

Nucleophilicity and Nucleofugality of Phenylsulfinate (PhSO₂[−]): A Key to Understanding its Ambident Reactivity

Mahiuddin Baidya, Shinjiro Kobayashi, and Herbert Mayr*

Department Chemie, Ludwig-Maximilians-Universität München, Butenandtstrasse 5–13 (Haus F), 81377 München, Germany

Received December 3, 2009; E-mail: herbert.mayr@cup.uni-muenchen.de

Abstract: Second-order rate constants for the reactions of the phenylsulfinate ion PhSO₂[−] with benzhydrylium ions Ar₂CH⁺ have been determined in DMSO, acetonitrile, and aqueous acetonitrile solution using laser-flash and stopped-flow techniques. The rate constants follow the correlation equation log *k* (20 °C) = *s*(*N* + *E*), which allows the determination of the nucleophile-specific parameters *N* and *s* for PhSO₂[−] in different solvents. With *N* = 19.60, PhSO₂[−] is a slightly weaker nucleophile than malonate and azide ions in DMSO. While PhSO₂[−] reacts with highly stabilized benzhydrylium ions to give benzhydryl phenyl sulfones exclusively, highly reactive benzhydrylium ions give mixtures of sulfones Ar₂CH–SO₂Ph and sulfinates Ar₂CH–OS(O)Ph; the latter rearrange to the thermodynamically more stable sulfones through an ionization recombination sequence. Sulfones generated from PhSO₂[−] and stabilized amino-substituted benzhydrylium ions undergo heterolysis in aqueous acetonitrile and the rate of formation of the colored benzhydrylium ions was followed spectrophotometrically by stopped-flow techniques. The ranking of the electrofugalities of the benzhydrylium ions (i.e., the relative ionization rates of Ar₂CH–SO₂Ph) was not the inverse of the ranking of their electrophilicities (i.e., the relative reactivities of Ar₂CH⁺ with nucleophiles), which was explained by differences in Marcus intrinsic barriers. While sulfones are thermodynamically more stable than the isomeric sulfinates, the intrinsic barriers for the attack of benzhydrylium ions at the oxygen of PhSO₂[−] are significantly lower than the intrinsic barriers for S-attack, and the activation energies for the attack of carbocations at sulfur are only slightly smaller than those for attack at oxygen. Because reactions of PhSO₂[−] with carbocations of an electrophilicity *E* > −2 (i.e., carbocations which are more reactive than Ph₃C⁺) are diffusion-controlled, the regioselectivities of the reactions of PhSO₂[−] with “ordinary” carbocations do not reflect relative activation energies.

Introduction

Regioselectivities of ambident nucleophiles are usually rationalized by the principle of hard and soft acids and bases (HSAB)¹ or, more quantitatively, by the Klopman-Salem concept of charge and orbital controlled reactions.²

Using these concepts, the predominant S-methylation of the sulfinate ion **1** by the soft electrophile iodomethane³ has been explained by the greater softness of the sulfur center.^{4–6} The exclusive O-ethylation of **1** by the triethyloxonium ion, on the other hand, has been interpreted as the attack of the hard oxonium ion at the hard oxygen center (Table 1).⁷

Table 1. Reactions of Arylsulfinate Ions **1** with Hard and Soft Electrophiles

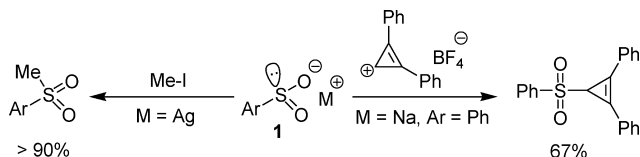
M ⁺	RX	condition	sulfone (%)	ester (%)	ref.
Na ⁺	MeI	DMF, 25 °C	93	7	3a
		MeOH, reflux	98	2	3a
		MeCN, rt	95	0	3b
		THF, 20 °C	93	0	3c
(<i>n</i> Bu) ₄ N ⁺	MeI	THF, 20 °C	93	0	3c
Poly-N ⁺ (Me) ₃ ^a	MeI	Benzene, reflux	95		3d
Na ⁺	Et ₃ O ⁺ BF ₄ [−]	CH ₂ Cl ₂ , rt	0	95	7

^a Supported on Amberlyst A-26.

On the other hand, examples have been reported that do not follow these concepts. Thus, S-methylation of arylsulfinate ions was observed when the silver salt of *p*-tolylsulfinic acid was treated with iodomethane, though silver ions have been claimed to shift methylations with MeI toward the S_N1 mechanism.^{3a,8} When sodium phenylsulfinate was combined with diphenylcyclopropenyl tetrafluoroborate, also S-attack took place,⁹ in spite of the fact that carbenium ions are generally considered to be hard electrophiles (Scheme 1).¹

In previous work, we have demonstrated that the ambident nucleophiles NCS[−], NC[−], NO₂[−], and NCO[−], prototypes for the application of the HSAB model or the Klopman-Salem concept,

- (1) (a) Pearson, R. G. *J. Am. Chem. Soc.* **1963**, 85, 3533–3539. (b) Pearson, R. G. *Science* **1966**, 151, 172–177. (c) Pearson, R. G.; Songstad, J. *J. Am. Chem. Soc.* **1967**, 89, 1827–1836. (d) Pearson, R. G. *J. Chem. Educ.* **1968**, 45, 581–587. (e) Pearson, R. G. *J. Chem. Educ.* **1968**, 45, 643–648. (f) Pearson, R. G. *Chemical Hardness*; Wiley: New York, 1997.
- (2) (a) Klopman, G. *J. Am. Chem. Soc.* **1968**, 90, 223–234. (b) Salem, L. *J. Am. Chem. Soc.* **1968**, 90, 543–552. (c) Fleming, I. *Frontier Orbitals and Organic Chemical Reactions*; Wiley: Chichester, 1976.
- (3) (a) Meek, J. S.; Fowler, J. S. *J. Org. Chem.* **1968**, 33, 3422–3424. (b) Kobayashi, M.; Toriyabe, K. *Sulfur Lett.* **1985**, 3, 117–122. (c) Veenstra, G. E.; Zwaneburg, B. *Synthesis* **1975**, 519–520. (d) Manescalchi, F.; Orena, M.; Savoia, D. *Synthesis* **1979**, 445–446. (e) Weber, J. V.; Schneider, M.; Faller, D. P. *Sulfur Lett.* **1985**, 3, 45–50.

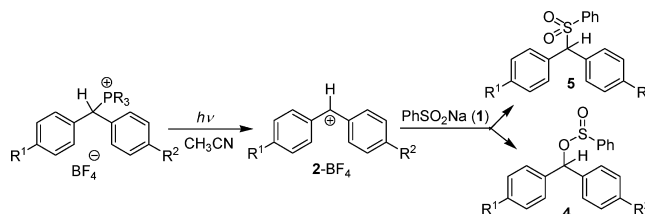
Scheme 1. Reactions of Arylsulfinate Ion **1** with Hard Electrophiles at the Sulfur Center

do not react as predicted by these models.¹⁰ Because these concepts have also been employed to rationalize the ambident reactivity of the phenylsulfinate ion **1**,¹¹ we have now investigated the reactivity of PhSO_2^- (**1**) toward benzhydrylium ions (Ar_2CH^+) of variable electrophilicity. We observed a change of regioselectivities in this reaction series, which is in disagreement with the HSAB model, and we will discuss consequences of these observations for rationalizing the ambident reactivity of PhSO_2^- in general. Furthermore, we will characterize the leaving group ability of the phenylsulfonyl group, which is fundamental for understanding the chemistry of sulfones.

Results

Rates for the reactions of the phenylsulfinate ion **1** with benzhydrylium ions were determined either by studying the kinetics of laser-flash photolytically generated benzhydrylium ions or by stopped-flow techniques using stable benzhydrylium tetrafluoroborates.

Kinetic Studies with Photolytically Generated Ar_2CH^+ . For the study of fast reactions, the method described in Scheme 2 was employed. Solutions of the benzhydrylphosphonium tetrafluoroborates ($\text{Ar}_2\text{CH-PR}_3^+\text{BF}_4^-$) in CH_3CN were irradiated

Scheme 2. Reactivity of the Phenylsulfinate Ion (**1**) toward Benzhydrylium Ions Determined by Laser-Flash Photolytic Techniques (refs 12 and 13)

with 6.5-ns laser pulses (266 nm, 40–60 mJ) to give benzhydrylium ions (Table 2), which were identified by their UV–vis spectra.

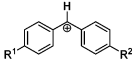
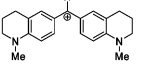
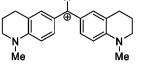
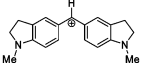
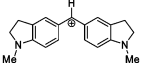
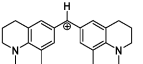
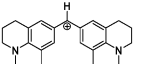
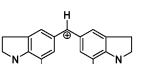
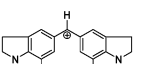
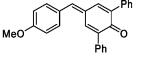
As specified in Table 2, differently substituted phosphines PR_3 have been used as photoleaving groups. Whereas the nature of PR_3 is not crucial for the use of phosphonium ions from highly electrophilic benzhydrylium ions, the situation is different for phosphonium ions from highly stabilized benzhydrylium ions. Because phosphonium salts from Ph_3P and strongly donor-substituted benzhydrylium ions (for example $(\text{jul})_2\text{CH-PPh}_3^+$) easily dissociate into Ar_2CH^+ and PPh_3 , it is not possible to prepare solutions of such phosphonium ions in the presence of PhSO_2^- . In such solutions, benzhydryl phenyl sulfones are formed rapidly, which do not yield benzhydrylium ions upon irradiation with 266 nm laser pulses. We have, therefore, used the more stable tributylphosphonium ions $\text{Ar}_2\text{CH-PBu}_3^+$ as precursors for the photolytic generation of highly stabilized benzhydrylium ions.

When the irradiation of the benzhydrylphosphonium ions was performed in the presence of PhSO_2Na (**1-Na**) in CH_3CN (containing 15-crown-5), the generated benzhydrylium ions reacted with the phenyl sulfinate ion. As **1** was used in high excess, the absorbances of the benzhydrylium ions decrease monoexponentially (Figure 1), and the pseudofirst-order rate

- (4) S-attack in $\text{S}_{\text{N}}2$ and $\text{S}_{\text{N}}2'$ reactions: (a) Colombani, D.; Navarro, C.; Castaing, M. D.; Maillard, B. *Synth. Commun.* **1991**, *21*, 1481–1487. (b) Kabalka, G. W.; Venkataiah, B.; Dong, G. *Tetrahedron Lett.* **2003**, *44*, 4673–4675. (c) Chandrasekhar, S.; Saritha, B.; Narsimulu, C.; Vijay, D.; Sarma, G. D.; Jagadeesh, B. *Tetrahedron Lett.* **2006**, *47*, 2981–2984. (d) Cheng, W.-C.; Halm, C.; Evarts, J. B.; Olmstead, M. M.; Kurth, M. J. *J. Org. Chem.* **1999**, *64*, 8557–8562. (e) Wu, J.-P.; Emeigh, J.; Su, X.-P. *Org. Lett.* **2005**, *7*, 1223–1225. (f) Culvenor, C. C. J.; Davies, W.; Heath, N. S. *J. Chem. Soc.* **1949**, 278–282. (g) Aleksiev, D. I.; Ivanova, S. *Phosphorus, Sulfur, Silicon* **1995**, *101*, 103–108. (h) Abrunhosa, I.; Gulea, M.; Masson, S. *Synthesis* **2004**, 928–934. (i) Hu, Y.; Chen, Z.-C.; Le, Z.-G.; Zheng, Q.-G. *Synth. Commun.* **2004**, *34*, 4031–4035. (j) Suryakiran, N.; Reddy, T. S.; Ashalatha, K.; Lakshman, M.; Venkateswarlu, Y. *Tetrahedron Lett.* **2006**, *47*, 3853–3856. (k) Crozet, M. D.; Remusat, V.; Curti, C.; Vanelle, P. *Synth. Commun.* **2006**, *36*, 3639–3646. (l) Guan, Z.-H.; Zuo, W.; Zhao, L.-B.; Ren, Z.-H.; Liang, Y.-M. *Synthesis* **2007**, 1465–1470. (m) Payne, R. J.; Peyrot, F.; Kerbarh, O.; Abell, A. D.; Abell, C. *ChemMedChem* **2007**, *2*, 1015–1029. (n) Kanai, T.; Kanagawa, Y.; Ishii, Y. *J. Org. Chem.* **1990**, *55*, 3274–3277. (o) Pyne, S.; David, D. M.; Dong, Z. *Tetrahedron Lett.* **1998**, *39*, 8499–8502. (p) Murakami, T.; Furusawa, K. *Synthesis* **2002**, 479–482. (q) Bordwell, F. G.; Mecca, T. G. *J. Am. Chem. Soc.* **1972**, *94*, 5829–5837. (r) Szabo, R.; Crozet, M. D.; Vanelle, P. *Synlett* **2008**, 2836–2840. (s) Kornblum, N.; Kestner, M. N.; Boyd, S. D.; Cattran, L. C. *J. Am. Chem. Soc.* **1973**, *95*, 3356–3361.
- (5) S-attack in transition-metal catalyzed allylations and arylations: (a) Gais, H.-J.; Jagusch, T.; Spalthoff, N.; Gerhards, F.; Frank, M.; Raabe, G. *Chem.—Eur. J.* **2003**, *9*, 4202–4211. (b) Jegelka, M.; Plietker, B. *Org. Lett.* **2009**, *11*, 3462–3465. (c) Watanabe, S.; Kurosawa, H. *Organometallics* **1998**, *17*, 479–482. (d) Baskin, J. M.; Wang, Z. *Org. Lett.* **2002**, *4*, 4423–4425. (e) Yokogi, M.; Kuwano, R. *Tetrahedron Lett.* **2007**, *48*, 6109–6112.
- (6) S-attack in nucleophilic aromatic substitutions: (a) Ulman, A.; Urankar, E. *J. Org. Chem.* **1989**, *54*, 4691–4692. (b) Grushin, V. V.; Kantor, M. M.; Tolstaya, T. P.; Shcherbina, T. M. *Russ. Chem. Bull.* **1984**, *33*, 2130–2135. (c) Baron, A.; Sandford, G.; Slater, R.; Yufit, D. S.; Howard, J. A. K.; Vong, A. J. *Org. Chem.* **2005**, *70*, 9377–9381. (d) Koumbis, A. E.; Kyzsa, C. M.; Savva, A.; Varvoglis, A. *Molecules* **2005**, *10*, 1340–1350. (e) Finley, K. T.; Kaiser, R. S.; Reeves, R. L.; Werimont, G. J. *Org. Chem.* **1969**, *34*, 2083–2090.

- (7) Kobayashi, M. *Bull. Chem. Soc. Jpn.* **1966**, *39*, 1296–1297.
- (8) Reference 2c, pp 40–42.
- (9) Breslow, R.; Brown, J.; Gajewski, J. J. *J. Am. Chem. Soc.* **1967**, *89*, 4383–4390.
- (10) For NCS^- : (a) Loos, R.; Kobayashi, S.; Mayr, H. *J. Am. Chem. Soc.* **2003**, *125*, 14126–14132. For NC^- : (b) Tishkov, A. A.; Mayr, H. *Angew. Chem., Int. Ed.* **2005**, *44*, 142–145. For NO_2^- : (c) Tishkov, A. A.; Schmidhammer, U.; Roth, S.; Riedle, E.; Mayr, H. *Angew. Chem., Int. Ed.* **2005**, *44*, 4623–4626. For NCO^- : (d) Schaller, H. F.; Schmidhammer, U.; Riedle, E.; Mayr, H. *Chem.—Eur. J.* **2008**, *14*, 3866–3868.
- (11) For examples of ambident reactivity of phenyl sulfinate ion: (a) Stirling, C. J. M. *Int. J. Sulfur Chem., Part B* **1971**, *6*, 277–320. (b) Kielbasinski, P.; Zurawinski, R.; Drabowicz, J.; Mikolajczyk, M. *Tetrahedron* **1988**, *44*, 6687–6692. (c) Hogg, D. R.; Robertson, A. J. *Chem. Soc., Perkin Trans. 1* **1979**, 1125–1128. (d) Michalski, J.; Modro, T.; Wiczorkowski, J. *J. Chem. Soc.* **1960**, 1665–1670. (e) Kondratenko, N. V.; Sambur, V. P.; Yagupol'skii, L. M. *Z. Org. Khim.* **1971**, *7*, 2382–2388. (f) Oda, M.; Kajioaka, T.; Uchiyama, T.; Nagara, K.; Okujima, T.; Ito, S.; Morita, N.; Sato, T.; Miyatake, R.; Kuroda, S. *Tetrahedron* **1999**, *55*, 6081–6096. (g) Grossert, J. S.; Dubey, P. K.; Elwood, T. *Can. J. Chem.* **1985**, *63*, 1263–1267. (h) Schank, K.; Weber, A. *Chem. Ber.* **1972**, *105*, 2188–2196. (i) Basava, V.; Flores, B.; Giovine, M.; Liscisyn, T.; Walck, K.; Boyko, W.; Giuliano, R. *J. Carbohydr. Chem.* **2008**, *27*, 389–400.
- (12) (a) Kobayashi, S.; Hari, Y.; Hasako, T.; Koga, K.; Yamataka, H. *J. Org. Chem.* **1996**, *61*, 5274–5279. (b) Kobayashi, S.; Roth, S.; Riedle, E.; Tishkov, A. A.; Mayr, H. *Rev. Sci. Instrum.* **2005**, *76*, 093111. (c) McClelland, R. A. In *Reactive Intermediate Chemistry*; Moss, R. A.; Platz, M. S.; Jones, M., Jr., Eds.; Wiley: New York, 2004; Chapter 1, pp 3–40. (d) Das, P. K. *Chem. Rev.* **1993**, *93*, 119–144. (e) Peters, K. *Annu. Rev. Phys. Chem.* **1987**, *38*, 253–270.
- (13) Baidya, M.; Kobayashi, S.; Brotzel, F.; Schmidhammer, U.; Riedle, E.; Mayr, H. *Angew. Chem., Int. Ed.* **2007**, *46*, 6176–6179.

Table 2. Electrophilicity Parameters E of the Benzhydrylium Ions (Ar_2CH^+) **2** and the Quinone Methide (QM) **3** and Second-Order Rate Constants (k) for their Combination Reactions with PhSO_2^- (**1**) in CH_3CN at 20 °C

						
	Ar_2CH^+	R^1	R^2	E^a	PR_3^b	$k [\text{L mol}^{-1} \text{s}^{-1}]$
2a	Ph_2CH^+	H	H	5.90		
2b	$(\text{tol})_2\text{CH}^+$	Me	Me	3.63	PPh_3	1.87×10^{10}
2c	$(\text{pop})(\text{Ph})\text{CH}^+$	OPh	H	2.90	PPh_3	1.92×10^{10}
2d	$(\text{ani})(\text{Ph})\text{CH}^+$	OMe	H	2.11	PPh_3	2.11×10^{10}
2e	$(\text{ani})(\text{tol})\text{CH}^+$	OMe	Me	1.48		
2f	$(\text{ani})(\text{pop})\text{CH}^+$	OMe	OPh	0.61		
2g	$(\text{ani})_2\text{CH}^+$	OMe	OMe	0	$\text{P}(4\text{-ClC}_6\text{H}_4)_3$	1.24×10^{10}
2h	$(\text{fur})(\text{ani})\text{CH}^+$			-0.56	PPh_3	1.07×10^{10}
2i	$(\text{fur})_2\text{CH}^+$			-1.36	$\text{P}(4\text{-ClC}_6\text{H}_4)_3$	1.01×10^{10}
2j	$(\text{pfa})_2\text{CH}^+$	$\text{N}(\text{Ph})\text{CH}_2\text{CF}_3$	$\text{N}(\text{Ph})\text{CH}_2\text{CF}_3$	-3.14	PPh_3	3.98×10^9
2k	$(\text{mfa})_2\text{CH}^+$	$\text{N}(\text{CH}_3)\text{CH}_2\text{CF}_3$	$\text{N}(\text{CH}_3)\text{CH}_2\text{CF}_3$	-3.85	PPh_3	1.53×10^9
2l	$(\text{dpa})_2\text{CH}^+$	NPh_2	NPh_2	-4.72	PPh_3	1.04×10^9
2m	$(\text{mor})_2\text{CH}^+$	$\text{N}(\text{CH}_2\text{CH}_2)_2\text{O}$	$\text{N}(\text{CH}_2\text{CH}_2)_2\text{O}$	-5.53	$\text{P}(4\text{-OMeC}_6\text{H}_4)_3$	1.66×10^8
2n	$(\text{mpa})_2\text{CH}^+$	$\text{N}(\text{Ph})\text{CH}_3$	$\text{N}(\text{Ph})\text{CH}_3$	-5.89	$\text{P}(4\text{-OMeC}_6\text{H}_4)_3$	2.19×10^8
2o	$(\text{dma})_2\text{CH}^+$	$\text{N}(\text{CH}_3)_2$	$\text{N}(\text{CH}_3)_2$	-7.02	$\text{P}(4\text{-OMeC}_6\text{H}_4)_3$	4.22×10^7
2p	$(\text{pyr})_2\text{CH}^+$	$\text{N}(\text{CH}_2)_4$	$\text{N}(\text{CH}_2)_4$	-7.69	$\text{P}(n\text{Bu})_3$	1.97×10^7
2q	$(\text{thq})_2\text{CH}^+$			-8.22	$\text{P}(n\text{Bu})_3$	1.01×10^7
2r	$(\text{ind})_2\text{CH}^+$			-8.76	$\text{P}(n\text{Bu})_3$	4.38×10^6
2s	$(\text{jul})_2\text{CH}^+$			-9.45	$\text{P}(n\text{Bu})_3$	1.89×10^6
2t	$(\text{lil})_2\text{CH}^+$			-10.04	$\text{P}(n\text{Bu})_3$	7.37×10^5
3	QM			-12.18		

^a Empirical electrophilicity parameter from ref 14b, c. ^b Photoleaving group for the photolytic generation of Ar_2CH^+ from $\text{Ar}_2\text{CH-PR}_3^+\text{BF}_4^-$.

constants k_{obs} were obtained by fitting the decays of the absorbances to the monoexponential function $A_t = A_0 e^{-k_{\text{obs}} t} + C$. From the slopes of the linear plots of k_{obs} vs **[1]** (Figure 1) the second-order rate constants k ($\text{L mol}^{-1} \text{s}^{-1}$) were derived and are listed in Table 2. The intercepts of the k_{obs} vs **[1]** plots reflect the background reaction. They are small for highly stabilized benzhydrylium ions and increase with increasing electrophilicities of the benzhydrylium ions.

Kinetic Studies with Persistent Benzhydrylium Salts $\text{Ar}_2\text{CH}^+\text{BF}_4^-$. Rate constants $k \leq 10^6 \text{ L mol}^{-1} \text{s}^{-1}$ have been determined by mixing solutions of $\text{Ar}_2\text{CH}^+\text{BF}_4^-$ and PhSO_2Na in a stopped-flow apparatus and following the decay of the electrophiles' absorbances spectrophotometrically using the

equipment described previously.^{14,15} Phenylsulfonate ion **1** was generally used in high excess over $\text{Ar}_2\text{CH}^+\text{BF}_4^-$ to achieve

- (14) (a) Mayr, H.; Patz, M. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 938–957. (b) Mayr, H.; Bug, T.; Gotta, M. F.; Hering, N.; Irrgang, B.; Janker, B.; Kempf, B.; Loos, R.; Ofial, A. R.; Remennikov, G.; Schimmel, H. *J. Am. Chem. Soc.* **2001**, *123*, 9500–9512. (c) Lucius, R.; Loos, R.; Mayr, H. *Angew. Chem., Int. Ed.* **2002**, *41*, 91–95. (d) Mayr, H.; Ofial, A. R. In *Carbocation Chemistry*; Olah, G. A., Prakash, G. K. S., Eds.; Wiley: Hoboken, NJ, 2004; Chapter 13, pp 331–358.
- (15) (a) Mayr, H.; Kempf, B.; Ofial, A. R. *Acc. Chem. Res.* **2003**, *36*, 66–77. (b) Mayr, H.; Ofial, A. R. *Pure Appl. Chem.* **2005**, *77*, 1807–1821. (c) Mayr, H.; Ofial, A. R. *J. Phys. Org. Chem.* **2008**, *21*, 584–595.

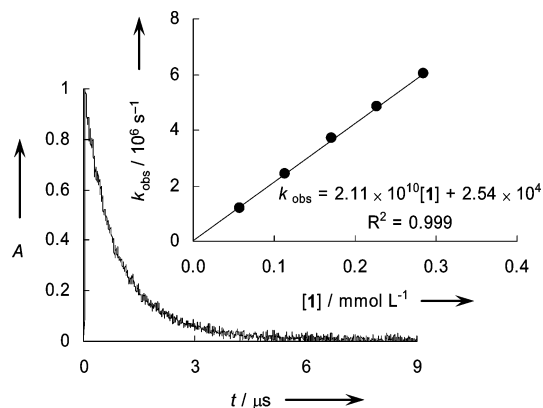


Figure 1. Exponential decay of the absorbance A at 455 nm and linear correlation of the pseudofirst-order rate constants k_{obs} vs $[1]$ for the reaction of (ani)(Ph)CH⁺ with **1** in CH₃CN at 20 °C.

Table 3. Second-Order Rate Constants (k) for the Reactions of PhSO₂[−] (**1**) with the Benzhydrylium Ions (Ar₂CH⁺) and the Quinone Methide (QM) at 20 °C

solvent	N, s^a	Ar ₂ CH ⁺	k [L mol ^{−1} s ^{−1}]
DMSO	19.60, 0.60	(ind) ₂ CH ⁺	2.43×10^6
		(jul) ₂ CH ⁺	1.61×10^6
		(lil) ₂ CH ⁺	6.85×10^5
			7.38×10^{5b}
		QM	2.57×10^4
CH ₃ CN	20.11, 0.59	Ar ₂ CH ⁺	see Table 2
50W50AN ^d	13.75, 0.68	(dma) ₂ CH ⁺	3.48×10^4
		(pyr) ₂ CH ⁺	1.46×10^4
		(thq) ₂ CH ⁺	6.16×10^3
		(ind) ₂ CH ⁺	2.27×10^3
	14.09, 0.66 ^e	(dma) ₂ CH ⁺	4.41×10^{4c}
		(pyr) ₂ CH ⁺	1.86×10^{4c}
		(thq) ₂ CH ⁺	8.24×10^{3c}
		(ind) ₂ CH ⁺	3.09×10^{3c}

^a Nucleophile-specific parameters N and s according to eq 3; for determination see below. ^b In the presence of 1.06 equiv of 15-crown-5. ^c Rate constants at 25 °C. ^d 50W50AN = 50% water and 50% acetonitrile (v/v). ^e N and s parameters correspond to 25 °C.

pseudofirst-order conditions. As mentioned for the laser-flash experiments, the plots of k_{obs} versus the concentration of PhSO₂[−] were linear, with the second-order rate constants (Table 3) being the slopes of the correlation lines. While in DMSO all benzhydrylium ions react quantitatively with PhSO₂[−], in 50% aqueous acetonitrile (50W50AN) only highly electrophilic benzhydrylium ions were found to react with PhSO₂[−]. The corresponding reactions with less electrophilic benzhydrylium ions ($E < -8$) are reversible, and in some cases the degree of ion combination was so small that rate constants for the cation–anion combinations could not be measured. To compare the reactivities in 50W50AN with other kinetic data, some of which refer to 20 °C and others to 25 °C, kinetic studies in this solvent were performed at both temperatures.

Product Studies. Addition of PhSO₂Na to the blue solutions of (lil)₂CH⁺BF₄[−] or (dma)₂CH⁺BF₄[−] in DMSO-*d*₆ leads to decolorization, and the NMR spectra revealed the exclusive formation of the sulfones (lil)₂CH–SO₂Ph and (dma)₂CH–SO₂Ph, respectively (Table 4). The crystal structure of (dma)₂CH–SO₂Ph unambiguously demonstrates the S-attack of the carbocation on the phenylsulfinate ion.¹⁶ Attempts to isolate (lil)₂CH–SO₂Ph by aqueous

Table 4. Benzhydrylations of PhSO₂Na (**1**-Na) in DMSO or in DMSO-*d*₆ at Room Temperature (Details of the Individual Experiments are Given in the Supporting Information)

entry	Ar ₂ CH-X	R ¹	R ²	time	4:5	δ_{H} [ppm]
						4 ^b 5 ^c
1	2t -BF ₄	(lil) ₂ CH ⁺ ^a		1 min	0:100	5.51
2				3 h	0:100	
3	2o -BF ₄	NMe ₂	NMe ₂	1 min	0:100	5.66
4				3 h	0:100 ^d	
5	2m -BF ₄	(mor) ₂ CH ⁺ ^a		20 min	0:100 ^e	5.43
6	2g -Cl	OMe	OMe	1 min	46:54	6.41 5.95
7	2g -Br			1 min	33:67 ^j	
8	2g -Cl			1 h	0:100 ^f	
	or -Br					
9	2f -Cl	OMe	OPh	1 min	56:44	6.46, 6.47 ⁱ 6.04
10	2f -Br			1 min	43:57 ^j	
11	2f -Cl			10 h	0:100	
	or -Br					
12	2e -Cl	OMe	Me	1 min	63:37	6.41, 6.42 ⁱ 5.96
13	2e -Br			1 min	51:49 ^j	
14	2e -Cl			1 d	0:100	
	or -Br					
15	2d -Cl	OMe	H	1 min	67:33 ^g	6.46, 6.47 ⁱ 6.03
16	2d -Br			1 min	56:44 ^j	
17	2d -Cl			12 d	0:100	
	or -Br					
18	2b -Cl	Me	Me	1 min	67:33 ^g	6.42 5.99
19	2b -Br			1 min	67:33 ^j	
20	2a -Cl	H	H	4 h/70 °C	0:100 ^h	6.06

^a For structure, see Table 2. ^b δ_{H} (DMSO-*d*₆) for Ar₂CH–OS(O)Ph. ^c δ_{H} (DMSO-*d*₆) for Ar₂CH–SO₂Ph; **5m** in CD₃CN. ^d Isolated yield of **5o**: 49%. ^e Isolated yield of **5m**: 32%; reaction in CH₃CN/15-crown-5. ^f Isolated yield of **5g**: 86%. ^g This ratio is approximate because of partial overlap of the proton of benzhydryl chloride (Ar₂CH–Cl). ^h Isolated yield of **5a**: 82%. ⁱ A mixture of diastereomers (1:1) was formed. ^j In DMSO-*d*₆/CD₃CN (≈1:1).

workup were unsuccessful because of its rapid heterolysis leading to the regeneration of (lil)₂CH⁺ and PhSO₂[−].

Because benzhydrylium tetrafluoroborates of electrophilicity $E > -7$ (Table 2) react with DMSO, it was not possible to study the reactions of (mor)₂CH⁺ and of alkoxy-substituted benzhydrylium ions by combining the corresponding tetrafluoroborates Ar₂CH⁺BF₄[−] with PhSO₂Na in DMSO solution. However, (mor)₂CH–SO₂Ph was formed and isolated when (mor)₂CH⁺BF₄[−] was reacted with PhSO₂Na/15-crown-5 in CH₃CN (Table 4). Product studies with methoxy- and methyl-substituted benzhydryl derivatives were carried out by treating the corresponding benzhydryl bromides and chlorides (Ar₂CH–Hal) with PhSO₂Na in DMSO.

As shown in Table 4, amino substituted benzhydrylium ions (entries 1–5) on the one hand, and methoxy- and methyl-substituted substituted benzhydryl derivatives (entries 6–17) on the other, showed a different pattern of reactivity. While the NMR spectra measured just after mixing (~1 min) of PhSO₂Na with 1 equiv of (lil)₂CH⁺BF₄[−] or (dma)₂CH⁺BF₄[−] in DMSO-*d*₆ were identical to those observed after several hours (entries 1–4), changes of the NMR spectra with time were observed, when more electrophilic benzhydrylium ions were combined with PhSO₂Na (entries 6–17). Thus, the ¹H NMR spectrum

(16) Baidya, M.; Mayr, H.; Mayer, P. *Acta Crystallogr., Sec. E: Struct. Rep. Online* **2009**, 65, o3035.

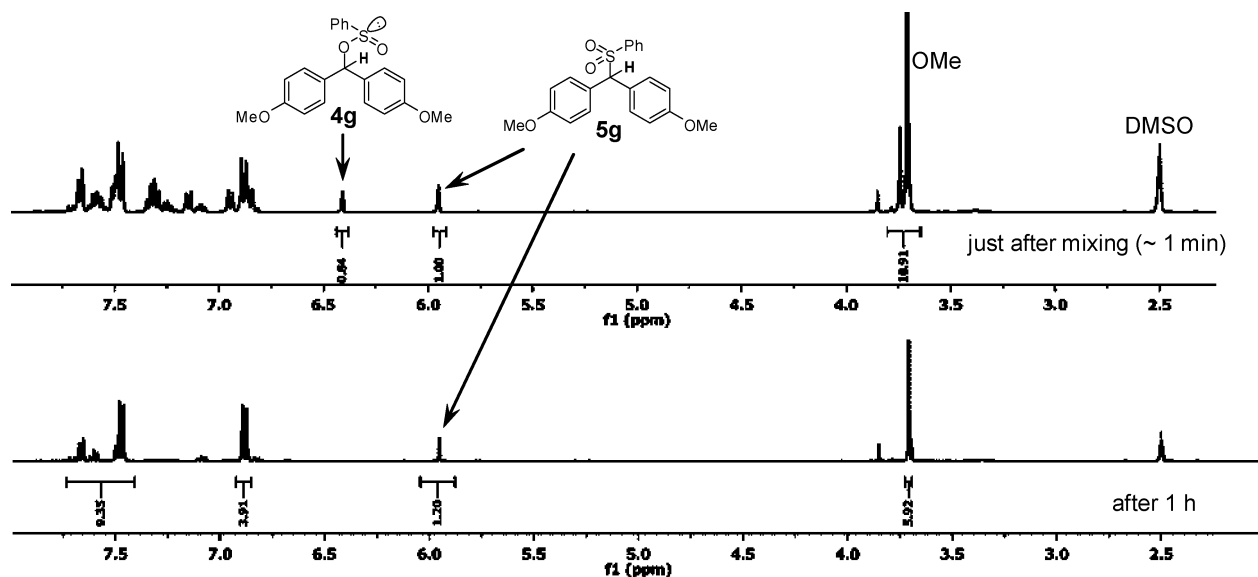


Figure 2. ^1H NMR spectra taken 1 min (top) and 1 h (bottom) after combining PhSO_2Na with $(\text{ani})_2\text{CHCl}$ (**2g-Cl**) in $\text{DMSO}-d_6$.

observed immediately after mixing equimolar amounts of **2g-Cl** or **2g-Br** and PhSO_2Na in $\text{DMSO}-d_6$ showed signals of two compounds, which were assigned to the sulfinate ester $(\text{ani})_2\text{CH}-\text{OS}(\text{O})\text{Ph}$ (**4g**) and the sulfone $(\text{ani})_2\text{CH}-\text{SO}_2\text{Ph}$ (**5g**, Figure 2, Table 4, entries 6 and 7). The spectrum taken after 1 h showed the complete conversion of **4g** into sulfone **5g** (Figure 2, Table 4, entry 8). Side products were not observed in any of the reactions described in Table 4.

Under the same conditions, the combination of the unsymmetrical benzhydryl chloride **2f-Cl** with PhSO_2Na gave a 28: 28: 44 mixture of the two diastereomers **4f** and **4f'** and the sulfone **5f** (Table 4, entry 9). Page S11 in the Supporting Information shows two signals at $\delta = 6.46$ and $\delta = 6.47$ ppm for the benzhydrylium protons of the diastereomeric sulfonates **4f** and **4f'** and the signal at $\delta = 6.04$ ppm for the benzhydrylium proton of the sulfone **5f**. In addition, three methoxy signals were observed, two for the diastereomeric sulfonates ($\delta = 3.75$ and 3.72 ppm), and one for the sulfone at $\delta = 3.71$ ppm. The assignment of these signals to the products of O-attack (**4f**, **4f'**) and S-attack (**5f**) is corroborated by the ^{13}C NMR signals for the benzhydryl carbons of **4f** and **4f'** at $\delta = 79.3$ and 79.6 ppm and one signal for the benzhydryl carbon of the sulfone **5f** ($\delta = 71.7$ ppm). After 10 h at room temperature, only the signals for sulfone **5f** remained (Table 4, and entry 11). Similar phenomena have been observed for **2f-Br** and for the unsymmetrical benzhydryl systems **2d-Cl**, **Br** and **2e-Cl**, **Br** (Table 4, entries 12–17 and Supporting Information pp S12–S27). The sulfones **5d–g**, which were formed after extended reaction times were stable and could be purified by column chromatography. The dimethyl substituted benzhydryl halides **2b-Cl**, **Br** gave 2: 1 mixtures of **4b** and **5b**. The rearrangement **4b** $\rightarrow$ **5b** was very slow at room temperature, and after 10 days the NMR spectrum showed the presence of **4b**, **5b**, and unidentified decomposition products. The parent benzhydryl chloride **2a-Cl** did not react with **1** at room temperature in DMSO. Heating at 70°C for 4 h gave 82% of the sulfone **5a**, the structure of which was confirmed by X-ray analysis.¹⁷ Details are given in the Supporting Information.

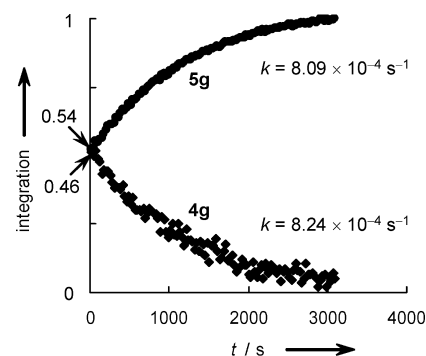


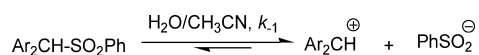
Figure 3. NMR spectroscopic determination of the rate of rearrangement of $(\text{ani})_2\text{CH}-\text{OS}(\text{O})\text{Ph}$ (**4g**) into $(\text{ani})_2\text{CH}-\text{SO}_2\text{Ph}$ (**5g**) in DMSO at 20°C .

Kinetics of the Sulfinate–Sulfone Rearrangement. As shown in the preceding section, the reaction of $(\text{ani})_2\text{CHCl}$ with PhSO_2Na in DMSO yields a 46:54 mixture of the sulfinate **4g** and the sulfone **5g**, which was eventually converted into pure sulfone **5g**. From the NMR integrals of the benzhydrylium protons one can derive the rate of the isomerization **4g** $\rightarrow$ **5g** (Figure 3). The first-order rate constant derived from the decay of the benzhydrylium proton of **4g** ($k = 8.24 \times 10^{-4} \text{ s}^{-1}$) agreed within experimental error with that derived from the growth of the benzhydrylium proton of **5g** ($k = 8.09 \times 10^{-4} \text{ s}^{-1}$).

When this rearrangement was studied in the presence of variable concentrations of PhSO_2Na in $\text{DMSO}-d_6$, the observed rate constants k were found to be independent of the concentration of PhSO_2Na (Supporting Information p S51). This observation excludes that the rearrangement results from a bimolecular process, that is, backside attack of the S-atom of **1** at the benzhydryl carbon of **4g** and suggests an ionization recombination mechanism, in agreement with earlier suggestions.¹⁸

(17) Baidya, M.; Mayr, H.; Mayer, P. *Acta Crystallogr., Sec. E: Struct. Rep. Online* **2009**, *65*, o3224.

(18) For rearrangement of sulfinate esters see: (a) Drawish, D.; McLaren, R. *Tetrahedron Lett.* **1962**, *3*, 1231–1237. (b) Darwish, D.; Preston, E. A. *Tetrahedron Lett.* **1964**, *5*, 113–118. (c) Arcus, C. L.; Balfe, M. P.; Kenyon, J. J. *Chem. Soc.* **1938**, 485–493. (d) Wragg, A. H.; McFadyen, J. S.; Stevens, T. S. *J. Chem. Soc.* **1958**, 3603–3605. (e) Cope, A. C.; Morrison, D. E.; Field, L. *J. Am. Chem. Soc.* **1950**, *72*, 59–67. (f) Ciuffarin, E.; Isola, M.; Fava, A. *J. Am. Chem. Soc.* **1968**, *90*, 3594–3595.

Scheme 3. Heterolysis of $\text{Ar}_2\text{CH}-\text{SO}_2\text{Ph}$ 

Heterolyses of Benzhydryl Phenyl Sulfones. As mentioned above, the highly stabilized benzhydrylium ions $(\text{lil})_2\text{CH}^+$ and $(\text{jul})_2\text{CH}^+$ combine with PhSO_2^- in anhydrous CH_3CN and DMSO to give sulfones almost quantitatively, while no reaction takes place in 50% aqueous acetonitrile. This observation suggested the possibility of determining the rates of the heterolysis reactions of benzhydryl phenyl sulfones (Scheme 3).¹⁹

For that purpose, colorless solutions of benzhydryl phenyl sulfones were generated by combining benzhydrylium tetrafluoroborates ($E < -8.0$) with 4 to 40 equivalents of PhSO_2Na in CH_3CN in the presence of 15-crown-5. When these solutions were mixed with pure distilled water or aqueous acetonitrile, the blue color of benzhydrylium ions appeared due to heterolysis of the sulfones (Scheme 3). Monitoring this process by UV-vis spectroscopy with a stopped-flow instrument showed that the increase of the benzhydrylium absorbances generally followed single exponentials (eq 1, Figure 4) from which the rate constants k_{obs} were derived.

$$[\text{Ar}_2\text{CH}^+] = [\text{Ar}_2\text{CH}^+]_{\text{eq}}(1 - e^{-k_{\text{obs}}t}) \quad (1)$$

The end absorbances A_∞ obtained from $(\text{lil})_2\text{CH}-\text{SO}_2\text{Ph}$ and $(\text{jul})_2\text{CH}-\text{SO}_2\text{Ph}$ in 50W50AN and 40W60AN decreased slightly when the heterolyses were performed in the presence of increasing concentrations of phenylsulfinate ions; concomitantly the first-order rate constants k_{obs} increased slightly (Figure 5, lower line). These effects were more pronounced when $(\text{ind})_2\text{CH}-\text{SO}_2\text{Ph}$ and $(\text{thq})_2\text{CH}-\text{SO}_2\text{Ph}$ were exposed to aqueous acetonitrile under the same conditions (Figure 5, upper line) indicating reversible ionization processes. As the observed rate constants (k_{obs}) for reversible reactions are the sum of forward (k_{-1}) and backward (k) reactions (eq 2),²⁰ the ionization rate constants k_{-1} (Table 5) were obtained as the intercepts of the plots of k_{obs} versus the concentrations of PhSO_2Na . Table 5 shows that the ionization rate constants k_{-1} are generally higher in 50W50AN than in 40W60AN solvent mixtures.

$$k_{\text{obs}} = k_{-1} + k[\text{PhSO}_2^-] \quad (2)$$

According to formal kinetics²⁰ the slopes of the plots of k_{obs} vs $[\text{PhSO}_2^-]$ of the heterolysis reactions (Figure 5) reflect the second-order rate constants of the reverse reactions, that is, the

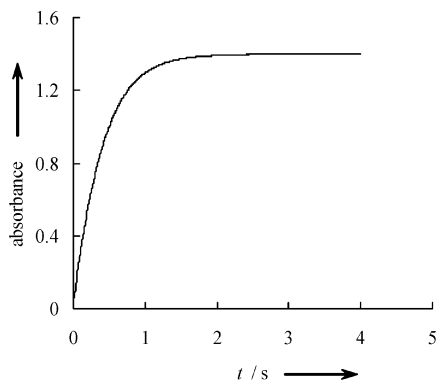


Figure 4. Increase of absorbance at 632 nm during the heterolysis of $(\text{lil})_2\text{CH}-\text{SO}_2\text{Ph}$ in 50W50AN at 25 °C.

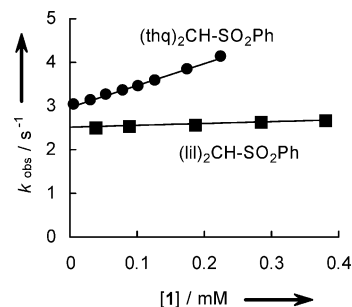


Figure 5. Dependence of the observed rate constants (k_{obs}) for the ionization of $(\text{lil})_2\text{CH}-\text{SO}_2\text{Ph}$ and $(\text{thq})_2\text{CH}-\text{SO}_2\text{Ph}$ on the concentration of PhSO_2Na (1) in 50W50AN at 25 °C.

Table 5. Ionization Rate Constants k_{-1} of Benzhydryl Phenyl Sulfones in Different Solvents at 25 °C

$\text{Ar}_2\text{CH}-\text{SO}_2\text{Ph}$	$k_{-1} [\text{s}^{-1}]$		
	50W50AN	40W60AN ^a	20W80AN ^b
$(\text{lil})_2\text{CH}-\text{SO}_2\text{Ph}$	2.51	1.67	
	1.54 ^c	1.04 ^c	0.49 ^c
$(\text{jul})_2\text{CH}-\text{SO}_2\text{Ph}$	10.9	6.02	
$(\text{ind})_2\text{CH}-\text{SO}_2\text{Ph}$	1.14	0.77	
$(\text{thq})_2\text{CH}-\text{SO}_2\text{Ph}$	2.97		

^a 40W60AN = 40% water and 60% acetonitrile (v/v). ^b 20W80AN = 20% water and 80% acetonitrile (v/v). ^c At 20 °C.

rate constants for the ion combinations. For the reactions of $(\text{ind})_2\text{CH}^+$ and $(\text{thq})_2\text{CH}^+$ with PhSO_2^- in 50W50AN, these second-order rate constants have independently been determined from the decay of the benzhydrylium absorbances at high concentrations of PhSO_2^- (Table 3). The observation that the rate constants for the ion combinations, which are derived from the heterolysis reactions (e.g., upper line in Figure 5), are 1.7–1.8 times smaller than the directly measured ones (Table 3) is probably due to the fact that the term $k[\text{PhSO}_2^-]$ in eq 2 is small compared to k_{-1} and, therefore, does not give access to reliable rate constants for the reverse reactions. From the linear correlation between k_{obs} and $[\text{PhSO}_2^-]$ (Figure 1 and Supporting Information pp S43–S47), we can exclude that this discrepancy is due to variable ion strength.

Discussion

Nucleophilicity of Phenyl Sulfinate. In previous work, we have shown that the reactions of carbocations with nucleophiles can be described by eq 3, where k is a second-order rate constant, E is a nucleophile-independent electrophilicity parameter, and N and s are electrophile-independent nucleophile-specific parameters.^{14,15}

- (19) Reactions involving PhSO_2^- as a leaving group: (a) Koutek, B.; Pavlickova, L.; Soucek, M. *Synth. Commun.* **1976**, *6*, 305–308. (b) Ito, S.; Tanaka, Y.; Kakehi, A.; Kondo, K.-I. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 1920–1923. (c) Das, B.; Damodar, K.; Bhunia, N. *J. Org. Chem.* **2009**, *74*, 5607–5609. (d) Rossen, K.; Jakubec, P.; Kiesel, M.; Janik, M. *Tetrahedron Lett.* **2005**, *46*, 1819–1821. (e) Chang, Y.-F.; Jiang, Y.-R.; Cheng, W.-C. *Tetrahedron Lett.* **2008**, *49*, 543–547. (f) Ghera, E.; Yechezkel, T.; Hassner, A. *J. Org. Chem.* **1990**, *55*, 5977–5982. (g) Nozaki, H.; Yamamoto, Y.; Nisimura, T. *Tetrahedron Lett.* **1968**, *9*, 4625–4626. (h) Richter, D.; Hampel, N.; Singer, T.; Ofial, A. R.; Mayr, H. *Eur. J. Org. Chem.* **2009**, 3203–3211.
- (20) (a) Maskill, H. *The Investigation of Organic Reactions and Their Mechanisms*; Blackwell Publishing: Oxford, 2006. (b) Schmid, R.; Sapunov, V. N. *Non-Formal Kinetics*; Verlag Chemie: Weinheim, 1982.

$$\log k_{20^\circ\text{C}} = s(N + E) \quad (3)$$

To determine the parameters N and s for phenyl sulfinate **1**, the second-order rate constants of their reactions with benzhydrylium ions have been plotted against the corresponding electrophilicity parameters E (Figure 6).

Figure 6 shows that the reactions of the carbocations **2** with **1** generally follow eq 3 in the activation controlled region. However, when highly reactive carbocations are used, the diffusion-controlled plateau is reached ($k \approx 10^{10} \text{ L mol}^{-1} \text{ s}^{-1}$). From the linear increase of $\log k$ with E , one can derive the parameters N (from the intercepts on the abscissa) and s (from the slopes) for the phenylsulfinate ion in different solvents (Table 3). The rate constants in acetonitrile and DMSO are almost identical. In 50% aqueous acetonitrile (v/v), phenylsulfinate is approximately 10^3 times less reactive.

Can the product studies reported in Table 4 be employed to partition the gross rate constants given in Tables 2 and 3 into partial rate constants for S- and O-attack? This is possible for the reactions of PhSO_2^- with the benzhydrylium ions **2f** and **2g**, because previous investigations indicate that **2f**-Br and **2g**-Br react via $\text{S}_{\text{N}}1$ mechanisms.^{21a} Table 4 unequivocally shows that the [5]/[4] ratios observed with these carbocations after short reaction times reflect kinetic product control. However, these reactions proceed with diffusion rates, and the observed product ratios do not give information about the relative reactivity of sulfur and oxygen in activation controlled reactions.

The change of the $k_{\text{s}}/k_{\text{o}}$ ratio from 1.3 for **2f** (Table 4, entry 10) to 2.0 for **2g** (Table 4, entry 7) shows that the percentage of kinetically controlled S-attack increases further as one moves to better stabilized benzhydrylium ions. Even if the ratio $k_{\text{s}}/k_{\text{o}}$ would not increase beyond 2.0 (as determined for **2g**, entry 7) for less electrophilic carbocations, one can derive that the gross nucleophilicity N for **1** (sum of S- and O-attack) which is given in Table 3 had only to be reduced by $\Delta N = 0.35$ to obtain the S-specific nucleophilicity parameter N for PhSO_2^- .^{21b} If the $k_{\text{s}}/k_{\text{o}}$ ratio increases further, the correction term will be even smaller. While the O-nucleophilicity of PhSO_2^- cannot be precisely be assigned, the formation of comparable amounts of **4g** and **5g** from **2g** and PhSO_2^- indicates that the O-nucleophilicity of PhSO_2^- cannot be much lower than its S-nucleophilicity. If one assumes similar values of s for both sites of attack, the ratio $[\text{5g}]/[\text{4g}] = 2.0$ can only be reached if the N value for O-attack is not more than approximately 4 logarithmic units smaller than that for S-attack (see Figure 6).

Figure 7 compares the nucleophilicity of phenylsulfinate **1** with that of other nucleophiles. One can see that its reactivity in DMSO and CH_3CN is comparable to that of stabilized carbanions (e.g., malonate), azide, and DABCO. It is about 3 orders of magnitude more nucleophilic than acetate, benzoate, and CN^- (all in CH_3CN). Hydration has a much larger effect on the nucleophilicity of PhSO_2^- than on the reactivity of ester-stabilized carbanions. While the change from DMSO to water reduces the N value of malonate by 4 units, the nucleophilicity of PhSO_2^- is reduced by $\Delta N = 6.4$ when 50% water is added to the solution in acetonitrile. Figure 7 shows that the nucleophilicities of PhSO_2^- and Br^- are almost equal in 50% aqueous

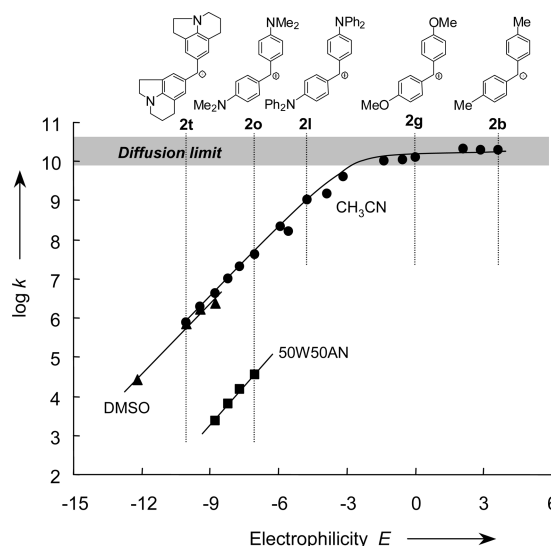


Figure 6. Plots of $\log k$ for the reactions of phenyl sulfinate **1** with benzhydrylium ions and a quinone methide (Tables 2, 3) versus their electrophilicity parameters E (Table 2) in different solvents at 20°C .

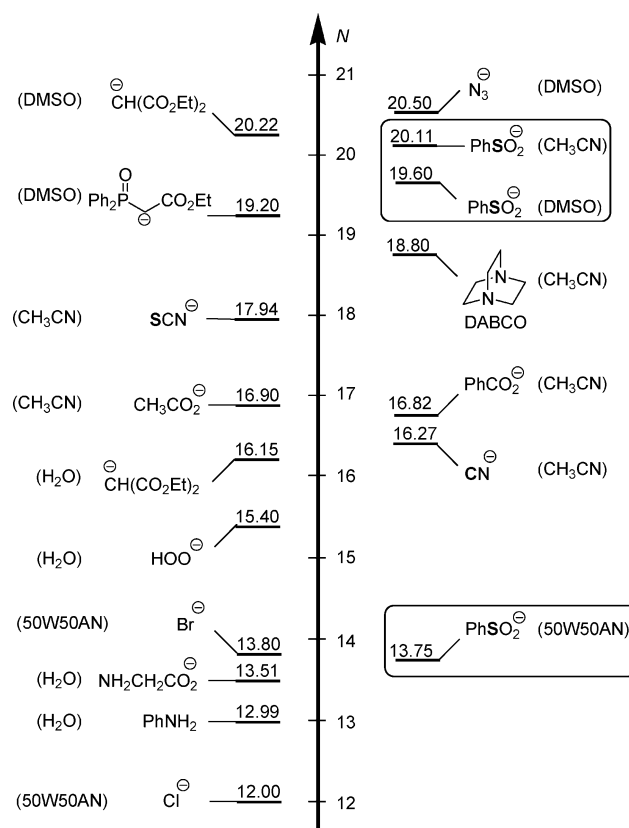


Figure 7. Comparison of the nucleophilic reactivity of the phenyl sulfinate ion (**1**) with other types of nucleophiles (N values from refs 10a, b, 13, 22, and 23).

acetonitrile, a fact which will be taken up again in the discussion of leaving group abilities.

Nucleofugality of Phenyl Sulfinate. Since the rate of the rearrangement of $(\text{ani})_2\text{CH}-\text{OS}(\text{O})\text{Ph}$ into the corresponding sulfone does not depend on the concentration of phenyl sulfinate

(21) (a) Phan, T. B.; Nolte, C.; Kobayashi, S.; Ofial, A. R.; Mayr, H. *J. Am. Chem. Soc.* **2009**, *131*, 11392–11401. (b) $\Delta N = 1/(s \log ([\text{5g}]/[\text{4g}] + [\text{4g}]))$.

(22) Schaller, H. F.; Tishkov, A. A.; Feng, X.; Mayr, H. *J. Am. Chem. Soc.* **2008**, *130*, 3012–3022.

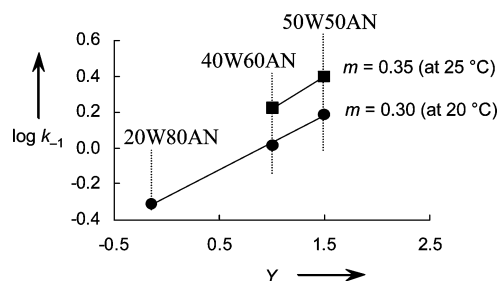


Figure 8. Correlation of ionization rate constants (k_{-1}) for $(\text{lil})_2\text{CH}-\text{SO}_2\text{Ph}$ with solvent ionizing power Y .

ions **1** in the solution, one can conclude that the rate constants derived from Figure 3 correspond to the ionization step (C–O cleavage). The increasing times for the rearrangement **4** $\rightarrow$ **5** with decreasing stabilization of the carbocations (**2g** $\rightarrow$ **2d**, Table 4) are in line with this interpretation.

The heterolyses of the corresponding sulfones (C–S cleavage) are considerably slower and can only be observed in aqueous solvents of high ionizing power. The Winstein–Grunwald equation (eq 4) correlates logarithms of solvolysis rate constants (k_s) with the solvent ionizing power Y in which k_s and k_0 refer to solvolysis rate constants for a substrate R–X in a given solvent and in an 80% ethanol/water mixture, respectively.²⁴ Because m values had been found to be close to 1 for most $\text{S}_{\text{N}}1$ reactions ($t\text{BuCl}$: $m = 1.00$) and <0.5 for $\text{S}_{\text{N}}2$ reactions, m values had been suggested as a tool for discriminating between $\text{S}_{\text{N}}1$ and $\text{S}_{\text{N}}2$ processes.^{24,25}

$$\log(k_s/k_0) = mY \quad (4)$$

Figure 8 shows a linear correlation between the ionization rate constants k_{-1} for $(\text{lil})_2\text{CH}-\text{SO}_2\text{Ph}$ (Table 5) with the solvent ionizing power Y .²⁶ The small slopes of these correlations ($m = 0.30\text{--}0.35$) which undoubtedly refer to rate-limiting ionization processes indicate noncarbocation like transition states. m -Values of similar magnitude have previously been observed for the ionizations of amino-substituted benzhydryl carboxylates in aqueous acetone.²²

It is remarkable that the heterolysis rate constants of the benzhydryl phenyl sulfones do not show the inverse order of the electrophilicities of the corresponding benzhydrylium ions (Figure 9). More than a hundred reaction series, including the reactions of benzhydrylium ions with phenyl sulfinate reported in this work (Tables 2 and 3) have shown the electrophilicity order $(\text{thq})_2\text{CH}^+ > (\text{ind})_2\text{CH}^+ > (\text{jul})_2\text{CH}^+ > (\text{lil})_2\text{CH}^+$.^{14,15} In contrast, the order of electrofugalities is completely different,

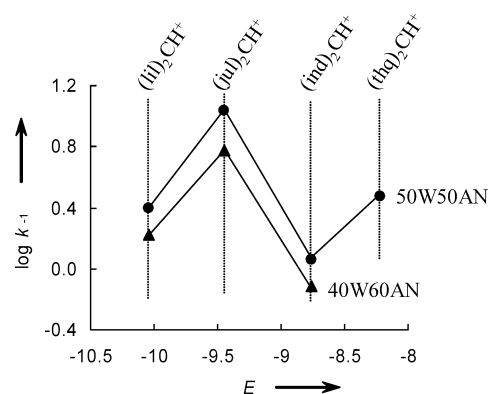


Figure 9. Plots of heterolysis rate constants ($\log k_{-1}$) for $\text{Ar}_2\text{CH}-\text{SO}_2\text{Ph}$ at 25 °C versus the electrophilicity parameters $E^{14,15}$ of Ar_2CH^+ .

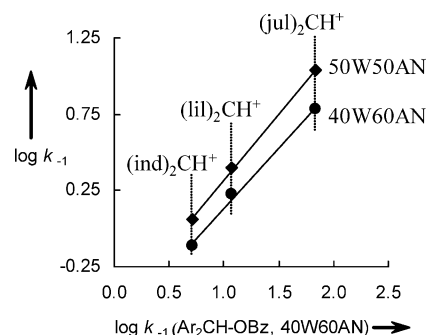


Figure 10. Correlations of the ionization rate constants of benzhydryl sulfones ($\text{Ar}_2\text{CH}-\text{SO}_2\text{Ph}$) versus the ionization rate constants of benzhydryl benzoates ($\text{Ar}_2\text{CH}-\text{OBz}$ in 40W60AN, from ref 22).

and $(\text{lil})_2\text{CH}^+$, the weakest electrophile of this series, is far from being the best electrofuge (Table 5, Figure 9).

The consistency of the electrofugalities given in Table 5 and depicted in Figure 9 is confirmed by the fact that the ionization rate constants k_{-1} for sulfones (Table 5) correlate well with the previously reported ionization rate constants for benzoates ($\text{Ar}_2\text{CH}-\text{OBz}$) in 40W60AN (Figure 10).²² The electrofugality order of the benzhydrylium ions, therefore, differs systematically from the electrophilicity order, but appears to be independent of the nature of the nucleofuge. Because the heterolysis rate constants for the benzhydryl phenyl sulfones and the benzhydryl carboxylates have been studied with the same benzhydrylium systems in the same solvent (40W60AN), a direct comparison of the heterolysis rate constants is possible. The leaving group ability of the phenylsulfonyl group (PhSO_2^- , C–S cleavage) is 7–11 times lower than that of benzoate (PhCO_2^-) and 4–7 times lower than that of acetate (CH_3CO_2^-).²²

Solvolysis rates of benzhydryl bromides and chlorides have previously been investigated in 40W60AN.^{27a} From the first-order rate constants of $(\text{tol})_2\text{CHCl}$ (**2b-Cl**, 2.76 s^{-1}) and $\text{Ph}_2\text{CH-Br}$ (**2a-Br**, 0.14 s^{-1}) and structurally related benzhydryl halides^{27b} one can extrapolate that the phenylsulfonyl group is a 10^{10} times weaker leaving group than Br^- and a 10^8 times weaker leaving group than Cl^- in 40W60AN. On other hand, Figure 7 has shown that the S-nucleophilicity of PhSO_2^- is comparable to that of Br^- and Cl^- in 50W50AN. This discrepancy is again due to the high intrinsic barriers of the S-reactivity of PhSO_2^- which will be discussed in detail in the next section.

(23) Reactivities for carbanions: (a) Lucius, R.; Loos, R.; Mayr, H. *Angew. Chem., Int. Ed.* **2002**, *41*, 91–95. (b) Bug, T.; Mayr, H. *J. Am. Chem. Soc.* **2003**, *125*, 12980–12986. (c) Appel, R.; Loos, R.; Mayr, H. *J. Am. Chem. Soc.* **2009**, *131*, 704–714. For N_3^- : (d) Phan, T. B.; Mayr, H. *J. Phys. Org. Chem.* **2006**, *19*, 706–713. For HOO^- : (e) Minegishi, S.; Mayr, H. *J. Am. Chem. Soc.* **2003**, *125*, 286–295. For Cl^- and Br^- : (f) Minegishi, S.; Loos, R.; Kobayashi, S.; Mayr, H. *J. Am. Chem. Soc.* **2005**, *127*, 2641–2649. For glycine: (g) Brotzel, F.; Mayr, H. *Org. Biomol. Chem.* **2007**, *5*, 3814–3820. For aniline: (h) Brotzel, F.; Chu, Y. C.; Mayr, H. *J. Org. Chem.* **2007**, *72*, 3679–3688.

(24) (a) Grunwald, E.; Winstein, S. *J. Am. Chem. Soc.* **1948**, *70*, 846–854. (b) Fainberg, A. H.; Winstein, S. *J. Am. Chem. Soc.* **1956**, *78*, 2770–2777.

(25) Bentley, T. W.; Llewellyn, G. *Prog. Phys. Org. Chem.* **1990**, *17*, 121–158.

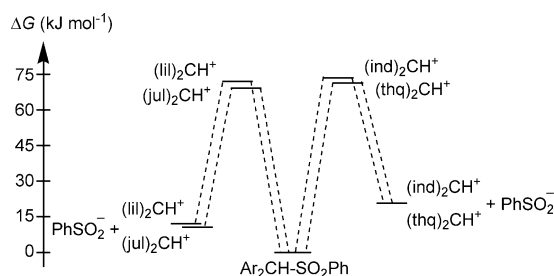
(26) Bentley, T. W.; Dau-Schmidt, J.-P.; Llewellyn, G.; Mayr, H. *J. Org. Chem.* **1992**, *57*, 2387–2392.

(27) (a) Streidl, N.; Antipova, A.; Mayr, H. *J. Org. Chem.* **2009**, *74*, 7328–7334. (b) Streidl, N.; Nolte, C.; Mayr, H. unpublished.

Table 6. Equilibrium Constants K , $\Delta G^\ddagger$, ΔG^0 , $\Delta G_0^\ddagger$, and Intrinsic Rate Constants (k_0) for the Ionization of $\text{Ar}_2\text{CH}-\text{SO}_2\text{Ph}$ in 50W50AN at 25 °C

Ar_2CH^+	k [$\text{M}^{-1}\text{s}^{-1}$]	k_{-1} ^d [s^{-1}]	K ^e [M^{-1}]	$\Delta G^\ddagger$ ^f [kJ mol^{-1}]	ΔG^0 ^g [kJ mol^{-1}]	$\Delta G_0^\ddagger$ [kJ mol^{-1}]	k_0 ^h [s^{-1}]
(lil) ₂ CH ⁺	4.71×10^{2a}	2.51	1.88×10^2	70.7	13.0	64.1	3.6×10^1
(jul) ₂ CH ⁺	1.15×10^{3b}	10.9	1.06×10^2	67.1	11.6	61.2	1.2×10^2
(ind) ₂ CH ⁺	3.09×10^{3c}	1.14	2.71×10^3	72.7	19.6	62.5	6.9×10^1
(thq) ₂ CH ⁺	8.24×10^{3c}	2.97	2.77×10^3	70.3	19.6	60.1	1.8×10^2

^a k calculated by eq 3 from $E = -10.04$ (Table 2) and $N = 14.09$, $s = 0.66$ (Table 3). ^b k calculated by eq 3 from $E = -9.45$ (Table 2) and $N = 14.09$, $s = 0.66$ (Table 3). ^c From Table 3. ^d From Table 5. ^e $K = k/k_{-1}$. ^f $\Delta G^\ddagger$ for the ionization reaction were calculated by using Eyring equation. ^g ΔG^0 for the ionization process is given by $+RT \ln K$. ^h Intrinsic rate constants (k_0) from Eyring equation.

**Figure 11.** Gibbs free energy profiles for the reactions of the phenylsulfinate ion with amino-substituted benzhydrylium ions in 50W50AN at 25 °C (standard state 1 M).

Intrinsic Barriers. The availability of rate and equilibrium constants for several reactions of benzhydrylium ions with PhSO_2^- allows us to calculate Marcus' intrinsic barriers. According to Marcus' equation (eq 5), the activation free energy ($\Delta G^\ddagger$) of a reaction can be expressed as a combination of the reaction free energy (ΔG^0) and the intrinsic barrier ($\Delta G_0^\ddagger$).²⁸ The latter term has been defined as the activation free energy ($\Delta G^\ddagger$) of a process without thermodynamic driving force (i.e., for $\Delta G^0 = 0$). The work term has been neglected in eq 5.

$$\Delta G^\ddagger = \Delta G_0^\ddagger + 0.5\Delta G^0 + (\Delta G^0)^2/(16\Delta G_0^\ddagger) \quad (5)$$

Equilibrium constants for the reactions of the benzhydrylium ions **2q-t** with PhSO_2^- in 50W50AN have been calculated as the ratio of forward/backward reaction, that is, $K = k/k_{-1}$. While k_{-1} has directly been measured for these four sulfones (Table 5), the rate constants for the combination with PhSO_2^- (k) have only been measured for $(\text{thq})_2\text{CH}^+$ and $(\text{ind})_2\text{CH}^+$ (Table 3, last two entries). The high quality of the correlation between the rate constants for ion combination (k) and the electrophilicity E (illustrated by the lower line in Figure 6), justifies to employ eq 3 for calculating the rate constants k for the reaction of $(\text{lil})_2\text{CH}^+$ and $(\text{jul})_2\text{CH}^+$ with PhSO_2^- as specified in Table 6. The ionization rate constants (k_{-1}) and the equilibrium constants (K) at 25 °C were converted into $\Delta G^\ddagger$ and ΔG^0 (Table 6) and substitution of these values into eq 5 gives the intrinsic barriers $\Delta G_0^\ddagger$. Table 6 shows the same ranking of intrinsic barriers for the differently substituted benzhydryl systems $(\text{lil})_2\text{CH}^+ > (\text{ind})_2\text{CH}^+ > (\text{jul})_2\text{CH}^+ > (\text{thq})_2\text{CH}^+$ as previously reported for benzhydryl carboxylates.²²

The free energy diagrams in Figure 11 summarize the influence of intrinsic barriers on the different reactivities of these four systems. The free energy of ionization (ΔG^0) is the same for $(\text{ind})_2\text{CH}^+$ and $(\text{thq})_2\text{CH}^+$. It is the higher intrinsic barrier for $(\text{ind})_2\text{CH}^+$ (annulated five-membered ring) compared to $(\text{thq})_2\text{CH}^+$ (annulated six-membered ring), which accounts for the observation that $(\text{thq})_2\text{CH}^+$ reacts faster with nucleophiles than $(\text{ind})_2\text{CH}^+$, and at the same time is generated faster by the reverse reaction.

A similar trend in the intrinsic barriers for compounds with annulated five- and six-membered rings also controls the relative reactivities of $(\text{lil})_2\text{CH}^+$ and $(\text{jul})_2\text{CH}^+$. Though $(\text{jul})_2\text{CH}^+$ is thermodynamically more stable than $(\text{lil})_2\text{CH}^+$, the higher intrinsic barrier of the 5-membered ring-system $(\text{lil})_2\text{CH}^+$ accounts for the observation that $(\text{lil})_2\text{CH}^+$ is less electrophilic than $(\text{jul})_2\text{CH}^+$. Analogously, the lower rate of ionization of $(\text{lil})_2\text{CH}-\text{SO}_2\text{Ph}$ is due to the higher intrinsic barrier for the formation of 5-membered ring system $(\text{lil})_2\text{CH}^+$.

Ambident Reactivity of Phenyl Sulfinate. As shown in Figure 6, the rates of the reactions of benzhydrylium ions with PhSO_2^- proceed with almost equal rates in acetonitrile and DMSO. The rate constants for the reactions of $(\text{ani})_2\text{CH}^+$ with PhSO_2^- in acetonitrile ($1.24 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$, Table 2) can, therefore, be combined with the product ratio (**4**: **5** = 1: 2.0, Table 4, entry 7) to derive the partial rate constants $k = 2.05 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ for the reaction of *one* oxygen of PhSO_2^- with $(\text{ani})_2\text{CH}^+$. Combination of this rate constant with the ionization rate constant of $(\text{ani})_2\text{CH}-\text{OS}(\text{O})\text{Ph}$ ($k_{-1} = 8.16 \times 10^{-4} \text{ s}^{-1}$ from Figure 3) yields the equilibrium constant $K = k/k_{-1} = 2.51 \times 10^{12} \text{ M}^{-1}$ (20 °C, because the high combination rate constant k can be assumed to be temperature-independent) which corresponds to ΔG^0 (20 °C) = $-69.6 \text{ kJ mol}^{-1}$ for the formation of **4g** from **2g** and **1**. Substitution of these values into the Marcus equation yields an intrinsic barrier of $\Delta G_0^\ddagger = 48 \text{ kJ mol}^{-1}$ for the O-attack at PhSO_2^- by $(\text{ani})_2\text{CH}^+$. This value is significantly lower than $\Delta G_0^\ddagger$ for S-attack reported in Table 6. Though part of this difference is due to the variation of the benzhydrylium ion (solvent variation was found to have little influence on $\Delta G_0^\ddagger$),²² it is obvious that O-attack is intrinsically highly favored over S-attack. Taking into consideration that the combination rate constant $k = 1.24 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ used for the calculation of $\Delta G_0^\ddagger$ for O-attack of **1** at $(\text{ani})_2\text{CH}^+$ is controlled by transport and not by activation, the intrinsic barrier $\Delta G_0^\ddagger = 48 \text{ kJ mol}^{-1}$ has to be considered as upper limit; as a consequence, the intrinsic preference for O-attack may even be higher than derived above. Because the thermodynamic term ΔG^0 in the Marcus equation favors S-attack, we have to conclude that both terms cancel each other to account for the similar S- and O-reactivity of PhSO_2^- .

Conclusion

Phenylsulfinate PhSO_2^- is a strong nucleophile with a reactivity in DMSO comparable to N_3^- and stabilized carbanions as diethyl malonate. It undergoes diffusion-controlled reactions with carbocations of moderate and high reactivity ($E > -2$), and the ratio O- vs S-attack of these reactions cannot be explained by transition state models, because none of these reactions has an activation barrier. Highly reactive carbocations ($E > 0$) attack oxygen and sulfur with similar rates.

In reactions with less electrophilic carbenium ions, the ΔG^0 term, which favors S-attack, is gaining importance. While the

exclusive formation of sulfones from highly stabilized carbocations is due to thermodynamic product control, mixtures of sulfones and sulfinates are formed under conditions of kinetic control. The ambident reactivity of sulfinate PhSO_2^- thus is the result of a complex interplay of intrinsic and thermodynamic effects. It cannot be explained by the HSAB model or Klopman-Salem concept of charge and orbital control.

Experimental Section

Materials. Commercially available acetonitrile (VWR, Prolabo, HPLC-gradient grade) and DMSO (Acros, >99.8%, extra dry) were used as received. The benzhydrylium tetrafluoroborates $\text{Ar}_2\text{CH}^+\text{BF}_4^-$ were prepared as described before.^{14b} The benzhydrylphosphonium tetrafluoroborates and benzhydryl chlorides were synthesized according to literature procedures.^{29,30} PhSO_2Na (Acros, >98%) and 15-crown-5 (ABC R, 98%) were purchased and used directly without further purification.

Laser-Flash Photolysis. Laser-flash photolysis was employed for determining the rates of the reactions of Ar_2CH^+ with PhSO_2^- in acetonitrile at 20 °C. For that purpose, benzhydrylium ions were generated by irradiation of benzhydrylphosphonium tetrafluoroborates ($\text{Ar}_2\text{CH-PR}_3^+\text{BF}_4^-$) in acetonitrile with an Innolas SpitLight 600 Nd:YAG laser (fourth harmonic at $\lambda = 266$ nm; power/pulse of 40–60 mJ, pulse length = 6.5 ns) in a quartz cell. The rate constants were determined by observing the time-dependent decay of the UV–vis absorptions of the benzhydrylium ions. The pseudofirst-order rate constants were obtained by fitting the decay of the UV–vis absorptions to the exponential function $A_t = A_0 e^{-k_{\text{obs}}t} + C$.

Determination of the Rates of the Combinations of Benzhydrylium Ions with PhSO_2^- . The reactions of PhSO_2^- with the colored benzhydrylium ions (Ar_2CH^+) in DMSO and aqueous acetonitrile were followed photometrically at the absorption maxima of Ar_2CH^+ by UV–vis spectroscopy using stopped-flow instruments (Hi-Tech SF-61DX2 or Applied Photophysics SX.18MV-R). All experiments were performed under pseudofirst-order conditions (excess of PhSO_2^-) and the pseudofirst-order rate constants k_{obs} were obtained by least-squares fitting of the absorbances to the monoexponential function $A_t = A_0 e^{-k_{\text{obs}}t} + C$. Temperature of the solutions during all kinetic studies was kept constant (20 or 25 °C) using a circulating bath thermostat.

Determination of Ionization Rates. The ionizations reactions were followed photometrically by UV–vis spectroscopy using a stopped-flow instrument (Hi-Tech SF-61DX2). The single mixing technique was employed where a colorless solution of $\text{Ar}_2\text{CH-SO}_2\text{Ph}$ obtained by mixing $\text{Ar}_2\text{CH}^+\text{BF}_4^-$ with excess PhSO_2Na in CH_3CN containing 15-crown-5 was used in one syringe and the another syringe contained pure distilled water or aqueous acetonitrile. Mixing of the colorless solution of $\text{Ar}_2\text{CH-SO}_2\text{Ph}$ in CH_3CN with an equal volume of pure water or aqueous acetonitrile inside the mixer provokes the ionization of the $\text{Ar}_2\text{CH-SO}_2\text{Ph}$. The rates of the ionizations were followed photometrically at the absorption maxima of Ar_2CH^+ . Each measurement was repeated at least five times with variable excess of the PhSO_2Na . The appearance of the benzhydrylium absorbances generally followed the monoexponential equation $[\text{Ar}_2\text{CH}^+] = [\text{Ar}_2\text{CH}^+]_{\text{eq}} (1 - e^{-k_{\text{obs}}t})$, from which the rate constants k_{obs} were derived. Temperature of the solutions during heterolysis studies was kept constant (20 or 25 °C) using a circulating bath thermostat.

Acknowledgment. Dedicated to Professor Paul von Rague Schleyer on the occasion of his 80th birthday. We thank the Deutsche Forschungsgemeinschaft for financial support (SFB 749) and Dr. Armin R. Ofial, Konstantin Troshin, and Roland Appel for discussions.

Supporting Information Available: Details of kinetic experiments and product studies. This material is available free of charge via the Internet at <http://pubs.acs.org>.

JA9102056

- (28) (a) Marcus, R. A. *J. Phys. Chem.* **1968**, *72*, 891–899. (b) Albery, W. J. *Annu. Rev. Phys. Chem.* **1980**, *31*, 227–263. (c) Bernasconi, C. F. *Acc. Chem. Res.* **1987**, *20*, 301–308. (d) Bernasconi, C. F.; Terrier, F. *J. Am. Chem. Soc.* **1987**, *109*, 7115–7121. (e) Guthrie, J. P. *J. Am. Chem. Soc.* **1996**, *118*, 12878–12885. (f) Guthrie, J. P. *J. Am. Chem. Soc.* **1996**, *118*, 12886–12890. (g) Guthrie, J. P. *Can. J. Chem.* **2005**, *83*, 1–8. (h) Uggerud, E. *J. Chem. Soc., Perkin Trans. 2*, **1999**, 1459–1463. (i) Uggerud, E. *J. Chem. Soc., Perkin Trans. 2*, **1999**, 1465–1467. (j) Lewis, E. S.; Shen, C. C.; More O’Ferrall, R. A. *J. Chem. Soc., Perkin Trans. 2*, **1981**, 1084–1088. (k) Lawlor, D. A.; More O’Ferrall, R. A.; Rao, S. N. *J. Am. Chem. Soc.* **2008**, *130*, 17997–18007. (l) Richard, J. P.; Amyes, T. L.; Toteva, M. M. *Acc. Chem. Res.* **2001**, *34*, 981–988.
- (29) Kempf, B.; Mayr, H. *Chem.—Eur. J.* **2005**, *11*, 917–927.
- (30) Denegri, B.; Streiter, A.; Juric, S.; Ofial, A. R.; Kronja, O.; Mayr, H. *Chem.—Eur. J.* **2006**, *12*, 1648–1656.