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Scope and Limitations of Cyclopropanations with Sulfur Ylides

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Abstract: The rates of the reactions of the stabilized and semistabilized sulfur ylides **1a**−**g** with benzhydrylium ions (**2a**−**e**) and Michael acceptors (**2f**−**v**) have been determined by UV−vis spectroscopy in DMSO at 20 °C. The second-order rate constants (log k_2) of these reactions correlate linearly with the electrophilicity parameters E of the electrophiles **2** as required by the correlation log $k_2 = s(N + E)$, which allowed us to calculate the nucleophile-specific parameters N and s for the sulfur ylides **1a**−**g**. The rate constants for the cyclopropanation reactions of sulfur ylides with Michael acceptors lie on the same correlation line as the rate constants for the reactions of sulfur ylides with carbocations. This observation is in line with a stepwise mechanism for the cyclopropanation reactions in which the first step, nucleophilic attack of the sulfur ylides at the Michael acceptors, is rate determining. As the few known pK_{aH} values for sulfur ylides correlate poorly with their nucleophilic reactivities, the data reported in this work provide the first quantitative approach to sulfur ylide reactivity.

Introduction

Sulfur ylides have emerged to an important class of reagents in organic synthesis. Though the first report on the isolation of a sulfur ylide by Ingold and Jessop was already published in 1930,[1] a systematic investigation of sulfur ylides started only in the 1960s when these compounds were recognized as versatile reagents for the preparation of three-membered carbo- and heterocycles.[2] Eventually, the use of chiral sulfur ylides or chiral electrophilic substrates gave rise to a variety of stereoselective sulfur ylide-mediated cyclization reactions.[3] Detailed investigations of epoxidation,[4] cyclopropanation,[4b,5] and aziridination reactions[6] revealed a common mechanistic course. In all cases, the sulfur ylide initially attacks at an electrophilic carbon center (i.e., aldehyde, imine, or Michael acceptor) to form a betaine intermediate, which undergoes an intramolecular nucleophilic displacement to yield an epoxide, an aziridine, or a cyclopropane, respectively (Scheme 1).

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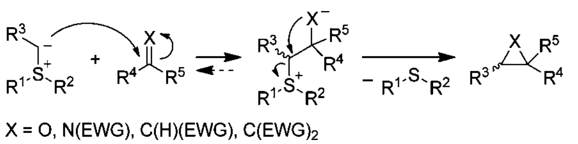
Scheme 1. Mechanism of the Sulfur Ylide-Mediated Epoxidation-, Aziridination-, and Cyclopropanation Reaction (Corey−Chaykovsky Reaction)[4−6]



Depending on the reactivities of the sulfur ylides, the initial addition step of the sulfur ylide to an aldehyde or an imine has been shown to be reversible or irreversible.[2k,4b,k−n,6a,c,d] Stabilized sulfur ylides, i.e., acetyl-, benzoyl-, and ester-substituted sulfur ylides, are considerably less reactive than the so-called semistabilized sulfur ylides, i.e., aryl-substituted sulfur ylides, and do not undergo epoxidation reactions with aldehydes or react only under harsh conditions.[2k,p,4k] Obviously, the nucleophilicities of the ylides play an important role for their synthetic applicability. Previous rationalizations of structure−reactivity relationships of sulfur ylides focused on their basicities.[5d,7] However, due to the small amount of available pK_{aH} values of sulfur ylides and the poor correlation between basicity and nucleophilicity of carbon-centered nucleophiles,[8] a quantitative comparison of the nucleophilicities of variably substituted sulfur ylides as well as a comparison with other classes of nucleophiles has so far not been possible.

In recent years, we have shown that the rates of the reactions of carbocations and Michael acceptors (some of them are depicted in Table 1) with n-, π-, and σ-nucleophiles can be described by eq 1, where $k_{20\,°C}$ is the second-order rate constant in $M^{-1}\,s^{-1}$, s is a nucleophile-specific sensitivity parameter, N is a nucleophilicity parameter, and E is an electrophilicity parameter.

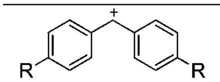
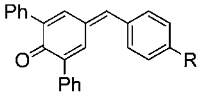
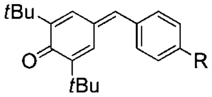
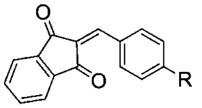
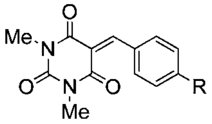
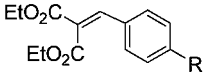
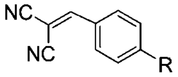
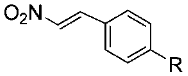
$$\log k_{20\,°C} = s(N + E) \qquad (1)$$

On the basis of this linear free-energy relationship, we have developed the most comprehensive nucleophilicity and electrophilicity scale presently available.[8,9] We have now employed this method for characterizing the nucleophilicities of stabilized and semistabilized sulfur ylides **1a**−**g** (Scheme 2), and we will discuss the impact of these results for predicting scope and limitations of cyclopropanation reactions of Michael acceptors with sulfur ylides.

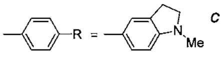
Results

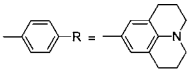
Reactions with Benzhydrylium Ions. In order to establish the course of the reactions, which were studied kinetically, we have characterized products of the reactions of the sulfur ylides **1a**−**g** with the benzhydrylium ion **2a**. Owing to their low stability, the initially formed addition products **3a**−**f** were not isolated but immediately treated with thiophenolate to afford the neutral addition products **4a**−**f**, which are fully characterized in the Supporting Information (Scheme 3).

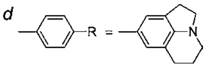
Table 1. Benzhydrylium Ions **2a**−**e**, Michael Acceptors **2f**−**v**, and their Electrophilicity Parameters *E*

Electrophile		R	E^a
	**2a**	NMe_2	−7.02
	2b	$N(CH_2)_4$	−7.69
	2c	ind[b]	−8.76
	2d	jul[c]	−9.45
	2e	lil[d]	−10.04
	**2f**	OMe	−12.18
	2g	NMe_2	−13.39
	**2h**	Me	−15.83
	2i	OMe	−16.11
	2j	NMe_2	−17.29
	2k	jul[c]	−17.90
	**2l**	OMe	−11.32
	2m	NMe_2	−13.56
	2n	jul[c]	−14.68
	**2o**	OMe	−10.37
	2p	NMe_2	−12.76
	2q	jul[c]	−13.84
	**2r**	NO_2	−17.67
	2s	CN	−18.06
	2t	*m*Cl	−18.98
	**2u**	NMe_2	−13.30
	**2v**	OMe	−14.70

[a] Electrophilicity parameters *E* of **2a**−**e** were taken from ref 9b, of **2f**−**k** from ref 9c, of **2l**−**n** from ref 9g, of **2o**−**q** from ref 9h, of **2r**−**t** from ref 9i, of **2u** from ref 9d, and of **2v** from ref 9k.

b 

c 

d 

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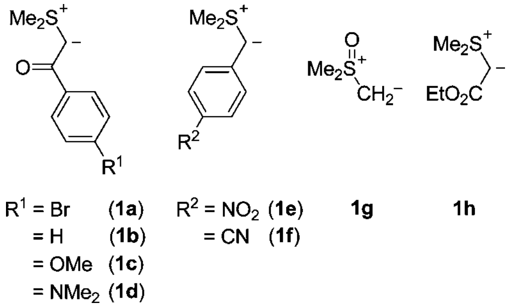
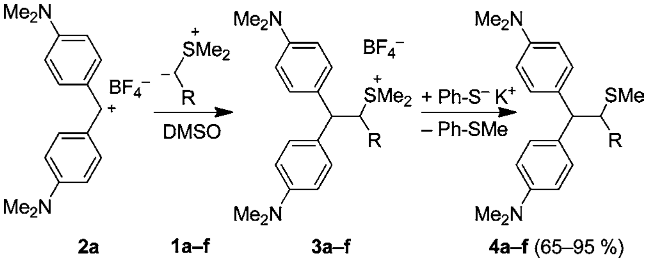
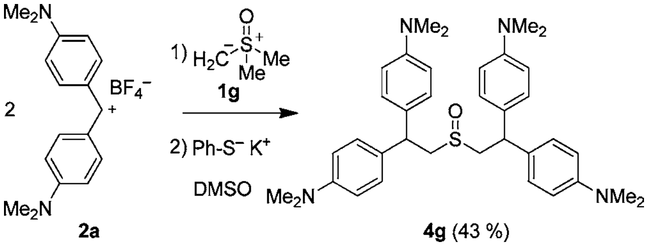
Scheme 2. Benzoyl-Stabilized Sulfur Ylides **1a**−**d**, Semistabilized Sulfur Ylides **1e**−**g**, and Ester-Stabilized Sulfur Ylide **1h**



Scheme 3. Reactions of the Sulfur Ylides **1a**−**f** with Benzhydrylium Tetrafluoroborate **2a**-BF$_4$



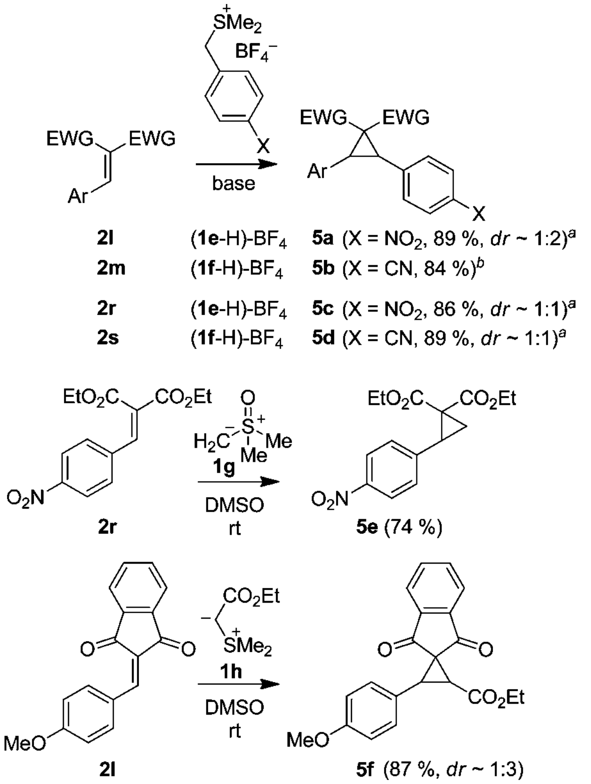
Scheme 4. Reaction of the Sulfur Ylide **1g** with Benzhydrylium Tetrafluoroborate **2a**-BF$_4$



Treatment of **2a** with the dimethylsulfoxonium ylide **1g** and subsequent addition of thiophenolate yielded the 2:1-product **4g** (Scheme 4). Obviously, the initially generated 1:1-addition product from **2a** and **1g** is rapidly deprotonated to give another sulfur ylide which reacts with a second molecule of the electrophile **2a**. Eventually, demethylation by thiophenolate (according to Scheme 3) yields **4g**.

Reactions with Michael Acceptors. As the reactions of sulfur ylides with Michael acceptors had already been known to yield cyclopropane derivatives (Scheme 1), product analyses have only been performed for representative combinations of the sulfur ylides **1** with Michael acceptors. The reactions of the semistabilized sulfur ylides **1e**−**g** with the benzylideneindandiones **2l**,**m** and the diethyl benzylidenemalonates **2r**,**s** as well as the reaction of the stabilized sulfur ylide **1h** with benzylideneindandione **2l** yielded the expected cyclopropane derivatives **5** (Scheme 5). Due to the high tendency of dimethylsulfoxonium ylide **1g** for multiple addition (see Scheme 4), complex mixtures of products were formed in the reactions of **1g** with the other types of Michael acceptors. The treatment of the benzylidenebarbituric acids **2o**,**p** with the sulfur ylides **1f** and **1h** did not yield cyclopropanes, but the dihydrofuran derivatives **6a**,**b**. As indicated in Scheme 6, the direct nucleophilic displacement of dimethylsulfide by a carbonyl oxygen of the initially formed zwitterion would lead to dihydrofurans **6′**, which have a different substitution pattern than was actually found for the compounds **6a**,**b** (derived by 2D-NMR experiments). These findings suggest that the dihydrofurans **6a**,**b** are formed via a rearrangement of an intermediate cyclopropane species **6″**.

Scheme 5. Reactions of the Semistabilized Sulfur Ylides **1e**−**g** and the Stabilized Sulfur Ylide **1h** with Different Michael Acceptors



[a] Reaction conditions: KO*t*Bu, DMSO, rt. [b] Reaction conditions: K$_2$CO$_3$ (aq)/CHCl$_3$, rt; only one diastereomer isolated.

In analogy to previous reports,[10,11] the reaction of the benzoyl-stabilized sulfur ylide **1c** with *trans*-4-methoxy-*β*-nitrostyrene (**2v**) does not give a cyclopropane but a dihydroisoxazole *N*-oxide, which has been identified as described in the Supporting Information.

Kinetic Investigations have been performed in analogy to earlier studies.[10] However, because of the low stability of the semistabilized ylides **1e**,**f**, several modifications were needed as described in detail in the Supporting Information. Table 2

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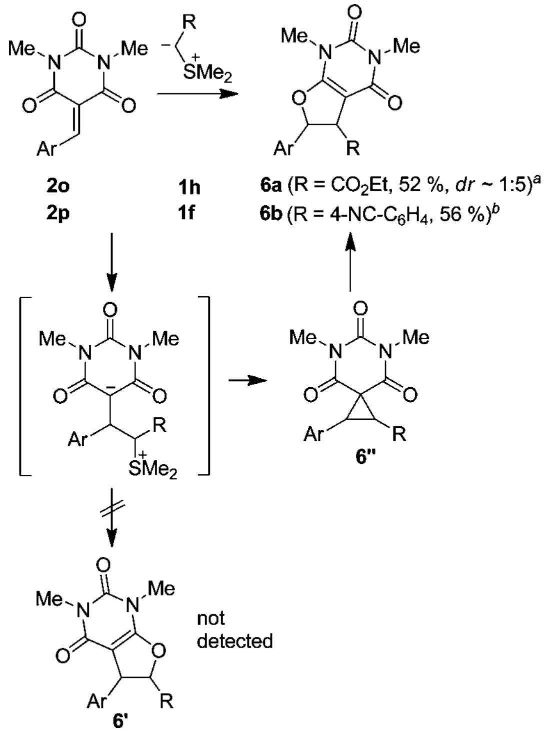
Scheme 6. Reactions of the Sulfur Ylides **1f** and **1h** with the Benzylidenebarbituric Acids **2o** and **2p**



[a] Reaction conditions: **1h**, DMSO, rt. [b] Reaction conditions: (**1f**-H)-BF$_4$, K$_2$CO$_3$ (aq)/CHCl$_3$, rt; only one diastereomer isolated.

shows a summary of the second-order rate constants, which have been determined for the reactions of the sulfur ylides **1a**−**h** with the benzhydrylium ions **2a**−**e** and the Michael acceptors **2f**−**v**.

Discussion

Correlation Analysis. In order to determine the nucleophile-specific parameters N and s of the sulfur ylides **1a**−**g**, the second-order rate constants (log k_2) of their reactions with the electrophiles **2** (see Table 2) were plotted against the electrophilicity parameters E of **2a**−**v**, which have previously been derived from the rates of the reactions of **2a**−**v** with electron-rich ethylenes and carbanions.[9b−d,g−i,k] In Figure 1 these correlations are shown exemplarily for the stabilized sulfur ylides **1b**,**d** and the semistabilized sulfur ylides **1e**,**f**. The correlations for the other nucleophiles investigated in this work (**1a**,**c**,**g**) are of similar quality (see Table 2 and Supporting Information) and allow the calculation of the nucleophile-specific parameters N and s, which are listed in Table 2. The small deviations between the calculated and experimental rate constants in Table 2 (72% less than a factor of 1.5, 87% less than a factor of 3.0, and 100% less than a factor of 5) confirms that the rate-determining step of these reactions is analogous to that from which the electrophilicity parameters E of **2a**−**v** have been derived. The same electrophilicity parameters E of carbocations and Michael acceptors, which have previously been demonstrated to be suitable for predicting the rates of their reactions with aliphatic and aromatic π-systems, carbanions, hydride donors, phosphines, and amines[8,9] have thus been found to be also suitable for predicting the rates of their reactions with stabilized and semistabilized sulfur ylides.

The similarities of the slopes of the correlations for the dimethylsulfonium ylides **1a**−**f** (Figure 1 and Supporting Information), which are numerically expressed by the s-parameters in Table 2, imply that the relative nucleophilicities of the dimethylsulfonium ylides **1a**−**f** depend only slightly on the electrophilicity of the reaction partners. Consequently, the N parameters can be used to compare the relative reactivities of these compounds (Figure 2). The considerably lower s parameter for the dimethylsulfoxonium ylide **1g** indicates that the rates of its reactions are less influenced by a change of the electrophilicity of the reaction partners than the corresponding reactions of the dimethylsulfonium ylides **1a**−**f**. As a consequence, the relative reactivities of dimethylsulfonium ylides **1a**−**f** in comparison to dimethylsulfoxo-

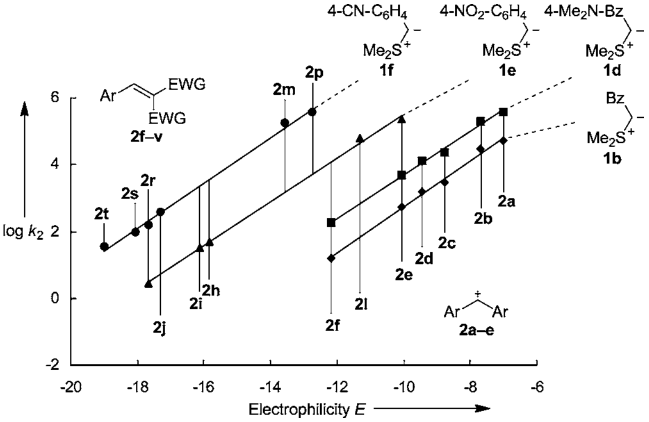


Figure 1. Plots of log k_2 for the reactions of the stabilized sulfur ylides **1b**,**d** and the semistabilized sulfur ylides **1e**,**f** with the electrophiles **2** (in DMSO at 20 °C) versus the electrophilicity parameters E of **2**. For the sake of clarity, the correlation lines for the ylides **1a**,**c**,**g** are only shown in the Supporting Information.

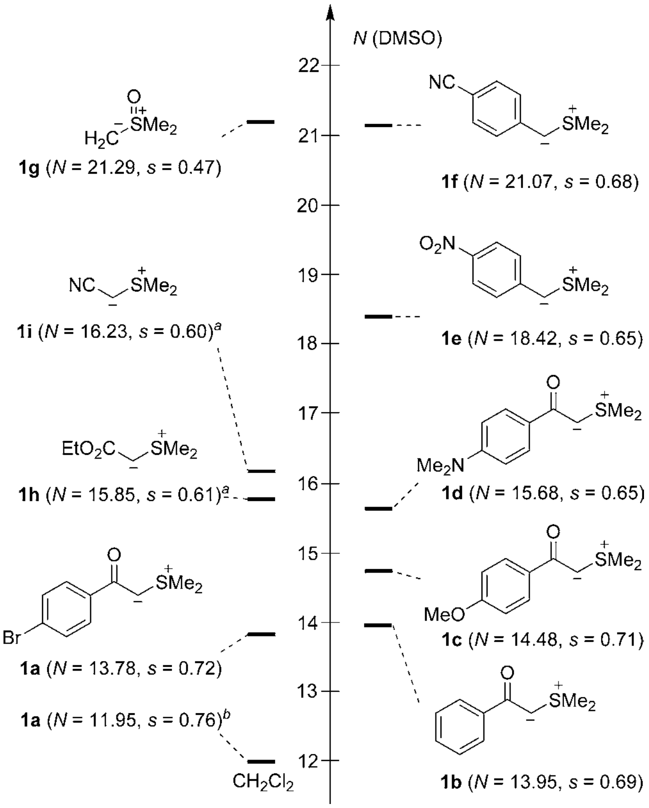
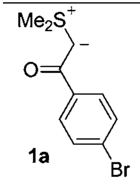
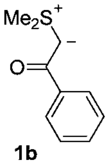
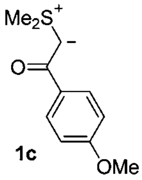
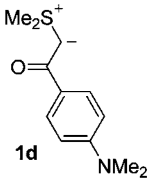
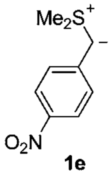
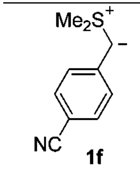
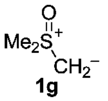
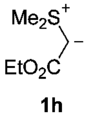


Figure 2. Comparison of the nucleophilicity parameters N (in DMSO at 20 °C) of stabilized sulfur ylides (**1a**−**d**,**h**,**i**) and semistabilized sulfur ylides (**1e**−**g**). [a] Taken from ref 10; [b] taken from ref 12.

Table 2. Experimental and Calculated Second-Order Rate Constants (M^{-1} s^{-1}) for the Reactions of the Sulfur Ylides **1** with the Electrophiles **2** in DMSO at 20 °C

Nucleophile N / s[a]	Electrophile	k_2^{exp}	k_2^{calcd}[b]
 **1a** 13.78 / 0.72	**2a**	5.71×10^4	7.37×10^4
	2b	3.34×10^4	2.43×10^4
	2c	3.03×10^3	4.12×10^3
	2d	1.73×10^3	1.31×10^3
	2e	5.72×10^2	4.93×10^2
	2f	1.23×10^1	1.42×10^1
 **1b** 13.95 / 0.69	**2a**	5.15×10^4	6.05×10^4
	2b	3.06×10^4	2.09×10^4
	2c	2.98×10^3	3.81×10^3
	2d	1.53×10^3	1.27×10^3
	2e	5.18×10^2	4.99×10^2
	2f	1.62×10^1	1.66×10^1
 **1c** 14.48 / 0.71	**2a**	1.46×10^5	1.98×10^5
	2b	7.54×10^4	6.62×10^4
	2c	8.06×10^3	1.15×10^4
	2d	4.61×10^3	3.73×10^3
	2e	1.50×10^3	1.42×10^3
	2f	5.01×10^1	4.30×10^1
	2v	5.80×10^{-1}	6.98×10^{-1}
 **1d** 15.68 / 0.65	**2a**	3.83×10^5	4.26×10^5
	2b	2.02×10^5	1.56×10^5
	2c	2.29×10^4	3.15×10^4
	2d	1.31×10^4	1.12×10^4
	2e	5.05×10^3	4.63×10^3
	2f	1.82×10^2	1.88×10^2
 **1e** 18.42 / 0.65	**2e**	2.28×10^5	2.80×10^5
	2h	5.16×10^1	4.83×10^1
	2i	3.27×10^1	3.17×10^1
	2l	5.96×10^4	4.12×10^4
	2r	2.81	3.07
 **1f** 21.07 / 0.68	**2j**	3.97×10^2	3.72×10^2
	2m	1.77×10^5	1.28×10^5
	2p	3.70×10^5	4.48×10^5
	2r	1.51×10^2	2.05×10^2
	2s	9.69×10^1	1.11×10^2
	2t	3.48×10^1	2.64×10^1
 **1g** 21.29 / 0.47	**2d**	1.63×10^5	3.67×10^5
	2e	6.38×10^4	1.94×10^5
	2e	6.36×10^4[c]	1.94×10^5
	2f	1.65×10^4	1.91×10^4
	2g	3.53×10^3	5.16×10^3
	2h	2.19×10^2	3.68×10^2
	2i	1.36×10^2	2.72×10^2
	2j	3.51×10^1	7.59×10^1
	2k	1.82×10^1	3.92×10^1
	2m	8.27×10^3	4.30×10^3
	2n	2.47×10^3	1.28×10^3
	2p	3.27×10^4	1.02×10^4
	2q	9.55×10^3	3.17×10^3
	2r	7.84×10^1	5.03×10^1
	2u	6.69×10^3	5.69×10^3
 **1h** (15.85 / 0.61)[d]	**2l**	2.41×10^3	5.80×10^2
	2m	1.14×10^2	2.49×10^1
	2o	1.06×10^4	2.20×10^3

[a] Nucleophilicity parameters N and s derived by using eq 1, determination see below. [b] Calculated by using eq 1 and the N and s parameters for the ylides **1** (column 1 of this Table) as well as the electrophilicity parameters E for the benzhydrylium ions **2a**−**e** and the Michael acceptors **2f**−**v** (see Table 1). [c] Deprotonation of the conjugate CH-acid Me_3SO^+ I^- with 0.482 equiv of KO*t*Bu (for details see Supporting Information). [d] Taken from ref 10.

nium ylide **1g** depend significantly on the electrophilicity of the reaction partner.

Structure−Reactivity Relationships. As shown in Figure 2, the nucleophilic reactivities of the sulfur ylides **1a**−**i** in DMSO cover a range of 7 orders of magnitude.

The reactivities of the benzoyl-stabilized ylides **1a**−**d**, which are the least reactive species in this series, correlate moderately

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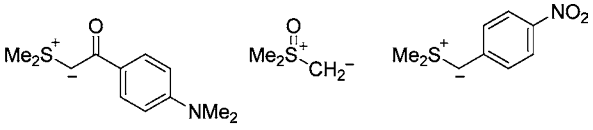
(12) Lakhdar, S.; Appel, R.; Mayr, H. *Angew. Chem., Int. Ed.* **2009**, *48*, 5034–5037.

Scheme 7. Relative Reactivities of the Nucleophiles **1d**,**e**,**g** towards the Benzhydrylium Ion **2e** and the Quinone Methide **2h** (DMSO, 20 °C)



	1d	**1g**	**1e**
k_{rel} (toward **2e**)	1.0	13	45
k_{rel} (toward **2h**)	1.0 [a]	274	65

[a] Absolute rate constant ($k_2 = 0.799$ M^{-1} s^{-1}) calculated by eq 1 using $N = 15.68$ and $s = 0.65$ for ylide **1d** as well as the electrophilicity parameters $E = -15.83$ for the electrophile **2h**.

with Hammett's σ_p as shown on p S43 of the Supporting Information. For $s = 0.7$, one derives a Hammett reaction constant of $\rho = -1.3$ which indicates a moderate increase of reactivity by electron-donating substituents.

The ethoxycarbonyl- and cyano-substituted ylides **1h** and **1i** show nucleophilic reactivities, which lie in between those of benzoyl- and aryl-substituted ylides. The semistabilized ylides **1e**,**f** are the strongest nucleophiles in this series despite the presence of strongly electron-withdrawing groups at the *p*-position of the phenyl ring.

As the nucleophile-specific slope parameter *s* of the dimethylsulfoxonium ylide **1g** differs significantly from those of the dimethylsulfonium ylides **1a**−**f**,**h**,**i**, the relative nucleophilic reactivities of these different types of sulfur ylides have to be compared with respect to a certain reaction partner. Scheme 7 thus shows that **1g** reacts 13 times faster with the benzhydrylium ion **2e** than the most reactive benzoyl-stabilized ylide **1d**, but 3 times more slowly than the benzylic ylide **1e**. In reactions with the weaker electrophile **2h**, **1g** exceeds the reactivity of the benzoyl-substituted sulfur ylide **1d** by more than 10^2 and is even more reactive than the aryl-stabilized sulfur ylide **1e** (Scheme 7).

As indicated in Figure 2, the sulfur ylide **1a** is significantly more nucleophilic in DMSO ($\varepsilon = 46.45$)[13] than in CH_2Cl_2 ($\varepsilon = 8.93$)[13] solution.[12] Obviously, the formation of a sulfonium ion from a delocalized benzhydrylium ion and a sulfur ylide is accompanied by a significant localization of charge; as a result the rates of the reactions of **1a** with benzhydrylium ions increase with increasing solvent polarity.

Figure 3 compares the nucleophilic reactivities of ethoxycarbonyl- and *p*-nitro-phenyl-stabilized sulfur ylides with those of analogously substituted carbanions. Both columns show that Me_2S^+ substitution reduces the nucleophilicity of a carbanionic center more than a cyano group. The right column indicates that a nitro group reduces the reactivity even more than a dimethylsulfonium group. It should be noted, however, that relative stabilizing effects of different groups thus derived, cannot be generalized, because geminal substituent effects are not strictly additive.

A rather poor correlation is found between the nucleophilic reactivities of different classes of carbanions and ylides[8,9c,14] and their pK_{aH} values[7c,15] (Figure S2 of the Supporting Information). Thus Brønsted basicities are also a poor guide for the prediction of nucleophilicities for ylides, as previously shown for acceptor-stabilized carbanions[8] as well as for amide and imide anions.[16]

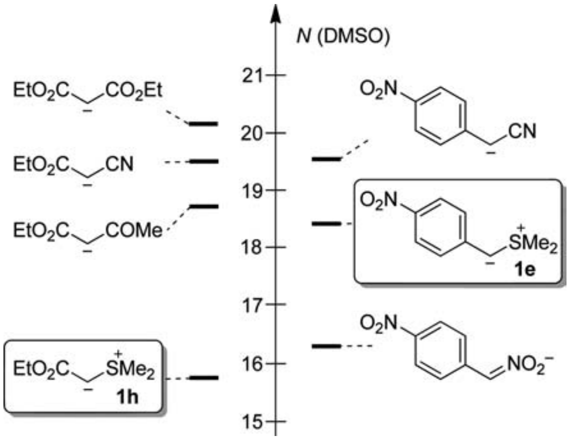


Figure 3. Comparison of the nucleophilicities of different ethoxycarbonyl- and *p*-nitro-phenyl-stabilized carbanions and sulfur ylides in DMSO at 20 °C.

Conclusion

Though the reactions of sulfur ylides with carbocations (see Schemes 3 and 4) yield products which differ from those obtained with Michael acceptors (see Schemes 5 and 6), the rate constants for both types of reactions lie on the same correlation lines (Table 2 and Figure 1), which allow us to include sulfur ylides into the nucleophilicity scale on the basis of eq 1 (Figure 4).

The common correlation lines for carbocations and Michael acceptors furthermore imply that the rate-determining step of the investigated sulfur ylide-mediated cyclopropanations is the same as that for additions of sulfur ylides to carbocations. These findings are in line with a stepwise or highly asynchronous mechanism for the cyclopropanation of Michael acceptors with sulfur ylides, in which the formation of the first C−C bond is rate-determining.[5b,e] As a consequence, eq 1 and the derived nucleophilicity parameters *N* (and *s*) of sulfur ylides **1** can efficiently predict the rates of their reactions with Michael acceptors of known electrophilicity *E*. As previous mechanistic investigations have shown that cyclopropanation reactions with sulfur ylides usually proceed with rate-determining addition steps, followed by fast cyclizations (sometimes accompanied by preceding fast proton-transfer reactions),[5b,e] the rule of thumb that nucleophile−electrophile combinations at room temperature only occur when

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(13) Reichardt, C. *Solvents and Solvent Effects in Organic Chemistry*; Wiley-VCH: Weinheim, 2003.

(14) Bug, T.; Lemek, T.; Mayr, H. *J. Org. Chem.* **2004**, *69*, 7565–7576.

(15) (a) Keeffe, J. R.; Morey, J.; Palmer, C. A.; Lee, J. C. *J. Am. Chem. Soc.* **1979**, *101*, 1295–1297. (b) Olmstead, W. N.; Bordwell, F. G. *J. Org. Chem.* **1980**, *45*, 3299–3305. (c) Arnett, E. M.; Harrelson, J. A. *J. Am. Chem. Soc.* **1987**, *109*, 809–812. (d) Bordwell, F. G. *Acc. Chem. Res.* **1988**, *21*, 456–463. (e) Bordwell, F. G.; Branca, J. C.; Bares, J. E.; Filler, R. *J. Org. Chem.* **1988**, *53*, 780–782. (f) Bordwell, F. G.; Cheng, J.-P.; Bausch, M. J.; Bares, J. E. *J. Phys. Org. Chem.* **1988**, *1*, 209–223. (g) Bordwell, F. G.; Harrelson, J. A.; Satish, A. V. *J. Org. Chem.* **1989**, *54*, 3101–3105. (h) Zhang, X.-M.; Bordwell, F. G. *J. Am. Chem. Soc.* **1994**, *116*, 968–972. (i) Bordwell, F. G.; Satish, A. V. *J. Am. Chem. Soc.* **1994**, *116*, 8885–8889. (j) Goumont, R.; Kizilian, E.; Buncel, E.; Terrier, F. *Org. Biomol. Chem.* **2003**, *1*, 1741–1748. (k) For a comprehensive database of pK_a-values in DMSO, see http://www.chem.wisc.edu/areas/reich/pkatable/.

(16) Breugst, M.; Tokuyasu, T.; Mayr, H. *J. Org. Chem.* **2010**, *75*, 5250–5258.

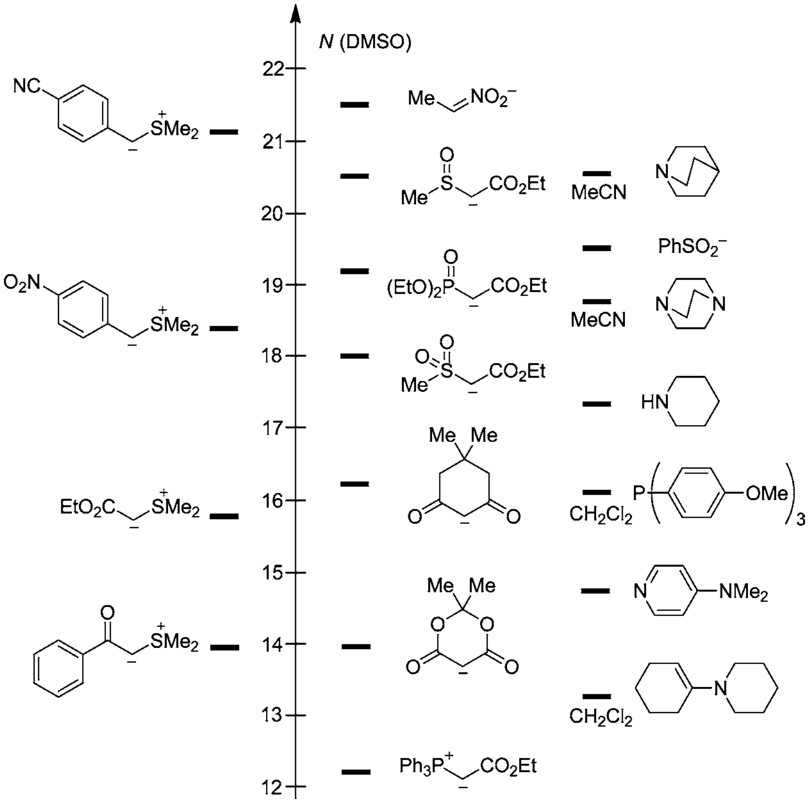

Figure 4. Comparison of the nucleophilicity parameters *N* (in DMSO at 20 °C) of different sulfur ylides with other classes of nucleophiles (data referring to other solvents are marked).

$E + N > -5$ can be employed[9c] to predict whether a certain cyclopropanation reaction is likely to take place.

Experimental Section

Product Analysis. Detailed synthetic procedures for the preparation of the addition products **4**, the cyclopropanes **5**, the dihydrofurans **6** as well as those for the reaction of the benzoyl-stabilized sulfur ylide **1c** with *trans*-4-methoxy-β-nitrostyrene (**2v**) are given in the Supporting Information.

Kinetics. The rates of all reactions were determined photometrically in dry DMSO (H_2O content <50 ppm). The temperature was kept constant (20.0 ± 0.1 °C) by using a circulating bath thermostat. All reactions have been performed under first-order conditions, and a detailed description of the procedure is given in the Supporting Information.

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Supporting Information Available: Details of the kinetic experiments, synthetic procedures, and NMR spectra of all characterized compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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