**Ambident Anions** 

## Ambident Reactivity of the Nitrite Ion Revisited\*\*

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Dedicated to Professor Horst Kessler on the occasion of his 65th birthday

Extensive investigations on the reactions of the nitrite ion with alkylating agents<sup>[1]</sup> led Kornblum to the conclusion "*The greater the carbonium contribution to the transition state the greater is the yield of nitrite ester and the smaller is the yield of nitroparaffin.*"<sup>[1a]</sup> However, Pearson's specification of this rule, " $tC_4H_9Cl$  reacts with the hard oxygen atom of  $NO_2^-$ , while the softer  $CH_3I$  reacts with the softer nitrogen atom,"<sup>[2a]</sup> which was expressed by Equation (1) in later theoretical treatments of ambident reactivity,<sup>[2b–d]</sup> is not in line with experimental findings, because  $CH_3I$  and other primary haloalkanes yield mixtures of alkyl nitrites and nitroalkanes with either NaNO<sub>2</sub> or AgNO<sub>2</sub>.<sup>[1,2e]</sup>

$$MeNO_{2} \xrightarrow{Mel} \ominus_{O} \overset{"}{N_{\geq O}} \xrightarrow{tBuCl} tBuONO$$
(1)

Fleming's statement "Although silver nitrite does react with alkyl halides to give nitrites, sodium nitrite gives more nitroalkane than alkyl nitrite" [Eqs. (2) and (3)]<sup>[3a]</sup> is contradicted by Streitwieser, Heathcock, and Kosower, who compare the reactions of iodoalkanes with NaNO<sub>2</sub> and AgNO<sub>2</sub> and conclude "Yields of nitroalkane are higher when silver nitrite is used, but this added economy is tempered by the cost of silver salt" [Eq. (4)].<sup>[3b]</sup>

$$AgNO_2 + RBr \to RONO \tag{2}$$

$$NaNO_2 + RBr \to RNO_2 \tag{3}$$

$$\begin{array}{c} CH_{3}(CH_{2})_{6}CH_{2}I + AgNO_{2} \rightarrow CH_{3}(CH_{2})_{6}CH_{2}NO_{2} \ (83 \%) \\ + CH_{3}(CH_{2})_{6}CH_{2}ONO \ (11 \%) \end{array}$$
(4)

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This confusion prompted us to reinvestigate the ambident reactivity of the nitrite ion with emphasis on absolute rate constants.

We have recently reported that the knowledge of absolute rate constants and of the diffusion control limit is a key to understanding the ambident reactivity of the thiocyanate<sup>[4a]</sup> and cyanide ions<sup>[4b]</sup> in alkylation reactions. These ambident anions are preferentially attacked at the soft S or C termini by hard and soft alkylating agents. Only when diffusion control is reached, can the attack of carbocations at the hard nitrogen compete with attack at sulfur (SCN<sup>-</sup>) or carbon (CN<sup>-</sup>), respectively. We now report on the kinetics and selectivities of alkylations of the nitrite ion.

Reactions of the blue benzhydrylium salts (1a-d)-BF<sub>4</sub> (see Table 1) with  $nBu_4N^+NO_2^-$  in anhydrous acetonitrile [Eq. (5)], which gave colorless adducts, were followed photo-

$$Ar \stackrel{H}{\oplus} Ar \stackrel{BF_{4}^{\ominus}}{\to} Ar + nBu_{4}N \stackrel{\oplus}{\to} NO_{2}^{\ominus} \xrightarrow{-nBu_{4}N \stackrel{\oplus}{\oplus} BF_{4}^{\ominus}} Ar \stackrel{H}{\to} Ar \stackrel{NO_{2}}{\to} Ar \stackrel{H}{\to} Ar \stackrel{NO_{2}}{\to} Ar \stackrel{H}{\to} Ar \stackrel{ONO}{\to} (5)$$

metrically using the stopped-flow technique described previously.<sup>[5]</sup> For  $[\mathbf{1a-d}]_0 = (1-10) \times 10^{-6} \text{ M}$  and  $[\text{NO}_2^{--}]_0 = (1-100) \times 10^{-5} \text{ M}$ , pseudo-first-order conditions were employed resulting in exponential decays of the benzhydrylium absorptions, from which the pseudo-first-order rate constants  $k_{1\psi}$ (s<sup>-1</sup>) were derived. The second-order rate constants  $k_2$ ( $\mathbf{m}^{-1}\mathbf{s}^{-1}$ ) listed in Table 1 were obtained as the slopes of the plots of  $k_{1\psi}$  vs.  $[\text{NO}_2^{--}]$ .<sup>[6]</sup> From the linearity of these correlations one can infer that ion pairing does not play a role under these conditions.

The reactions with the highly electrophilic benzhydrylium ions 1e-k (see Table 1) were too fast to be followed by stopped-flow techniques. Therefore, these carbocations were generated photolytically in the presence of the nitrite ion. For this purpose, solutions of (1e-h)-NO<sub>2</sub> (obtained according to

**Table 1:** Rate constants of the reactions of nitrite ions with the benzhydrylium cations 1 a-k (20°C, MeCN).

Benzhyc	drylium ion		<b>E</b> <sup>[a]</sup>	k <sub>2</sub> [м <sup>-1</sup> s <sup>-1</sup> ]
	n = 1	1a	-10.04	1.58×10 <sup>5</sup>
	n=2	16	-9.45	3.30×10 <sup>5</sup>
Ĥ	<i>n</i> =1	1c	-8.76	9.85×10⁵
	n = 2	1 d	-8.22	2.76×10 <sup>6</sup>
Mé	Ňe			
	$R = NMe_2$	1e	-7.02	$1.56 \times 10^{7}$
н	R = NMePh	1 f	-5.89	$1.49 \times 10^{8}$
	$R = NMe(CH_2CF_3)$	1g	-3.85	$1.09 \times 10^{9}$
Ĩ I I I I I I I I I I I I I I I I I I I	$R = NPh(CH_2CF_3)$	1ĥ	-3.14	$3.41 \times 10^{9}$
	R=OMe	1i	0.00	_[b]
K - K	R = Me	1j	3.63	$2.50 \times 10^{10}$
	R = H	1 k	5.90	$2.2 \times 10^{10}$ [c]

[a] Electrophilicity parameter as defined by Equation (6), see ref. [5a]. [b] Not determined. [c] From ref. [6].

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Eq. (5)) or **1j**-Cl and  $nBu_4N^+NO_2^-$  in acetonitrile were irradiated by laser pulses (<1 ps, ca. 1.5 µJ, center wavelengths between 250 and 300 nm) to yield the benzhydrylium ions **1e–j** in less than 2 ps. The behavior of these transients ( $\lambda_{max} = 460-612$  nm) was monitored on different timescales, and we detected reactions with 10 ms >  $\tau_{\frac{1}{2}}$  > 10 ns.<sup>[7]</sup> As in the stopped-flow experiments, these reactions were also performed under pseudo-first-order conditions [Ar<sub>2</sub>CH<sup>+</sup>]  $\leq$  [NO<sub>2</sub><sup>-</sup>], and the second-order rate constants listed in Table 1 were again derived from plots of  $k_{1\Psi}$  vs. [NO<sub>2</sub><sup>-</sup>].

In previous work we have shown that the reactions of carbocations with nucleophiles can be described by Equation (6), where k is the second-order rate constant, E is a

$$\log k_{20^{\circ}\mathrm{C}} = s(E+N) \tag{6}$$

nucleophile-independent electrophilicity parameter, and N and s are electrophile-independent nucleophilicity parameters.<sup>[5,8]</sup> Figure 1 correlates the second-order rate constants listed in Table 1 with the previously determined electrophilicity parameters of benzhydrylium ions<sup>[5]</sup> and shows that the reactions of carbocations **1a–f** with NO<sub>2</sub><sup>-</sup> follow Equation (6).



**Figure 1.** Plot of  $\lg k_2$  for the reactions of the nitrite ion with the benzhydrylium ions **1 a**–**k** versus their electrophilicity parameters *E* (20 °C, MeCN).<sup>[Sa]</sup>

From the linear part of this correlation (**1a**–**f**) one can derive N = 17.2 and s = 0.72 for the nitrite ion in acetonitrile. For the more electrophilic benzhydrylium ions **1g–k**, a flattening of the curve can be seen, and the observed diffusion limit is in accord with the previously reported value of  $(2.2-2.7) \times 10^{10} \text{ m}^{-1} \text{ s}^{-1}$  for reactions of carbocations with anions in acetonitrile.<sup>[6]</sup>

Which reactions are responsible for the decay of the benzhydrylium absorbances? Addition of an excess of  $nBu_4N^+NO_2^-$  to solutions of benzhydrylium tetrafluoroborates (**1a–h**)-BF<sub>4</sub> in CD<sub>3</sub>CN gives rise to the exclusive formation of the nitromethanes (**1a–h**)-NO<sub>2</sub><sup>[9]</sup> (Scheme 1), as revealed by the characteristic <sup>1</sup>H NMR chemical shifts of the benzhydryl protons ( $\delta = 6.5-6.8$  ppm) and the <sup>15</sup>N NMR



**Scheme 1.** Reactions of benzhydrylium tetrafluoroborates with  $nBu_4N^+NO_2^-$  (equilibrium constants K in CH<sub>3</sub>CN at 20°C).

chemical shift of the nitro group ( $\delta = 3.8 \text{ ppm}$ ) in **1e**-NO<sub>2</sub>.<sup>[10]</sup> For the least reactive carbocations **1a**-c an excess of  $nBu_4N^+NO_2^-$  is needed to drive the reactions toward completion. The equilibrium constants, which were determined by UV/Vis spectroscopy (see the Supporting Information), are listed in Scheme 1.<sup>[11]</sup>

These observations clearly indicate that the photometrically monitored process for the reactions of 1a-c with NO<sub>2</sub><sup>-</sup> is N attack: Since alkyl nitrites are thermodynamically less stable than the corresponding nitro compounds,<sup>[12]</sup> the equilibrium constants for the formation of (1a-c)-ONO must be much smaller, and one can exclude that the observed rates of carbocation decay are due to the formation of (1a-c)-ONO, which rearrange to the observed nitro compounds (1a-c)-NO<sub>2</sub> in consecutive reactions.<sup>[13]</sup>

For the more electrophilic benzhydrylium ions **1d-h** one cannot a priori exclude the possibility that the UV/Vis spectroscopically monitored process is the formation of (1d-h)-ONO, which successively rearrange to the observed nitro compounds (1d-h)-NO<sub>2</sub>. However, since the obtained rate constants for the reactions of 1d-h with NO<sub>2</sub><sup>-</sup> are on the same correlation line as the rate constants for N attack at 1a-c (Figure 1), the observed rate constants are compatible only with exclusive N attack or with simultaneous N and O attacks that occur with similar rates. In none of these cases could a biexponential decay be observed as in the reactions of some benzhydrylium ions with SCN<sup>-</sup>, where the faster reversible S attack was followed by the slower irreversible N attack.<sup>[4a]</sup>

Pure benzhydrylium nitrites **1i**-ONO and **1j**-ONO were obtained by treatment of the corresponding benzhydrols with NOCl/ $Et_3N$  (Scheme 2), while analogous attempts to synthe-



**Scheme 2.** i: Ar = 4-MeOC<sub>6</sub>H<sub>4</sub>; j: Ar = 4-MeC<sub>6</sub>H<sub>4</sub>.

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size (**1a–h**)-ONO failed.<sup>[14]</sup> Whereas pure **1j**-ONO remained unchanged when stored at room temperature for several days, **1i**-ONO rearranged within two days at 0°C into **1i**-NO<sub>2</sub>, which decomposed to **2i** either spontaneously or upon treatment with  $nBu_4N^+NO_2^-$  in MeCN (Scheme 2).<sup>[15]</sup>

Both benzhydrylium nitrites **1i**-ONO and **1j**-ONO were recovered unchanged when kept in a solution of  $nBu_4N^+NO_2^$ in acetonitrile for 3 h. These experiments show that benzhydryl nitrites **1i**-ONO and **1j**-ONO are kinetically stable under the conditions of the experiment described in Scheme 3. Treatment of the benzhydrylium halides **1i**-Cl and **1j**-Br with





 $nBu_4N^+NO_2^-$  in MeCN gave 7:2 mixtures of **1i**-ONO and benzophenone **2i**, and **1j**-ONO and benzophenone **2j**, respectively, which were analyzed by comparison of the NMR spectra of the product mixtures with those of authentic compounds. Since **1i**-ONO and **1j**-ONO are stable under the conditions of the experiment, and the benzophenones **2i** and **2j** are consecutive products of the corresponding diarylnitromethanes **1i**-NO<sub>2</sub> and **1j**-NO<sub>2</sub>, the product ratios described in Scheme 3 imply a  $k_0/k_N$ ratio of 3.4 for the diffusion-controlled reactions of NO<sub>2</sub><sup>-</sup> with the benzhydrylium ions **1i** and **1j**.

We thus conclude that diffusion-controlled reactions of benzhydrylium ions with  $NO_2^-$  occur preferentially at the O terminus.<sup>[16]</sup> Since Figure 1 shows that carboca-

tions with E > 0 (i.e., carbocations less stabilized than **1i**) generally undergo diffusion-controlled reactions with NO<sub>2</sub><sup>-</sup>, it is evident that the reactions of NO<sub>2</sub><sup>-</sup> with most carbocations typically generated in S<sub>N</sub>1 processes (e.g., *tert*-alkyl, allyl, and benzyl cations) proceed without an activation barrier. Explanations of the ambident reactivity of NO<sub>2</sub><sup>-</sup> based on transition-state models, therefore, cannot apply. On the other hand, those benzhydryl nitrites, which are formed by activation-controlled reactions of benzhydrylium ions with NO<sub>2</sub><sup>-</sup>, are thermodynamically unstable and rapidly isomerize to the corresponding nitro compounds.

Let us now turn to  $S_N 2$  reactions with the nitrite ion. Silver ion was proven to assist the cleavage of the C–Hal bond during the reactions of AgNO<sub>2</sub> with alkyl halides.<sup>[1a]</sup> However, in contrast to statements in the secondary literature (e.g., see ref. [3a]) silver ions were reported not to exert a significant influence on the O/N selectivity (Table 2, entries 1-4).<sup>[2e]</sup> On the other hand, the methyl nitrite/nitromethane ratio is changed significantly by variation of the solvent (Table 2, entries 5-8).<sup>[17]</sup>

We have now studied the reactions of  $nBu_4N^+NO_2^-$  with soft (MeI) and hard (MeOSO<sub>2</sub>Me, MeOSO<sub>2</sub>CF<sub>3</sub>, and Me<sub>3</sub>O<sup>+</sup>BF<sub>4</sub><sup>-</sup>) methylating agents in CDCl<sub>3</sub>. The yields were determined by integration of the <sup>1</sup>H NMR spectra with MeOAc as the internal standard. Overall yields were close to quantitative in all cases, and the methyl nitrite/nitromethane ratios (Table 2, entries 9–12) clearly indicate that the effect of the leaving groups on the O/N selectivities is small. Changing from the soft methylating agent MeI to the hard Me<sub>3</sub>O<sup>+</sup> changes the O/N selectivities by only a factor of 2.4, while a larger difference is found among the hard methylating agents MeOSO<sub>2</sub>Me and MeOSO<sub>2</sub>CF<sub>3</sub>.

In conclusion, neither  $S_N1$  nor  $S_N2$  alkylations of the nitrite ion are satisfactorily described in the framework of perturbation molecular orbital theory (PMO). The reactions of carbocations with  $NO_2^-$  only yield kinetically controlled product mixtures when  $k > 1 \times 10^9 M^{-1} s^{-1}$ , that is, when they proceed without an activation barrier. Therefore PMO approaches, such as the Klopman–Salem model, which aim

Tahle 2.	O/N	selectivities	for	methylations	of	nitrite	ions	[a]
iudie 2.	O/N	Selectivities	101	methylations	0I	minie	ions.	

Entry	Nitrite	Methylation agent	Solvent	Me-ONO/Me-NO <sub>2</sub>
1	AgNO <sub>2</sub>	Mel	DMSO	46:54 <sup>[b]</sup>
2	NaNO <sub>2</sub>	Mel	DMSO	54:46 <sup>[b]</sup>
3	AgNO <sub>2</sub>	Mel	DMF	54:46 <sup>[b]</sup>
4	NaNO <sub>2</sub>	Mel	DMF	54:46 <sup>[b]</sup>
5	KNO <sub>2</sub> /[18]crown-6	MeOSO <sub>2</sub> Me	EtOH	30:70 <sup>[c]</sup>
6	KNO <sub>2</sub> /[18]crown-6	MeOSO <sub>2</sub> Me	MeCN	50:50 <sup>[c]</sup>
7	KNO <sub>2</sub> /[18]crown-6	MeOSO <sub>2</sub> Me	THF	92:8 <sup>[c]</sup>
8	KNO <sub>2</sub> /[18]crown-6	MeOSO <sub>2</sub> Me	$C_6H_6$	85:15 <sup>[c]</sup>
9	nBu₄N <sup>+</sup> NO₂ <sup>-</sup>	Mel	CDCl <sub>3</sub>	30:70 <sup>[d]</sup>
10	nBu <sub>4</sub> N <sup>+</sup> NO <sub>2</sub> <sup>-</sup>	MeOSO <sub>2</sub> Me	CDCl <sub>3</sub>	32:67 <sup>[d]</sup>
11	nBu₄N <sup>+</sup> NO₂ <sup>−</sup>	MeOMe <sub>2</sub> +BF <sub>4</sub> -		50:50 <sup>[d]</sup>
12	nBu <sub>4</sub> N <sup>+</sup> NO <sub>2</sub> <sup>-</sup>	MeOSO <sub>2</sub> CF <sub>3</sub>		59:41 <sup>[d]</sup>

[a] At room temperature. [b] Determined by LC with radioactivity detection for reactions of  ${}^{11}CH_3I$  (see ref. [2e]). [c] Determined by GC (see ref. [17]). [d] Determined by integration of  ${}^{1}H$  NMR spectra (this work, see the Supporting Information).

at comparing relative activation energies cannot be applied. Furthermore, O/N selectivities of the methylations of the nitrite ion (Table 2) also do not correlate well with the hardness of the methylating agents. Thus,  $NO_2^-$  is the third prototype of the ambident anions (after SCN<sup>-</sup> and CN<sup>-</sup>)<sup>[4]</sup> for which the previously accepted rationalization by frontier orbital theory has to be withdrawn.

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## Communications

- a) N. Kornblum, R. A. Smiley, R. K. Blackwood, D. C. Iffland, J. Am. Chem. Soc. 1955, 77, 6269–6280; b) N. Kornblum, H. O. Larson, R. K. Blackwood, D. D. Mooberry, E. P. Oliveto, G. E. Graham, J. Am. Chem. Soc. 1956, 78, 1497–1501; c) N. Kornblum, R. A. Smiley, H. E. Ungnade, A. M. White, B. Taub, S. A. Herbert, Jr., J. Am. Chem. Soc. 1955, 77, 5528– 5533; d) N. Kornblum, H. O. Larson, D. D. Mooberry, R. K. Blackwood, E. P. Oliveto, G. E. Graham, Chem. Ind. 1955, 78, 443; e) N. Kornblum, Organic Reactions, Vol. 12 1962, 101–156; f) N. Kornblum, L. Fishbein, R. A. Smiley, J. Am. Chem. Soc. 1955, 77, 6261–6266.
- [2] a) R. G. Pearson, J. Songstad, J. Am. Chem. Soc. 1967, 89, 1827–1836; b) G. Klopman, J. Am. Chem. Soc. 1968, 90, 223–234; c) R. F. Hudson, Angew. Chem. 1973, 85, 63–84; Angew. Chem. Int. Ed. Engl. 1973, 12, 36–57; d) S. J. Formosinho, L. G. Arnaut, J. Chem. Soc. Perkin Trans. 2 1989, 1947–1952; e) K.-O. Schoeps, C. Halldin, S. Stone-Elander, B. Långström, T. Greitz, J. Labelled Compd. Radiopharm. 1988, 25, 749–758.
- [3] a) I. Fleming, Frontier Orbitals and Organic Chemical Reactions, Wiley, Chichester, 1976, p. 41–42; b) A. Streitwieser, C. H. Heathcock, E. M. Kosower, Introduction to Organic Chemistry, Macmillan, New York, 1992, p. 779; This statement is in line with Kornblum's report (p. 114 in ref. [1e]): "In the synthesis of saturated primary nitro compounds, silver nitrite gives nitroparaffins in about 80% yield as against about 60% yields obtained with sodium nitrite. While silver nitrite is, therefore, the reagent of choice here, the lower cost and ready availability of sodium nitrite, the not very large disparity in yield, and the shorter reaction time all combine to make sodium nitrite an excellent second choice."
- [4] a) R. Loos, S. Kobayashi, H. Mayr, J. Am. Chem. Soc. 2003, 125, 14126-14132; b) A. A. Tishkov, H. Mayr, Angew. Chem. 2005, 117, 145-148; Angew. Chem. Int. Ed. 2005, 44, 142-145.
- [5] a) H. Mayr, T. Bug, M. F. Gotta, N. Hering, B. Irrgang, B. Janker, B. Kempf, R. Loos, A. R. Ofial, G. Remennikov, H. Schimmel, J. Am. Chem. Soc. 2001, 123, 9500–9512; b) H. Mayr, B. Kempf, A. R. Ofial, Acc. Chem. Res. 2003, 36, 66–77.
- [6] J. Bartl, S. Steenken, H. Mayr, J. Am. Chem. Soc. 1991, 113, 7710-7716.
- [7] The laser flash photolysis was performed using state-of-the-art femtosecond pulses as excitation and light-emitting diodes (LEDs) as sources of monitoring beams. New instrumentation was developed that is compatible with standard pump probe setups. Details of this method will be published separately: U. Schmidhammer, S. Roth, E. Riedle, A. A. Tishkov, H. Mayr, *Rev. Sci. Instrum.* 2005, submitted.
- [8] a) S. Minegishi, R. Loos, S. Kobayashi, H. Mayr, J. Am. Chem. Soc. 2005, 127, 2641–2649; b) S. Minegishi, H. Mayr, J. Am. Chem. Soc. 2003, 125, 286–295; c) R. Lucius, R. Loos, H. Mayr, Angew. Chem. 2002, 114, 97–102; Angew. Chem. Int. Ed. 2002, 41, 91–95; d) T. Bug, H. Mayr, J. Am. Chem. Soc. 2003, 125, 12980–12986; e) T. Bug, T. Lemek, H. Mayr, J. Org. Chem. 2004, 69, 7565–7576.
- [9] Because of the ease of the transformation of diarylnitromethanes into the corresponding benzophenones (see Scheme 2) these reactions were performed in NMR tubes and analyzed immediately after the reagents had been mixed.
- [10] D. M. Grant, R. K. Harris, Encyclopedia of Nuclear Magnetic Resonance, Vol. 5, Wiley, Chichester, 1996, p. 3232.
- [11] The nonobservance of tetraarylethanes indicates that electrontransfer processes do not occur under these conditions; see: a) N. Kornblum, L. Cheng, T. M. Davies, G. W. Earl, N. L. Holy, R. C. Kerber, M. M. Kestner, J. W. Manthey, M. T. Musser, H. W. Pinnick, D. H. Snow, F. W. Stuchal, R. T. Swiger, *J. Org. Chem.* **1987**, *52*, 196–204; b) N. Kornblum, T. M. Davies, G. W. Earl,

N. L. Holy, R. C. Kerber, M. T. Musser, D. H. Snow, J. Am. Chem. Soc. 1967, 89, 725-727.

- [12] a) J. F. Liebman, M. S. Campbell, S. W. Slayden in *The Chemistry of Amino, Nitroso, Nitro and Related Groups, Supplement F2* (Ed.: S. Patai), Wiley, Chichester, **1996**, chap. 8, p. 340; b) B. M. Rice, S. V. Pai, J. Hare, *Combust. Flame* **1999**, *118*, 445–458; c) "Neutral Thermochemical Data": H. Y. Afeefy, J. F. Liebman, S. E. Stein in *NIST Chemistry WebBook* (Eds.: P. J. Linstrom, W. G. Mallard), NIST Standard Reference Database Number 69, National Institute of Standards and Technology, Gaithersburg MD, 20899, **2003** (http://webbook.nist.gov).
- [13] These results disagree with the claim that malachite green ((4- $Me_2NC_6H_4)_2PhC^+$ ) reacts with  $NO_2^-$  in acetone and ethyl acetate yielding (4- $Me_2NC_6H_4)_2PhC$ -ONO as the kinetic product followed by slow (for a UV/Vis spectrometer with a regular mixing mode) irreversible formation of the more stable (4- $Me_2NC_6H_4)_2PhC$ -NO<sub>2</sub>: O. H. Abed, N. S. Isaacs, *J. Chem. Soc. Perkin Trans.* 2 **1983**, 839–842. Since the electrophilicity parameter of (4- $Me_2NC_6H_4)_2PhC^+$  (E = -10.29, ref. [8b]) is comparable to that of **1a** (E = -10.04), the rate constant reported by Isaacs for the reaction of (4- $Me_2NC_6H_4)_2PhC^+$  with  $NO_2^-$  in acetonitrile is more than six orders of magnitude smaller than expected for the formation of either (4- $Me_2NC_6H_4)_2PhC$ -NO<sub>2</sub> or (4- $Me_2NC_6H_4)_2PhC$ -ONO.
- [14] Addition of NOCl to solutions of benzhydrols (1 a-h)-OH in the presence of Et<sub>3</sub>N led to the immediate development of blue color characteristic for the corresponding benzhydryl cations.
- [15] a) Ph<sub>2</sub>CH-NO<sub>2</sub> was reported to convert into benzophenone spontaneously: H. Feuer, H. Friedman, J. Org. Chem. 1975, 40, 187–190; b) For the conversion of secondary nitro compounds into ketones in the presence of NO<sub>2</sub><sup>-</sup>, see: N. Kornblum, R. K. Blackwood, D. D. Mooberry, J. Am. Chem. Soc. 1956, 78, 1501–1504; c) A. Gissot, S. N'Gouela, C. Matt, A. Wagner, C. Mioskowski, J. Org. Chem. 2004, 69, 8997–9001.
- [16] Preferential or exclusive formation of nitrites was reported for reactions of *tert*-alkyl halides as well as 4-methoxybenzyl bromide and 1-phenylethyl chloride with AgNO<sub>2</sub> in Et<sub>2</sub>O (see refs. [1a, c, f]).
- [17] H. Lemmetyinen, L. Lehtinen, J. Koskikallio, *Finn. Chem. Lett.* 1979, 6, 72–75.