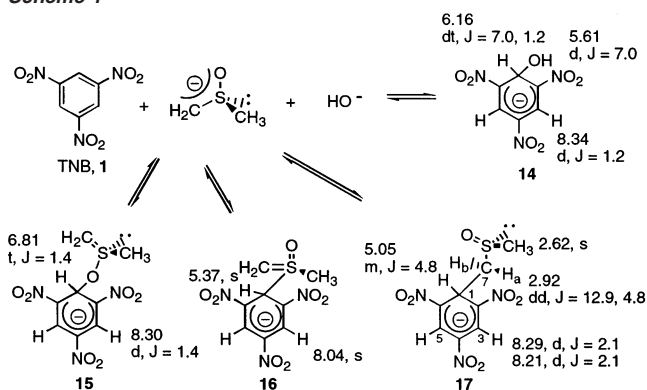


## Results and Discussion

The interaction of dimsyl anion with TNB (**1**) was investigated using three protocols: (1) Me<sub>4</sub>NOH/DMSO-*d*<sub>6</sub>, (2) K<sup>+</sup>dimsyl/DMSO, and (3) preformed sodium dimsyl tetrahydrofuranate. The key features of the three reaction regimes are as follows:

(1) In the tetramethylammonium hydroxide/DMSO-*d*<sub>6</sub> system, where the concentrations of both <sup>-</sup>OH and water ( $\geq 1$  M) are

Scheme 1



relatively high, the O-adduct of dimsyl anion with TNB, **15**, is observed initially as the major adduct but gives way to the hydroxide adduct, **14**, which is the final adduct in this system.

(2) In the K<sup>+</sup>dimsyl system, **15** is observed as the major adduct along with a new adduct that has been tentatively identified as the novel S-adduct, **16**; **14** is a minor component in the initial spectrum. However, over time, the intervention of hydroxide from adventitious H<sub>2</sub>O results in the disappearance of **15** and **16** in favor of **14**.

(3) Sequestering of the Na<sup>+</sup> counterion by tetrahydrofuran in the reaction of sodium dimsyl tetrahydrofuranate with TNB leads to the observation of the C-adduct **17** as well as the other dimsyl adducts, **15** and **16**; **17** is the thermodynamically most favored Meisenheimer adduct formed by dimsyl anion in this reaction system.

These points, including the basis of the structural assignments, are illustrated and amplified in the following sections. Structures of all adducts formed under the various experimental protocols are shown in Scheme 1, including <sup>1</sup>H NMR data for each. Selected <sup>13</sup>C resonances of the adducts are given in Table 1.

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**Table 1.** Selected  $^{13}\text{C}$  Resonances of the  $\sigma$ -Adducts of TNB in  $\text{DMSO}-d_6^a$ 

adduct	C(1)	C(2/6)	C(3/5)	C(4)	C(7)	C(8)
<b>14</b>	59.3	134.3	124.7	120.7		
<b>15</b>	66.4	133.6	124.6	121.3		
<b>16</b>	43.0	128.0	125.0			
<b>17</b>	33.8	132.2	128.0	121.3	57.5	

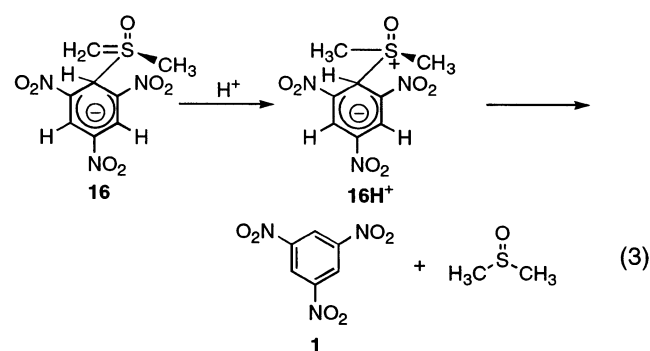
<sup>a</sup> Recorded at 100 MHz at ambient temperature.

**(1)  $\text{Me}_4\text{NOH}/\text{DMSO}-d_6$ .** Injection of 11  $\mu\text{L}$  of a 25 wt % solution of  $\text{Me}_4\text{NOH}$  in water into an NMR tube containing TNB in 490  $\mu\text{L}$  of  $\text{DMSO}-d_6$  (final  $[\text{TNB}] = 59.6 \text{ mM}$ , 95 mol %  $\text{DMSO}$ ) yielded an initial 400 MHz  $^1\text{H}$  NMR spectrum (recorded 3 min after mixing) displaying two  $\sigma$ -adducts in a 3:1 ratio, with the dominant adduct at  $\delta$  8.30 ppm (2H, d,  $J = 1.4 \text{ Hz}$ ) and 6.81 (1H, t,  $J = 1.4$ ). The minor adduct with peaks at 8.34 (2H, d,  $J = 1.2$ ), 6.16 (1H, dt,  $J = 7.0, 1.2$ ), and 5.61 (1H, d,  $J = 7.0$ ) could be assigned to the anticipated  $\text{TNB}\cdot\text{OH}^-$  complex, **14**, and it grew over time at the expense of the initially formed major complex ascribed to a deuterated dimsyl O-adduct **15** (vide infra) generated from equilibration of  $^-\text{OH}$  with the  $\text{DMSO}$  solvent (at 30 min, adducts **14** and **15** were present in a 3:2 ratio favoring **14**). Increasing the water content also favored formation of **14** (80 mol %  $\text{DMSO}-d_6$  resulted in a 4:1 ratio favoring **14**, while at 70 mol %  $\text{DMSO}-d_6$  only a trace of the dimsyl O-adduct **15** could be detected).

In a separate experiment, the acid lability of the  $\sigma$ -complexes was tested. Upon addition of 5  $\mu\text{L}$  of trifluoroacetic acid (TFA), the resonances due to **14** and the dimsyl O-adduct **15** disappeared with concomitant restoration of the singlet at  $\delta$  9.16 for TNB. Acid lability is characteristic of O-bonded TNB adducts,<sup>10,11a,18</sup> indicating that dimsyl anion reacted with TNB to produce the O-bonded complex **15**. Consistent with this assignment, the downfield shift of the sensitive  $\text{sp}^3 \text{C}(1)\text{-H}$  signal at  $\delta$  6.81 (t,  $J = 1.4$ ) was particularly diagnostic of an O-bonded adduct. We have characterized the TNB acetophenone O-bonded enolate adduct **2** in acetonitrile–dimethoxyethane ( $\text{MeCN}-d_3$ :  $\text{DME}-d_{10}$ , 1:1) at low temperature ( $-40 \text{ }^\circ\text{C}$ ); its  $\text{sp}^3 \text{C}(1)\text{-H}$  proton resonates at  $\delta$  6.93 (t,  $J = 1.3$ ).<sup>10</sup> Phenoxide O-adducts (i.e., **4** is similar to the enolate O-adduct **2** in that the attached oxygen center is also adjacent to the  $\text{sp}^2$ -hybridized carbon site) also have  $\text{C}(1)\text{-H}$  signals in the range of 6.7–7.0 ppm.<sup>11a</sup> In contrast, the  $\text{C}(1)\text{-H}$  signal of the C-adduct of the acetophenone enolate (**3**) resonates at  $\delta$  5.22 (tt,  $J = 0.8, 6.0$ );<sup>10</sup> note that phenoxide C-adducts (i.e., **5**) have  $\text{C}(1)\text{-H}$  signals at 5.0–5.5 ppm.<sup>11</sup> Because the dimsyl  $\sigma$ -adduct **15** was derived from  $\text{DMSO}-d_6$ , the  $^1\text{H}$  signals at 8.30 and 6.81 for the trinitrocyclohexadienide moiety were the only ones detected. The ring  $^{13}\text{C}$  NMR resonances of **14** and **15** were assigned also from the  $\text{Me}_4\text{NOH}/\text{DMSO}-d_6$  experiments (Table 1); the  $^{13}\text{C}$  chemical shifts for **15** were similar to the corresponding shifts for the O-bonded phenoxide complex **4**.<sup>11a</sup>

**(2)  $\text{K}^+\text{dimsyl}/\text{DMSO}$ .** Treatment of TNB (6.7 mg in 430  $\mu\text{L}$  of  $\text{DMSO}-d_6$ ) with  $\text{K}^+\text{dimsyl}/\text{DMSO}$  (70  $\mu\text{L}$  from 0.44 M stock solution) yielded an initial  $^1\text{H}$  NMR spectrum with signals ascribed to the O-bonded adduct **15** and trace amounts of the  $\text{TNB}\cdot\text{OH}^-$  complex **14**. However, an additional pair of broad, apparent singlets at 8.04 and 5.37 was also observed, and integration showed these peaks to be in a 2:1 ratio, suggesting an additional dimsyl  $\sigma$ -complex with  $\text{sp}^3 \text{C}(1)\text{-H}$  at 5.37 and  $\text{C}(3,5)\text{-H}$  at 8.04 ppm; the expected small (1–2 Hz)

$\text{H}(1)\text{-H}(3,5)$  coupling is not resolved. In the initial  $^1\text{H}$  spectrum, the integral ratio of the  $\text{sp}^3 \text{C}(1)\text{-H}$  at 6.81 for **15** and at 5.37 for the new adduct was 2:1. Over time (4 h), both dimsyl complexes gave way to the hydroxide complex **14**. Acidification with TFA resulted in the immediate disappearance of all peaks ascribed to  $\sigma$ -complex formation. The acid lability of the new complex combined with the lack of coupling observed in the  $\text{sp}^3 \text{C}(1)\text{-H}$  proton precluded C-attachment because C-bonded enolate adducts decompose only slowly in acidic media<sup>19</sup> and their  $\text{sp}^3 \text{C}(1)\text{-H}$  protons show coupling to the attached methylene group ( $J \approx 4\text{--}6 \text{ Hz}$ ).<sup>10,19</sup> On the basis of the known tendency of the parent  $\text{DMSO}$  to form S-alkylated products,<sup>7</sup> the resonances at  $\delta$  8.04 and 5.37 were tentatively assigned to the S-bonded  $\sigma$ -complex **16**. It is noteworthy that S-bonded  $\sigma$ -adducts generally do not exhibit acid lability.<sup>8d,20</sup> In the present system, however, protonation of **16** would occur on the methylene carbon with subsequent ejection of neutral dimethyl sulfoxide in an irreversible process, as illustrated by eq 3.



**(3) Sodium Dimsyl Tetrahydrofuranate.** In a typical experiment, a stock TNB solution (97 mM) was prepared in 200  $\mu\text{L}$  of freshly distilled  $\text{DMSO}$ . The  $\text{DMSO}$  solution was then added to 19 mg of solid sodium dimsylvetrahydrofuranate<sup>21</sup> in a glovebox. After dilution with 300  $\mu\text{L}$  of  $\text{DMSO}-d_6$ ,  $^1\text{H}$  NMR spectra of the solution were acquired. In a spectrum obtained 5 min after mixing the reagents, peaks ascribed to the O-bonded adduct **15** and the S-adduct **16** were noted, but unlike experiments with  $\text{K}^+\text{dimsyl}/\text{DMSO}$ , they did not represent the dominant peaks in the  $^1\text{H}$  spectrum. Instead, the upfield region of the spectrum showed an apparent triplet at 5.05 ppm ( $J = 4.8$ ) and a double doublet at 2.92 ( $J = 12.9, 4.8$ ). Decoupling experiments verified that these peaks were coupled, and integration showed them to be in a 1:2 ratio. These characteristics were reminiscent of the spectral features of the C-bonded enolate TNB adducts of acetophenone (**3**)<sup>10,19</sup> and acetone,<sup>22</sup> with the exception that the methylene protons (2.92 ppm) of the attached dimsyl moiety were nonequivalent due to the chiral sulfur atom. Thus, these resonances were assigned to the C-bonded dimsyl adduct **17**, and their observation showed that the attached dimsyl moiety had not undergone H/D exchange with the NMR solvent  $\text{DMSO}-d_6$ . At this early stage in the reaction, the integral ratio of  $^1\text{H}$  signals ascribed to  $\text{C}(1)\text{-H}$ )

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the dimsyl adducts at 6.81 (**15**), 5.37 (**16**), and 5.05 (**17**) was 1:2:3. In contrast to the peaks for **15** and the tentatively assigned S-adduct **16**, the signals at 5.05 and 2.92 survived acidification with TFA, as noted with C-bonded enolate complexes,<sup>19</sup> and were therefore assigned to **17**. Following acid decomposition of the other adducts, the full <sup>1</sup>H NMR assignment of **17** could be made. The ring protons (H<sub>3</sub>, H<sub>5</sub>) of the trinitrocyclohexanide moiety were also nonequivalent as a consequence of the chiral dimsyl moiety: <sup>1</sup>H (δ ppm, *J* Hz) 8.29 (1H, d, *J* = 2.1), 8.21 (1H, d, *J* = 2.1), 5.05 (1H, m, *J* = 4.8), 2.92 (2H, dd, *J* = 12.9, 4.8), 2.62 (3H, s); <sup>13</sup>C (δ ppm) 132.2, 130.1, 128.0, 127.9, 121.3 (C<sub>4</sub>), 57.5 (C<sub>7</sub>), 33.8 (C<sub>1</sub>).

The reaction of TNB with sodium dimsylvetrahydrofuranate was also monitored as a function of time. Following 2 h at ambient temperature, peaks ascribed to the O-bonded adduct **15** disappeared, and signals for TNB·OH<sup>-</sup> (**14**) were present. The peaks at 8.04 and 5.37 ascribed to the S-adduct **16** showed a slower rate of decomposition; by 6 h they had given way to **14**, but the intensity of signals for the C-bonded adduct **17** was unchanged. After 3 days (stored in the refrigerator), the C-adduct **17** remained as the sole complex derived from dimsyl anion in solution indicating its thermodynamic preference, as noted for the C-bonded enolate adduct of acetophenone.<sup>10</sup> Interestingly, the initial concentration of the C-bonded adduct **17** observed 5 min after mixing the reagents remained unchanged throughout the duration of these experiments (i.e., C-reactivity of dimsyl was observed only starting with the solid furanate salt). This observation differed from the reaction of TNB with acetophenone enolate where the initially formed O-bonded enolate adduct **2** gave way in time and as a function of temperature to the thermodynamically more favored C-bonded adduct **3**.<sup>10</sup>

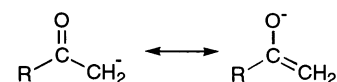
Of the σ-adducts presented in Scheme 1, formation of **14** from adventitious water in these systems has been amply established in previous work.<sup>10,11</sup> Interestingly, in a study by Fyfe et al. which employed 60 MHz NMR spectroscopy,<sup>23</sup> the species formed between TNB and dimsyl anion was claimed to be the C-bonded adduct; however, the NMR parameters reported for that species actually correspond to the O-bonded dimsyl adduct **15** observed in the present study.

Some comments are in order on reactivities under the three protocols described above. In the tetramethylammonium hydroxide/DMSO system (≥1 M in H<sub>2</sub>O), TNB is largely intercepted by hydroxide, and only the relatively free (uncomplexed by Me<sub>4</sub>N<sup>+</sup>) O-site of dimsyl is kinetically competitive with hydroxide. Proceeding to the K<sup>+</sup>dimsyl system with only adventitious H<sub>2</sub>O present, the decreased water content of this medium now permits observation of both the O- and the S-adducts of dimsyl with **1**. Finally, it is only in the sodium dimsyl tetrahydrofuranate system where the complexation of the sodium counterion by tetrahydrofuran permits the observation of all three adducts, **15**, **16**, and **17**, and reveals the full tridentate reactivity of dimsyl anion.

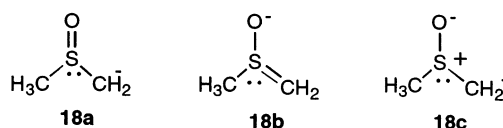
Following our first-time observation of the O- and C-bonded σ-adducts from the interaction of TNB with the enolate of acetophenone,<sup>10</sup> a similar ambident reactivity of dimsyl, resulting in the formation of O- and C-adducts, seemed probable. The results that were generated, as described above for the spectral characteristics of **15** and **17**, fully confirmed our expectations.

However, our experiments revealed the discovery of apparently yet another σ-adduct which is consistent with S-reactivity, in accord with Winstein's observation of S-alkylation of DMSO.<sup>7</sup> In this case, the NMR evidence is not fully conclusive because the protons of the attached dimsyl moiety in the S-adduct **16** undergo H/D exchange and hence problems making unambiguous <sup>13</sup>C NMR assignments due to overlap of solvent and σ-adduct peaks were encountered.

However, there is a clear contrast in the ambident reactivities of dimsyl and of enolates. As first noted by House,<sup>24</sup> O-alkylation of enolates is favored in non-H-bonding solvents and through metal ion complexation by crown ethers, whereas with dimsyl it was C-reactivity that was observed only on scrupulous removal of all but the last traces of H<sub>2</sub>O and using solid sodium dimsylvetrahydrofuranate where Na<sup>+</sup> is complexed by THF. Additionally, a more fundamental distinction between enolate and dimsyl anions is called for. The description of the enolate anion as a resonance hybrid of two canonical structures has received ample confirmation from a variety of theoretical investigations<sup>25</sup> as well as being in accord with the relatively low pK<sub>a</sub> of ketones as carbon acids.<sup>3</sup>



In contrast, the theoretical studies on dimsyl by Streitwieser and co-workers<sup>26</sup> as well as those by Hirst<sup>27</sup> show that the anionic charge of dimsyl is primarily localized on the methylene fragment, with a small transfer of charge to sulfur and almost no appreciable delocalization of charge to the oxygen center. Similarly, the earlier theoretical study by Wolfe<sup>28</sup> revealed a pyramidal configuration for the anionic carbon of dimsyl, again precluding charge delocalization. Thus, of the three valence bond structures (**18a**, **18b**, and **18c**) for dimsyl anion, it appears that **18c**, with pyramidal geometry about S and C, while in accord with theoretical calculations,<sup>26–28</sup> represents fully the tridentate reactivity of dimsyl.



Attention is further drawn to a juxtaposition of the tridentate reactivity of dimsyl as reported herein and the bidentate reactivity of its parent, dimethyl sulfoxide (DMSO). Early work by Smith and Winstein clearly demonstrates the ambident nature of DMSO (O- and S-reactivity) upon treatment with alkyl halides or arenesulfonates.<sup>7</sup> Reaction of DMSO with methyl iodide generated the O-alkyl product **19** in a kinetically favored process, while the S-alkylated product **20** was thermodynamically preferred. Further, treatment of **20** with NaH yields the dimethylsulfoxonium methyllide **21**,<sup>29</sup> which corresponds to the

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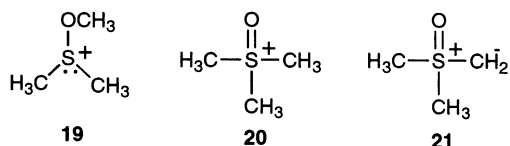
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alkylated analogue of the proposed S-adduct **16**. Thus, the present report that dimsyl anion acts as an O-, S-, and C-nucleophile in Meisenheimer complexation with TNB is fully consistent with the ambident reactivity of its parent, DMSO. The kinetic (**15** > **16** > **17**) and thermodynamic (**17** > **16** > **15**) preferences present interesting parallels to enolate and DMSO reactivity toward carbon-centered electrophiles.



## Conclusion

The present study constitutes a novel tridentate nucleophilic reactivity system in which the dimsyl anion behaves as an O-, S-, and C-nucleophile in reactions with 1,3,5-trinitrobenzene. To our knowledge, dimsyl represents a unique structure in which three adjoining atoms having unshared electron pairs utilize these in covalent bond formation. It would be of interest to extend this study to a family of sulfoxides with several potential anionic sites<sup>5</sup> and electron-deficient nitroaromatic substrates, which have already demonstrated multiple electrophilic sites.<sup>30</sup> Such sulfoxide/nitroaromatic interactions may permit new structure–reactivity relationships to be established for bi- and tridentate reactivity in this unique system.

## Experimental Section

**Materials and Methods.** 1,3,5-Trinitrobenzene (TNB, **1**) was prepared by nitrating 1,3-dinitrobenzene as described previously.<sup>11,31</sup> Dimethyl sulfoxide (DMSO, BDH) was refluxed and distilled under reduced pressure from  $\text{CaH}_2$  prior to use. Other solvents were purified using standard procedures. Potassium methylsulfinyl carbanion ( $\text{K}^+$ dimsyl) was prepared by adding 12 mL of freshly distilled DMSO to KH (0.27 g, 6.6 mmol) that had been washed several times with dry

hexane in an  $\text{N}_2$ -filled glovebox. The resulting suspension was stirred for 1 h under  $\text{N}_2$ , and the solution was standardized against potassium hydrogen phthalate (KHP, Aldrich) to yield 0.41 M  $\text{K}^+$ dimsyl in DMSO. Following the procedure described by Martin,<sup>21</sup> (methylsulfinyl)methyl-sodium tetrahydrofuranate (sodium dimsyl tetrahydrofuranate) was prepared by adding 20 mL of dry DMSO and 50 mL of dry THF to a  $\text{N}_2$ -purged flask containing 5 g of NaH. The gray suspension was refluxed for 3 h at 70 °C, cooled to 45 °C, and then allowed to stir for 12 h. The resulting gray precipitate was collected and handled in a glovebox.

**NMR Experiments.** The NMR experiments were carried out at ambient temperature on a Bruker AM-400 spectrometer ( $^1\text{H}$ , 400 MHz;  $^{13}\text{C}$ , 100 MHz) in  $\text{DMSO}-d_6$ . The  $\text{DMSO}-d_5\text{H}$  peak (d 2.49) served as reference and lock signal. Chemical shifts are given in parts per million (ppm), and coupling constants are in hertz (Hz). For  $^{13}\text{C}$  NMR experiments, spectra were acquired using the *J*-modulated (JMODO) pulse sequence.<sup>32</sup> Wilmad pp-507 NMR tubes (5 mm) were used in all experiments. All stock solutions and NMR tubes were capped with rubber septa and swept out with  $\text{N}_2$  prior to injection of the reactants.

**Representative NMR Experiment: Reaction of TNB with Sodium Dimsyl Tetrahydrofuranate.** A DMSO solution of TNB (20.7 mg in 200  $\mu\text{L}$  of dry DMSO) was added to a septum-capped vial in the glovebox containing 19 mg of dry sodium dimsyl tetrahydrofuranate. The resulting reddish-black solution was mixed and added in the drybox to an NMR tube containing 300  $\mu\text{L}$  of  $\text{DMSO}-d_6$  (final [TNB] = 0.19 M, final [dimsyl] = 0.22 M). The contents in the NMR tube were mixed and then frozen in a dry ice/acetone slurry for transfer to the NMR spectrometer. NMR ( $^1\text{H}$  and  $^{13}\text{C}$ ) spectra were acquired at various intervals until the reaction was deemed complete.

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