Quantification of the Electrophilicities of Diazonium Ions☆

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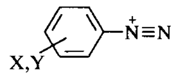
The kinetics of the reactions of arenediazonium ions with arenes, alkenes, allylsilanes, allylstannanes, and silyl ketene acetals have been studied in acetonitrile solution. The reactions follow second-order kinetics, and in several cases rate-determining attack of the diazonium ion has been proven by kinetic isotope effect studies (**1a** + **2b**), by the independence of the allylsilane reactivities of the rate of desilylation (**1a** + **10a**, **d**) and by the independence of the rate constants of the diazonium counterion. A decrease of the rate constant with increasing solvent donor ability (correlation with Gutmann's donor number) was found. The reactions of diazonium ions with π-nucleophiles roughly follow the correlation lg$k$ (20 °C) = s (E + N), previously derived for the reactions of carbocations with nucleophiles. With the E parameters derived for diazonium ions, rate constants for azo couplings with aromatic and nonaromatic π-nucleophiles can be predicted with an accuracy of $\approx 10^2$. On the basis of E, the electrophilic reactivities of diazonium ions can be compared with those of carbocations (Figure 9), and the combination with the nucleophilicity parameters N (Figure 10) gives a first clue on possible azo coupling reactions. Literature reports are discussed within this scheme.

"Diazonium ions are weak electrophiles and undergo azo couplings only with activated arenes." Statements of that type can be found in most textbooks of organic chemistry, and the question arises whether it is possible to quantify the electrophilic power of diazonium ions in order to make predictions of potential reaction partners. Since Ritchie reported that the reactions of diazonium ions and highly stabilized carbocations with OH^-, CN^-, N_3^- and related n-nucleophiles follow the same constant selectivity relationships[1] we were prompted to investigate whether the linear free energy relationships found for the reactions of carbocations with π-nucleophiles[2] also hold for the corresponding reactions of diazonium ions.

For this purpose, we have synthesized arenediazonium tetrafluoroborates of variable reactivity (Scheme 1) and studied the kinetics of their reactions with π-nucleophiles[3].

Scheme 1



X,Y	No	X,Y	No	X,Y	No
2,4-(NO_2)$_2$	**1a**	4-CN	**1f**	4-Br	**1k**
2-Cl, 4-NO_2	**1b**	4-CF_3	**1g**	4-H	**1l**
2-Cl, 4-CN	**1c**	3-Cl	**1h**	4-Me	**1m**
4-NO_2	**1d**	4-CO_2Me	**1i**	4-OMe	**1n**
3-NO_2	**1e**	4-Cl	**1j**	4-NMe_2	**1o**

1. Reaction Products

1.1 Arenes

Azo couplings with phenols are usually carried out at pH = 8, conditions under which phenolate ions act as reaction partners. Phenol ethers, which cannot be activated in this way, are considerably less reactive, and the benzenediazonium ion (**1l**) has been reported only to couple with highly nucleophilic alkoxyarenes such as 1,3,5-trimethoxybenzene (**2a**)[4]. It has been demonstrated that the more electrophilic 4-nitrobenzenediazonium ion (**1d**) also reacts with 1,3-dimethoxybenzene (**2b**)[4], and that the highly reactive 2,4-dinitrobenzenediazonium ion (**1a**) was needed to achieve azo coupling with anisole (**2d**)[5].

We have now investigated the reactions of various diazonium tetrafluoroborates with **2a**, **2b**, 1-methoxy-3-methylbenzene (**2c**) and **2d** in acetonitrile, the same solvent as used for most kinetic studies, and isolated the corresponding azo compounds **3** in high yield (Table 1).

1.2 Alkenes

Marxmeier and Pfeil[6] have reported on the reactions of the 2,4-dinitrobenzenediazonium tetrafluoroborate (**1a**-BF_4^-) with ordinary alkenes **4** in wet acetonitrile. Usually cleavage of the C−C double bond was observed, as illustrated for the reaction of **1a** with 2,3-dimethylbut-2-ene (**4a**) in Scheme 2.

We found that the C−C bond fission can be avoided by using methanol/acetonitrile (5:2, v/v) as solvent. Depending on the substitution pattern, the azo compounds **6** and/or **7** or the hydrazones **8** or **9** were isolated (Table 2, Scheme 3). Their formation is rationalized by Scheme 3 which suggests the initial formation of the carbocation **5** as a common intermediate, which either loses a proton or accepts

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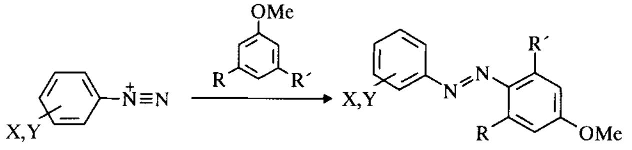
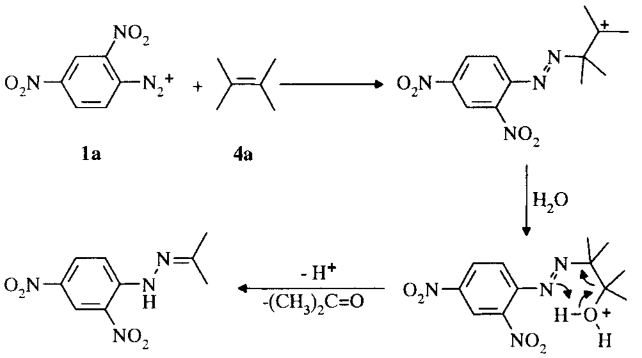
Table 1. Reactions of the diazonium salts **1a**-, **1b**- and **1d**-BF_4^- with arenes in acetonitrile at 20 °C



X, Y		R	R′			
2,4-$(NO_2)_2$	**1a**	OMe	OMe	**2a**	89%	**3aa**
		OMe	H	**2b**	80%	**3ab**
2-Cl, 4-NO_2	**1b**	OMe	OMe	**2a**	98%	**3ba**
		OMe	H	**2b**	75%	**3bb**
4-NO_2	**1d**	OMe	OMe	**2a**	54%	**3da**

Scheme 2



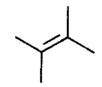
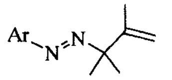
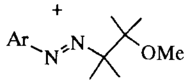
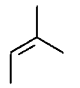
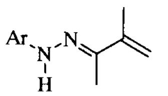
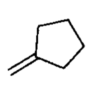
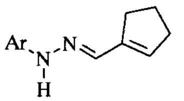
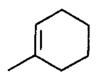
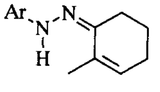
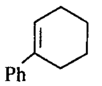
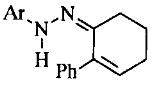
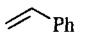
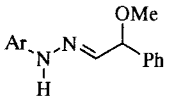
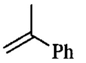
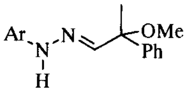
methanol to give the azo compounds **6** and **7**, respectively. These products were isolated when neither R^1 and R^2 were hydrogen. Otherwise tautomerization occurred, and the hydrazones **8** and **9** were isolated instead of the azo compounds.

This mechanistic sequence has not been corroborated, however. Compounds **6** and **8** may alternatively have been formed by elimination of methanol from **7** and **9**, respectively. The formation of compounds **8** by concerted ene reaction[7] of the diazonium ions with alkenes is a third possibility. We prefer the formulation given in Scheme 3 because of the analogy to the corresponding reactions of diazonium ions with allylsilanes (Scheme 4), where the initial formation of azo compounds and their successive tautomerization to hydrazones has been observed (see below).

1.3 Allylsilanes and Allylstannanes

In a preliminary communication[8], we have reported that diazonium ions, like other electrophiles, undergo S_E2' reactions with allylsilanes and allylstannanes. As shown in Scheme 4, the initially produced β-silyl or β-stannyl substituted carbenium ions **12** were demetallated to give the allylazo compounds **13** which tautomerized when either R^1 or R^2 was hydrogen to yield the hydrazones **14** as the final products. Though most of the combinations of diazonium salts with allylsilanes or allylstannanes produced **13** or **14** in good yields (Table 3), there were exceptions. While the reaction of **1a** with allyltributylstannane (**11a**) gave 65% of the hydrazone **14aa**, analogous to the corresponding reaction of **1a** with **10a**, all attempts to isolate products from the reactions of **11a** with **1d**-, **1f**-, **1i**-, **1k**-BF_4^- were unsuccessful. We observed evolution of nitrogen, but were unable to detect any products derived from phenyl radicals.

Table 2. Reactions of the 2,4-dinitrobenzenediazonium tetrafluoroborate (**1a**-BF_4^-) with alkenes in methanol/acetonitrile (5:2, v/v) at 20 °C [Ar = 2,4-$(NO_2)_2C_6H_3$)]

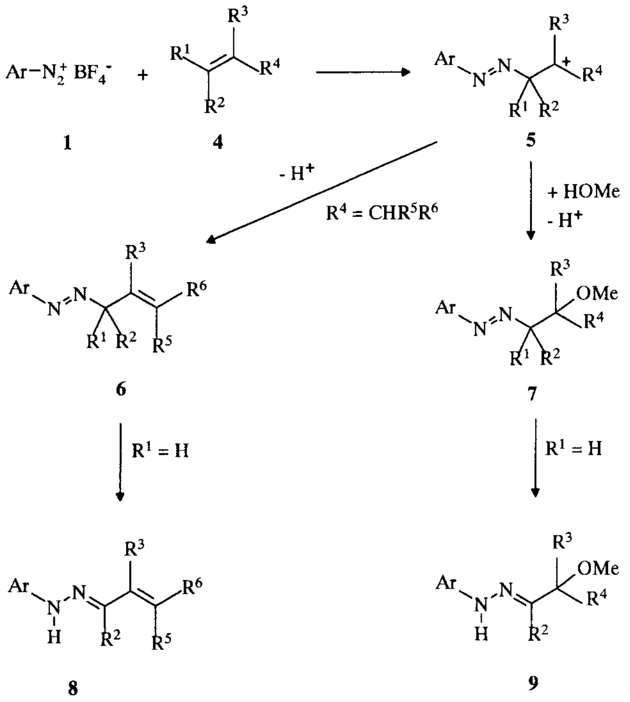
Alkene	Product	
 **4a**		**6aa** (43%)[a]
	+	+
		**7aa** (12%)
 **4b**		**8ab** (20%)
 **4c**		**8ac** (21%)
 **4d**		**8ad** (16%)
 **4e**		**8ae** (58%)
 **4f**		**9af** (13%)
 **4g**		**9ag** (52%)

[a] **1d**-BF_4^- yielded 60% of the corresponding azo compound **6da**.

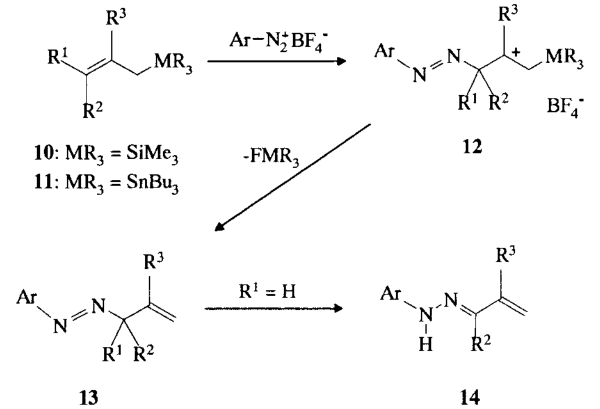
Stirring of trimethyl(2-methylallyl)silane (**10b**) with a suspension of **1a**-BF_4^- in acetonitrile at ambient temperature for one minute yielded 72% of the allylazo compound **13ab** which could be isolated by evaporation of the solvent at ambient temperature. The microcrystalline **13ab** could be stored in a refrigerator (−20 °C, dark) for months, but isomerized rapidly to the hydrazone **14ab** when the solid was heated at 60 °C or was dissolved in $CDCl_3$ (not specially deacidified) at room temperature.

Like other 3,3-disubstituted allylsilanes[8], compound **10c** reacted with **1a** and **1d** to give the stable allylazo compounds **13ac** and **13dc**, respectively. The analogous reaction of **10c** with the parent benzenediazonium ion **11** to give **13lc** could not be achieved, but this product was obtained by

Scheme 3



Scheme 4



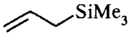
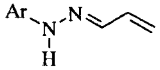
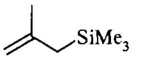
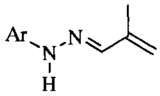
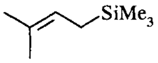
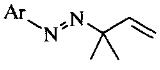
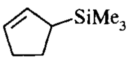
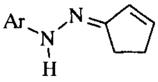
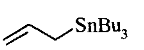
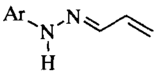
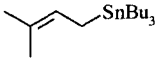
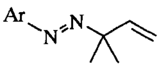
reaction of **1l** with the more nucleophilic allylstannane **11c**. The allylstannane **11c** is highly reactive and even combined with the donor substituted benzenediazonium ions **1m** and **1n** yielding the allylazo compounds **13mc** and **13nc**, respectively (Table 3).

1.4 Silyl Ketene Acetals

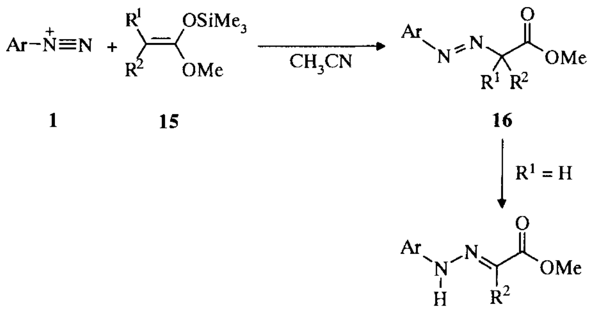
Sakakura and Tanaka[9,10] have reported on the reactions of arenediazonium ions with silyl ketene acetals in pyridine. As with the allylazo compounds above, the initially produced areneazo esters **16** tautomerized yielding the hydrazono esters when either R^1 or R^2 was hydrogen (Scheme 5).

We investigated the reactions of the diazonium ions **1n** and **1o** with 1-methoxy-2-methyl-1-trimethylsiloxypropene (**15a**) in acetonitrile and isolated the corresponding azo compounds **16** in good yields (Table 4).

Table 3. Reactions of various diazonium tetrafluoroborates [(**1a**–**1n**)-BF$_4^-$] with allylsilanes **10** and allylstannanes **11** in acetonitrile at 20°C

Ar–N$_2^+$	Allylsilane/-stannane	Product (Yield)
1a	 **10a**	 **14aa** (58%)
1a	 **10b**	 **14ab** (72%)
1d		**14db** (50%)
1a	 **10c**	 **13ac** (84%)
1d		**13dc** (72%)
1a	 **10e**	 **14ae** (67%)
1a	 **11a**	 **14aa** (65%)
1a	 **11c**	 **13ac** (57%)
1b		**13bc** (89%)
1d		**13dc** (55%)
1f		**13fc** (64%)
1g		**13gc** (39%)
1i		**13ic** (56%)
1j		**13jc** (51%)
1k		**13kc** (71%)
1l		**13lc** (67%)
1m		**13mc** (84%)
1n		**13nc** (59%)

Scheme 5

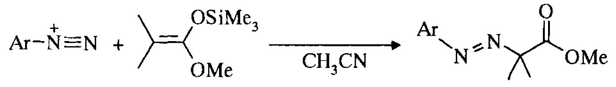


2. Kinetics

2.1 Methods

Two different methods have been employed for determining the rates of the reactions of diazonium ions with nucleophiles. In the initially used method, developed by Marx-

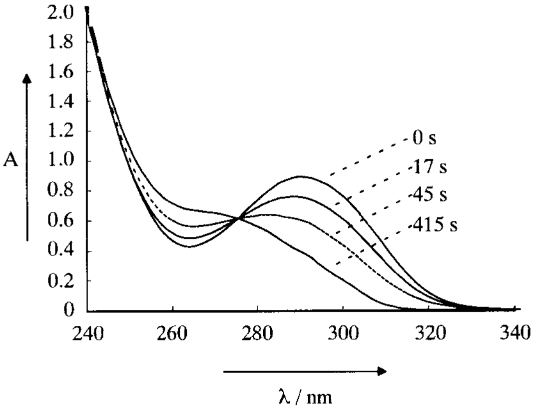
Table 4. Reactions of diazonium tetrafluoroborates **1n**- and **1o**-BF_4^- with 1-methoxy-2-methyl-1-trimethylsiloxypropene (**15a**) in acetonitrile at 20 °C



1n	**15a**	100%	**16na**
1o		80%	**16oa**

meier and Pfeil[11], a solution of diazonium salt and nucleophile in CH_3CN was kept in a thermostat, and after certain time intervals, samples of the solution were removed and added to a solution of the highly reactive 2-naphthylamine in acetonitrile. Photometric determination of the concentration of the instantaneously formed azo dye allowed the calculation of the concentration of the nonconsumed diazonium ion, and the results were independent of the concentration of the naphthylamine used for quenching.

Figure 1. UV-spectrophotometric determination of the rate of the reaction of 4-bromobenzenediazonium tetrafluoroborate (**1k**-BF_4^-) with tributyl(3-methylbut-2-enyl)stannane (**11c**) (CH_3CN at 20 °C)



The second method follows the decay of the diazonium absorbance at λ = 250−378 nm (Figure 1) or the formation of the azo dye (reactions with arenes) photometrically as a function of time.

$$-d[\mathbf{1}]/dt = k[\mathbf{1}][Nuc] \qquad (1)$$

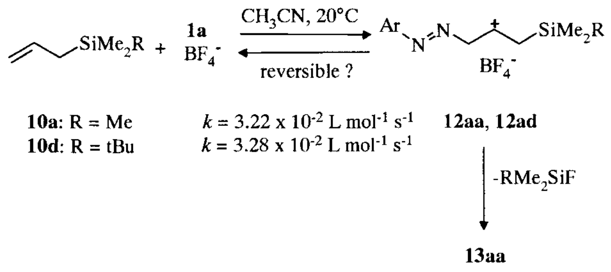
All reactions reported in this paper followed second-order kinetics and were linear with respect to diazonium ion and to nucleophile (eq. 1). In several cases, where both methods were employed, the indirect method was found to yield rate constants which were approximately 30% lower than the rate constants obtained by directly following the decay of the diazonium absorbance (Figure 1).

We consider the direct method to be more precise than the indirect method. If the products of the investigated reactions also weakly absorb at the wavelength of the azo dye obtained from the coupling of the diazonium ions with 2-naphthylamine, the photometric analysis gives a falsely high concentration of the azo dye. Since the amount of unreacted diazonium ions is derived from this concentration, the rate constants so calculated are too low.

2.2 The Rate-Determining Step

The observation of second-order kinetics (eq. 1) is in accord with rate-determining attack of the diazonium ion at the π-system as well as with reversible formation of the initial adducts (e.g. **5** or **12**) followed by rate-determining deprotonation or demetallation steps.

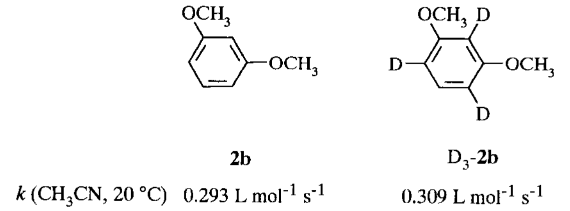
Scheme 6



If the first step of Scheme 6 were reversible, allyl-*tert*-butyldimethylsilane (**10d**) should be less reactive than allyltrimethylsilane (**10a**), since the desilylation step is retarded by steric shielding[12]. According to Scheme 6, both compounds are equally reactive, which indicates an irreversible attack of the diazonium ion at the π-system followed by rapid desilylation.

An irreversible attack of the diazonium ion at the π-system has also been deduced for the reaction of **1a**-BF_4^- with 1,3-dimethoxybenzene (**2b**) from kinetic isotope effect studies. As shown in Scheme 7, deuterated and non-deuterated **2b** react with similar rates, which excludes rate-determining deprotonation.

Scheme 7



Though the reactivity difference shown in Scheme 7 should not be overinterpreted because of the error limits of our experiments, it should be noted that the value k_H/k_D = 0.95 is of the order of magnitude expected for the secondary kinetic isotope effect of a reaction with $sp^2 \rightarrow sp^3$ rehybridization in the rate-limiting step.

In analogy to the reactions of benzhydryl cations with π-systems, the counterion only slightly affects the electrophilicities of the diazonium ions, and **1n**-BF_4^- was found to react only 1.14 times faster with **11c** than $(\mathbf{1n})_2ZnCl_4^{2-}$ (CH_3CN, 20 °C), again in agreement with rate-determining attack of **1n** at the double bond of **11c**. This observation is also in accord with Zollinger's report that **1m**-SO_4H^- and **1m**-BF_4^- show identical reactivities towards *N*,*N*-dimethylaniline in both acetonitrile and nitromethane solution[13].

2.3 Influence of the Solvent

In accordance with literature reports[14], we had found that solvent polarity had little influence on the rates of the reactions of carbocations with neutral π-nucleophiles[15] and hydride donors[16]. We rationalized this observation by the fact that charge is neither created nor destroyed in the rate-determining step[2,15,16].

The situation seems to be different for the analogous reactions of diazonium ions. While Zollinger[13] and Matsui[17] reported only moderate solvent effects on the rates of azo couplings (see below), Bagal et al., who studied the reactions of several diazonium tetrafluoroborates with *N*,*N*-dimethylaniline in various solvents, found the reaction of **1d**-BF_4^- to occur 4750 times faster in nitromethane than in HMPT[18]. A correlation of the rate constants with Gutmann's donor numbers[19] of the solvents was reported, and in accord with the assumption of a specific interaction of the diazonium ions with donor solvents, the magnitude of the solvent effects increases with increasing electrophilicity of the diazonium ions.

Since the question of solvent dependence of the rate constants is crucial for our reactivity model[2], where solvent effects have not yet been specifically considered, we have also studied the influence of solvent on the rates of two typical reactions (Table 5).

Table 5. Rate constants k(L mol^{-1} s^{-1}, 20°C) for the reactions of the diazonium tetrafluoroborates **1n**-BF_4^- and **1k**-BF_4^- with the tributyl(3-methylbut-2-enyl)stannane (**11c**) and *N*,*N*-dimethylaniline in various solvents

solvent	**1n** + **11c** k/ L mol^{-1} s^{-1}	**1k** + $Me_2NC_6H_5$ k/ L mol^{-1} s^{-1}
dichloromethane	1.55 x 10^1	8.50 x 10^2
acetonitrile	2.07 x 10^{-1}	2.20 x 10^0
propionitrile	1.71 x 10^{-1}	3.05 x 10^0
ethyl acetate	1.13 x 10^{-2}	2.54 x 10^{-1}
tetrahydrofuran	1.05 x 10^{-1}	6.23 x 10^{-1}
dimethylformamide	6.78 x 10^{-2}	-
dimethylsulfoxide	3.50 x 10^{-2}	2.74 x 10^{-1}

The fair correlation between the two reaction series in Figure 2 shows the internal consistency for the two sets of data given in Table 5. The slope of this correlation (1.2) is in accord with Bagal's statement that solvent effects are more pronounced for more electrophilic diazonium ions. Since these two reaction series also refer to different nucleophiles, however, additional effects may be responsible for the non-unity slope of the graph in Figure 2.

Though the correlations between lg$k$ and Gutmann's donor numbers are only of moderate quality (Figure 3), we did not find any other solvent parameter (ε, E_T(30), Z, μ)[19] that gave better correlations and, therefore, agree with Bagal's interpretation of the solvent effects. The high rates of reaction found in the weak donor solvent CH_2Cl_2 are in accord with the very fast phase transfer catalyzed coupling reactions in the two-phase system CH_2Cl_2/H_2O[20] or $CHCl_3/H_2O$[21].

Figure 2. Correlation of the rate constants k of the reaction of the 4-bromobenzenediazonium ion (**1k**) with *N*,*N*-dimethylaniline and of the 4-methoxybenzenediazonium ion (**1n**) with tributyl(3-methylbut-2-enyl)stannane (**11c**) in different solvents [lg$k_{(1k+Me_2NC_6H_5)}$ = 1.202 · lg$k_{(1n+11c)}$ + 1.329]; r^2 = 0.956

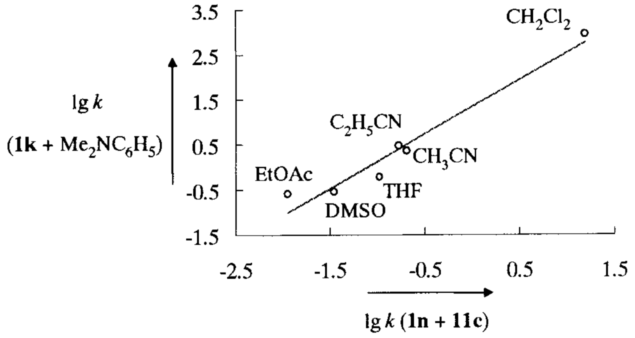
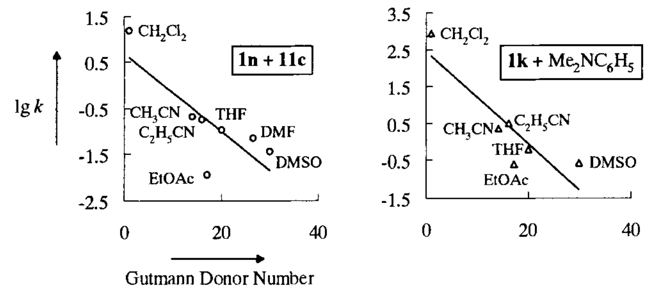


Figure 3. Correlation of the rate constants k of the reactions of the 4-methoxybenzenediazonium ion (**1n**-BF_4^-) with tributyl(3-methylbut-2-enyl)stannane (**11c**) and of the bromobenzenediazonium ion (**1k**-BF_4^-) with *N*,*N*-dimethylaniline versus the Gutmann donor number of the solvent[19]



The considerable influence of solvent donicity on the rates of these reactions implies that the electrophilicities of diazonium ions, unlike the electrophilicities of carbocations, have to be defined with respect to a certain solvent. We have now selected acetonitrile as the standard solvent. Since Zollinger[13] and Matsui[17] found azo couplings in water to be only 2–3 times faster than in acetonitrile, the reactivity data determined for acetonitrile should not differ greatly from those for water, the solvent in which most azo couplings have been performed.

2.4 Kinetics of the Reactions of the Diazonium Ion 1a with Various Aromatic, Aliphatic and Alicyclic π-Systems

In previous work[2] we have shown that the reactions of carbocations with noncharged nucleophiles follow the correlation (eq. 2), where E represents the reactivities of the electrophiles, while nucleophiles are characterized by the nucleophilicity parameter N and the slope parameter s.

$$\lg k = s(E + N) \qquad (2)$$

Figure 4 shows that the quotient (lg$k$)/s for the reactions of the 2,4-dinitrobenzenediazonium ion (**1a**) with nucleophiles correlates moderately with N as required by eq. 2. Though the standard deviation, which corresponds to a factor of about 7 in the rate constants, appears rather high at first glance, the basic message of Table 6 and Figure 4 should be noticed: Nucleophiles as different as, for example, allyltrimethylsilane (**10a**), α-methylstyrene (**4g**), and 1-methoxy-3-methylbenzene (**2c**), which have previously been reported to show similar reactivities towards carbenium ions[2,12,22], also have similar reactivities towards diazonium ions. Marked deviations from the correlation shown in Figure 4 have been found for π-nucleophiles with two alkyl groups at the position of the electrophilic attack, however, and nucleophiles of that type, e.g. 2,3-dimethylbut-2-ene (**4a**) and (3-methylbut-2-enyl)trimethylsilane (**10c**), have not been included for the construction of the correlation line. Probably because of steric reasons these nucleophiles react approximately 10^2-10^4 times faster with the "slim" electrophile **1a** than would be expected by extrapolation of their reactivities towards the sterically more demanding benzhydryl cations. Alternatively one can explain the unusually high reactivity of the highly alkylated π-systems by the greater importance of the electron transfer term in reactions of diazonium ions (see below).

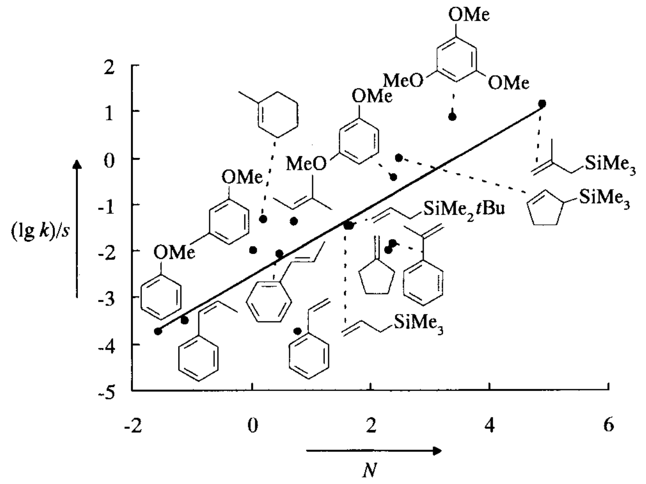
Table 6. Second-order rate constants *k* for the reactions of 2,4-dinitrobenzenediazonium tetrafluoroborate (**1a**-BF_4^-) with various nucleophiles (CH_3CN, 20 °C)

Nucleophile	*N*[2]	*s*[2]	*k*/ L mol^{-1} s^{-1}
1,3,5-Trimethoxy-benzene (**2a**)	3.40	1.30	1.32 x 10^{1}
1,3-Dimethoxy-benzene (**2b**)	2.40	1.20	2.93 x 10^{-1}
1-Methoxy-3-methyl-benzene (**2c**)	0.02	1.20	4.08 x 10^{-3}
Anisole (**2d**)	-1.56	1.17	4.37 x 10^{-5}
2,3-Dimethyl-but-2-ene (**4a**)	-0.96	1.44	1.12 x 10^{1}
2-Methyl-but-2-ene (**4b**)	0.71	1.16	2.58 x 10^{-2}
Methylene-cyclopentane (**4c**)	2.31	1.02	9.39 x 10^{-3}
1-Methyl-cyclohexene (**4d**)	0.20	1.10	3.53 x 10^{-2}
Styrene (**4f**)	0.78	0.97	2.33 x 10^{-4} [11]
Isopropenyl-benzene (**4g**)	2.39	1.00	1.43 x 10^{-2} [11]
(Z)-Propenyl-benzene	-1.12	1.20	6.33 x 10^{-5} [11]
(E)-Propenyl-benzene	-0.47	1.20	3.33 x 10^{-3} [11]
Allyl-trimethyl-silane (**10a**)	1.62	1.01	3.22 x 10^{-2} [a]
Trimethyl-(2-methyl-allyl)-silane (**10b**)	4.90	0.89	1.02 x 10^{1}
(3-Methyl-2-but-enyl)-trimethyl-silan (**10c**)	0.84	1.25	1.97 x 10^{0}
Allyl-*tert*-butyl-dimethyl-silane (**10d**)	1.65	1.00	3.28 x 10^{-2}
Cyclopent-2-enyl-trimethyl-silane (**10e**)	2.50	0.90	9.80 x 10^{-1}

[a] $\Delta H^{\neq} = (44.58 \pm 1.36)$ kJ mol^{-1}, $\Delta S^{\neq} = (-121.06 \pm 4.68)$ J mol^{-1} K^{-1}.

From the intercept of the correlation in Figure 4, the electrophilicity parameter $E(\mathbf{1a}) = -2.5 \pm 0.3$ is derived, which slightly differs from the preliminary value[2] because of the larger data basis used for the correlation in this work. The slope of the correlation line in Figure 4, which deviates from unity, manifests the limitations of our approach[2] to use only one parameter for the characterization of electrophiles. However, the moderate deviation of this slope from unity has little consequence for the use of eq. 2 by the practicing synthetic chemist, and we have decided not to introduce an additional slope parameter for electrophiles at present.

Figure 4. Correlation of the rate constants of the reactions of 2,4-dinitrobenzenediazonium tetrafluoroborate (**1a**-BF_4^-) with various nucleophiles with the corresponding nucleophilicities *N* [$(\lg k)/s = 0.734 \cdot N - 2.54$]



In principle the *E*-parameters for the other diazonium ions **1b**–**1o** might analogously be derived from the rate constants listed in Table 7. However, for many of these electrophiles only limited kinetic data are available, sometimes with atypical nucleophiles as **11c**, i.e. with systems that considerably deviate from eq. 2 (see discussion above). Depending on the choice of the nucleophiles this way of de-

Table 7. Second-order rate constants for the reactions of the arenediazonium ions **1b**–**1o** with π-nucleophiles (CH_3CN, 20 °C) and n-nucleophiles (H_2O, 23 °C)[23]

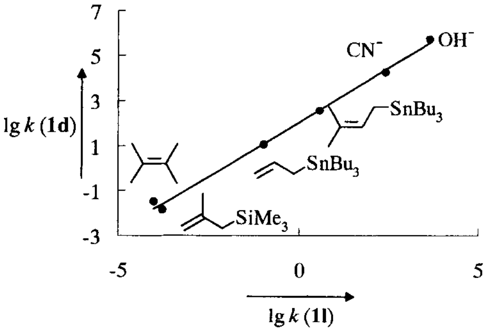
Diazonium Ion	Nucleophile	*k* L mol^{-1} s^{-1}	Diazonium Ion	Nucleophile	*k* L mol^{-1} s^{-1}
1b	**2a**	2.44 x 10^{0}	**1i**	**11a**	1.11 x 10^{0}
	2b	5.29 x 10^{-2}	**1j**	**4a**	5.44 x 10^{-4}
1d	**2a**	9.42 x 10^{-2}		**10b**	2.82 x 10^{-4}
	2b	3.06 x 10^{-4}		OH^-	1.6 x 10^{4} [23]
	4a	3.23 x 10^{-2}		CN^-	6.8 x 10^{2} [23]
	10b	1.27 x 10^{-2}	**1k**	**11a**	4.08 x 10^{-1}
	10c	6.53 x 10^{-3}		**11c**	1.82 x 10^{1}
	11a	1.14 x 10^{1}		OH^-	2.1 x 10^{4} [23]
	11c	3.30 x 10^{2} [a]		CN^-	6.5 x 10^{2} [23]
	OH^-	5.4 x 10^{5} [23]	**1l**	**4a**	9.80 x 10^{-5}
	CN^-	1.7 x 10^{4} [23]		**10b**	1.69 x 10^{-4}
1e	**11a**	9.98 x 10^{0}		**11a**	1.05 x 10^{-1}
1f	**11a**	6.28 x 10^{0}		**11c**	3.67 x 10^{0}
	11c	2.10 x 10^{2} [b]		OH^-	4.5 x 10^{3} [23]
	OH^-	4.2 x 10^{5} [23]		CN^-	2.6 x 10^{2} [23]
	CN^-	7.4 x 10^{3} [23]	**1m**	**11c**	1.12 x 10^{0}
1g	**4a**	6.98 x 10^{-3}		OH^-	1.2 x 10^{3} [23]
	10b	3.62 x 10^{-3}		CN^-	9.0 x 10^{1} [23]
1h	**11a**	1.59 x 10^{0}	**1n**	**11c**	2.07 x 10^{-1}
	OH^-	6.4 x 10^{4} [23]		**15a**	7.55 x 10^{1} [c]
	CN^-	1.8 x 10^{3} [23]	**1o**	**15a**	8.12 x 10^{-1}

[a] $\Delta H^{\neq} = (29.68 \pm 0.60)$ kJ mol^{-1}, $\Delta S^{\neq} = (-95.22 \pm 2.25)$ J mol^{-1} K^{-1}. – [b] $\Delta H^{\neq} = (31.81 \pm 0.92)$ kJ mol^{-1}, $\Delta S^{\neq} = (-91.50 \pm 3.40)$ J mol^{-1} K^{-1}. – [c] $\Delta H^{\neq} = (33.25 \pm 2.51)$ kJ mol^{-1}, $\Delta S^{\neq} = (-95.48 \pm 9.26)$ J mol^{-1} K^{-1}.

termining E-parameters might yield quite accidental results, because not all reactions of diazonium ions studied in this work follow exactly the same linear free enthalpy relationship (eq. 2) as the reactions of benzhydryl cations with the corresponding nucleophiles. We have tried to overcome this problem by employing the following procedure.

The reactivities of diazonium ions with all types of nucleophiles used in this study are interrelated by perfect linear free enthalpy relationships with unity slopes as shown for the couple **1d**/**1l** in Figure 5. Therefore, the relative reactivities of the diazonium ions towards any of the nucleophiles used in this work can be used to derive relative E-values. Consequently, we have combined the E-value for **1a** (−2.5), which is based on kinetic studies with a wide variety of structurally different nucleophiles, with the averaged relative reactivities of diazonium ions towards the nucleophiles accessible from Table 7, to derive the E-values for **1b**−**1o**. For this purpose we have used the equation $\lg k = \lg k_{1a} + (E - E_{1a})$, where $\lg k$ corresponds to the observed combination rate constant (Table 7), $\lg k_{1a}$ is the rate constant for the reaction of **1a** with the nucleophile under consideration, and $E_{1a} = -2.5$. Optimization with respect to $\lg k_{1a}$ and E yields the electrophilicity parameters E listed in Figure 9. By handling k_{1a} as a variable, the experimental error in k_{1a} is treated in the same way as the experimental error of the other rate constants.

Figure 5. Correlation of the rate constants of the reaction of **1d** and **1l** with various π-nucleophiles (CH_3CN, 20°C) and n-nucleophiles (H_2O, 23°C) [$\lg k(\mathbf{1d}) = 0.965 \cdot \lg k(\mathbf{1l}) + 2.034$]



3. Discussion

3.1 Correlations with the Electrophilicity Parameter E

The reactivities of substituted benzenediazonium ions have previously been reported to correlate with Hammett's σ-parameters[24]. Since their reactivities have now been expressed by the electrophilicity parameter E, the linear correlation between these two quantities which is shown in Figure 6 is an inevitable consequence.

Figure 7 shows that the correlation lines obtained for the reactions of different n- and π-nucleophiles with diazonium ions have very similar slopes, in contrast to their behavior towards benzhydryl cations, where π-systems with two alkyl groups at the attacked vinylic position are characterized by markedly larger slopes[25].

Figure 6. Correlation of the electrophilicity parameters E of substituted benzenediazonium ions with Hammett's σ constants [$E = 3.324\,\sigma - 7.613$]

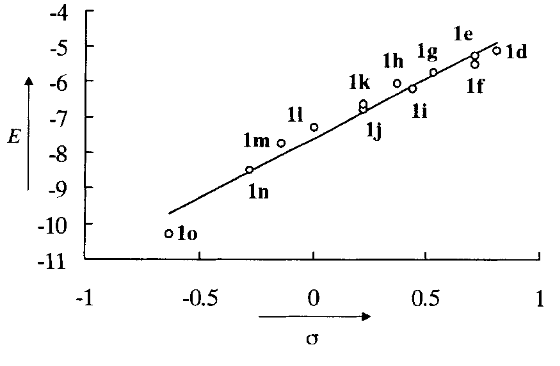
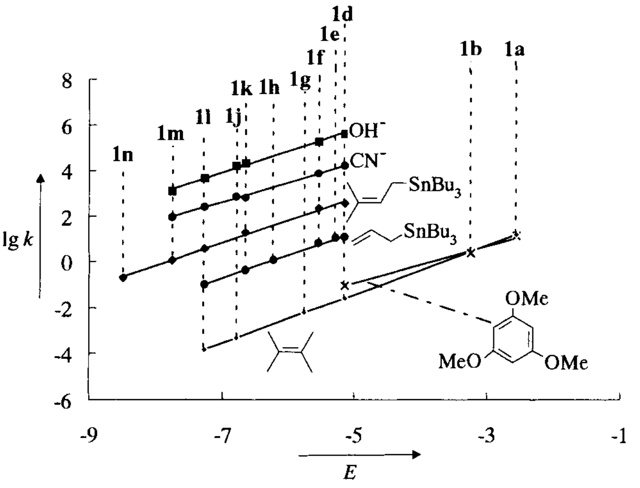


Figure 7. Correlation of the rate constants of the reactions of diazonium ions **1** with various nucleophiles with the electrophilicity parameters E



Combination of the correlations depicted in Figures 6 and 7 yields Hammett reaction constants ρ = 2.5−3.2, slightly smaller than reported for the majority of azo couplings[3,26,27]. Since Zollinger's review[26] on diazonium reactivities reports ρ values between 1.1 and 5.9, the narrow range of the slopes found for the different nucleophiles in this work (Figure 7) is surprising.

The different electronic effects of the aryl groups which are responsible for the different electrophilicities of the diazonium ions can also be seen in the ^{13}C-NMR spectra of the coupling products. Figure 8 reveals a linear correlation between $\delta_{C\text{-}1}$ of the (1,1-dimethylallyl)aryldiazenes and the E parameters of the corresponding diazonium ions, indicating the same electronic origin of both quantities.

3.2 Consequences for Organic Synthesis

While Hammett's σ-constants allow the comparison of the reactivities of various diazonium ions among each other, the definition of the E parameters now permits the direct comparison of the electrophilicities of diazonium ions with those of carbocations and transition metal π-complexes. Figure 9 shows that the 2,4-dinitrobenzenediazon-

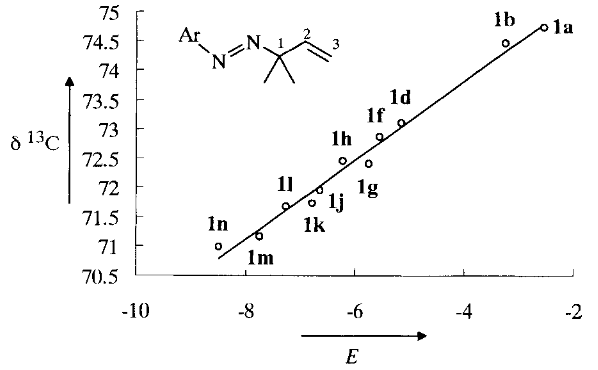


Figure 8. Correlation of the ^{13}C-NMR chemical shifts of C-1 of the (1,1-dimethylallyl)aryldiazenes with the electrophilicity parameters E [$\delta^{13}C = 0.673 \cdot E + 76.50$]

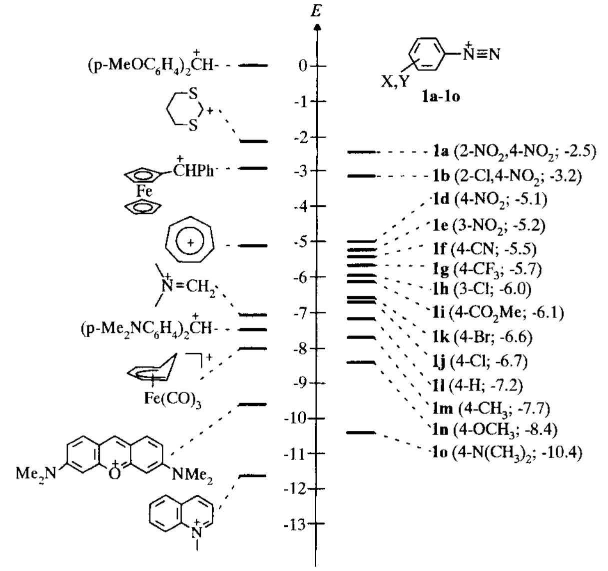


Figure 9. Comparison of the electrophilicities of benzenediazonium ions (substituents and E-parameters in parentheses), carbenium ions, and transition metal complexes (E-parameters taken from ref.[21])

ium ion (**1a**), the most electrophilic diazonium ion studied in this investigation, is comparable to the ferrocenylphenylmethylium ion, while the highly stabilized dimethylamino substituted benzenediazonium ion **1o** is slightly more electrophilic than the *N*-methylquinolinium ion. The electrophilicity of the parent benzenediazonium ion (**1l**) corresponds to that of the bis(*p*-dimethylamino)benzhydryl cation or the *N*,*N*-dimethylmethyleneammonium ion.

In previous work[2] we have shown that at first approximation the different slope parameters s in eq. 2 can be neglected, and that a graphic representation of electrophilic and nucleophilic reactivities as shown in Figure 10 allows a first orientation which electrophile-nucleophile combinations are going to take place. As discussed previously for other systems[2], one can expect reactions of diazonium ions with those nucleophiles which are placed below them in Figure 10.

On these premises, one would not expect reactions of the 2,4-dinitrobenzenediazonium ion (**1a**) with toluene or *m*-xylene, in accord with Meyer's report that **1a** reacts only slowly with the more nucleophilic mesitylene[5]. The reaction of **1a** with anisole, first reported by Meyer[5] has been observed in this work to be rather slow. In accord with the position of the less electrophilic 4-nitrobenzenediazonium ion (**1d**) in Figure 10, its azo coupling with anisole has been reported not to be possible[28]. The reaction of **1d** with 1-methoxy-3-methylbenzene (**2c**), two systems on the same level in Figure 10, has been observed by von Auwers[28].

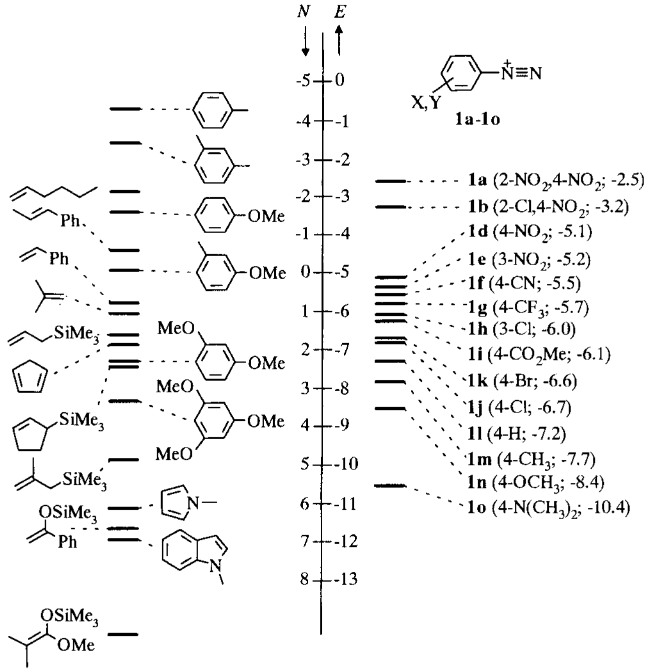


Figure 10. Which nucleophiles can be attacked by diazonium ions? (N-values taken from ref.[2,32])

The unsubstituted benzenediazonium ion (**1l**) has been reported not to react with 1,3-dimethoxybenzene (**2b**)[5], reaction partners at the same level in Figure 10. The borderline situation for this electrophile-nucleophile combination is illustrated by the fact, that 1,3-dimethoxybenzene (**2b**) was found to react with the 4-chlorobenzenediazonium ion (**1j**)[5], which is only slightly more reactive than **1l** according to Figure 10.

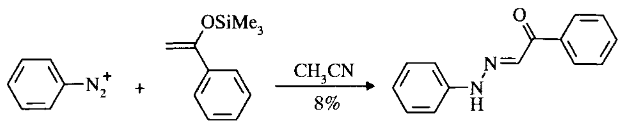
Because of its high nucleophilicity, 1,3,5-trimethoxybenzene (**2a**) reacts with **1l**[5] and even with the highly stabilized 4-methoxybenzenediazonium ion (**1n**), but the latter reaction was described to be very slow, as expected from the position of **1n** at the same level as **2a** in Figure 10[20].

It is not accidental that Marxmeier and Pfeil only reported on the reactions of the highly electrophilic 2,4-dinitrobenzenediazonium ion (**1a**) with alkenes[6,11]. Terentjew and Demidova had previously reported that the 4-nitrobenzenediazonium ion (**1d**) in contrast to **1a** does not react with isobutylene or trimethylethylene[29], reactions which are expected to be rather slow on the basis of Figure 10. Since 1,5-hexadiene can be expected to possess a similar nucleophilicity as 1-hexene (−2.02)[2], Terentjew's report that this nonconjugated diene does not even react with **1a** is also in accord with Figure 10.

If nucleophiles are positioned below certain diazonium ions in Figure 10, the corresponding azo coupling can be expected to be fast enough to take place within reasonable time at 20 °C. Since faster side reactions cannot be predicted by our analysis, one cannot rely on the formation of azo coupling products if Figure 10 indicates this reaction to be feasible.

The observation that **1l**-BF_4^- does not react with 1-phenyl-1-trimethylsiloxyethene (**17**) in toluene at 0 °C led Tanaka to the conclusion that the nucleophilicities of silylated enol ethers are not sufficient for reactions with diazonium ions as **1l**[10]. Since the reported quantitative recovery of 1-phenyl-1-trimethylsiloxyethene (**17**) after treatment with **1l**-BF_4^- in toluene for two hours[10] contrasted the predictions of Figure 10, we have repeated this reaction in acetonitrile, a better solvent for diazonium salts than toluene. Complete consumption of the reactants was observed under these conditions, but the expected hydrazone **18** was isolated in only 8% yield besides arylation products of **17** (Scheme 8). Obviously the competing radical pathway, previously described by Tanaka[10], is faster than the corresponding azo coupling reaction.

Scheme 8



1l **17** **18**

From the reduction potentials of the diazonium ions[30a] and the oxidation potentials of the π-systems used in this work[30b] one can calculate that the probability of outer sphere electron transfer processes is considerably higher than in the analogous reactions of carbocations[30b]. As a consequence, azo coupling is not the only possible reaction pathway, and in some cases other reactions take place.

As reported above, the expected azo coupling products of **1d**, **1f**, **1i** and **1k** with allyltributylstannane (**11a**) could not be isolated, but fast decompositions of the diazonium ions took place instead. Similarly, the 4-nitrobenzenediazonium ion (**1d**) was consumed in presence of allyltrimethylsilane (**10a**), as predicted by Figure 10, but coupling products could not be isolated. Analogously, undefined decomposition products were produced upon combination of the benzenediazonium ion (**1l**) with 2-methylallyltrimethylsilane (**10b**) while the expected azo coupling product could not be isolated.

Since 1,3-dienes and diazonium ions usually undergo cycloaddition reactions[31], a reaction type not treated by eq. 2, the kinetics of these reactions will be reported separately in the succeeding paper. An ordinary coupling reaction of cyclopentadiene with the 4-nitrobenzenediazonium ion (**1d**) has been described by Huisgen[31c], however, in accord with the relative positioning of these two reactants in Figure 10.

The reliability of eq. 2 and Figure 10 to predict potential azo coupling reactions can, perhaps, best be tested by comparison of the rates of azo coupling reactions described in the literature with those calculated from our correlations. From the nucleophilicity parameters of *N*-methylindole (N = 6.98)[32] and the electrophilicity parameters given in Figure 9, one calculates rate constants approximately 10 to 30 times greater than those observed[33] (Table 8). The deviations become slightly larger, when the different temperatures are considered. The analogous treatment of the reactions of diazonium ions with *N*-methylpyrrole (N = 6.18)[32] gives calculated rate constants 100–200 times smaller than observed[34] (Table 8).

Table 8. Comparison between calculated (20 °C, eq. 2) and observed (MI, 30 °C, CH_3CN[33]; MP, 20 °C, H_2O[34]) rate constants for the reactions of diazonium ions with *N*-methylindole (MI) and *N*-methylpyrrole (MP)

Nucleophile	Diazonium Ion	k_{obs} (L mol^{-1} s^{-1})	k_{calcd} (L mol^{-1} s^{-1})
MI	**1d**	6.61	76
N = 6.98	**1f**	3.72	30
s = 1.0	**1j**	1.18×10^{-1}	1.9
	1l	2.57×10^{-2}	6.0×10^{-1}
	1m	5.80×10^{-3}	1.9×10^{-1}
	1n	2.46×10^{-3}	3.8×10^{-2}
MP	**1l**	1.72×10^{1}	9.5×10^{-2}
N = 6.18	**1m**	3.93	3.0×10^{-2}
s = 1.0	**1n**	8.47×10^{-1}	6.0×10^{-3}

These examples show that the reactivity parameters E for diazonium ions derived in this work do not allow precise predictions of the rates of azo coupling reactions, as expected from the crudeness of our approach, but represent a useful qualitative guide to the synthetic potential of diazonium ions.

We thank Prof. *T. Sonoda*, Prof. *H. Zollinger*, Dr. *M. Patz* and Dr. *B. Dogan* for discussions and criticism. Financial support of this work by the *Deutsche Forschungsgemeinschaft* and the *Fonds der Chemischen Industrie* is gratefully acknowledged.

Experimental Section

Melting point (uncorrected): Büchi 530 and Büchi 510 instruments. – NMR spectra: Bruker WM 300 and Varian XL 200 spectrometers. – IR spectra: Perkin Elmer Spectrometer 197 and Shimadzu IR-435 spectrometer. – Mass spectra: Varian 311A and VG 70–250 instruments. – Microanalyses: Perkin Elmer 240 apparatus. – Solvents were dried according to literature procedures[6,35].

2,4-Dinitrobenzenediazonium tetrafluoroborate (**1a**-BF_4^-) was prepared by diazotation of 2,4-dinitroaniline with $NaNO_2$ in 50% H_2SO_4 and addition of $NaBF_4$[36]. The diazonium tetrafluoroborates **1b**–**1n** were prepared by treatment of the corresponding amines with $NaNO_2$ and conc. HBF_4 as described in ref.[37]. Diazonium tetrachlorozincate, $(\mathbf{1n})_2ZnCl_4^{2-}$ was obtained according to Flett[38] by diazotation of the amine and addition of zinc chloride.

Reactions of Arenediazonium Ions with 1,3,5-Trimethoxybenzene (**2a**)

Typical Procedure. – (2,4-Dinitrophenyl)(2,4,6-trimethoxyphenyl)diazene (**3aa**): 2,4-Dinitrobenzenediazonium tetrafluoroborate (**1a**-BF_4^-) (1.41 g, 5.00 mmol) was suspended in 10 ml of dry acetonitrile. After addition of **2a** (1.01 g, 6.00 mmol) the mixture was stirred at ambient temperature for 30 min. The precipitate was collected and recrystallized from ethanol to give 1.62 g (89%) of **3aa**, brown needles, m.p. 189.5–190.5 °C. – ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 3.93 (s, 9 H, OCH_3), 6.20 (s, 2 H, 3'-H), 7.79 (br. d, J = 7.4 Hz, 1 H, 6-H), 8.44 (br. d, J = 8.4 Hz, 1 H, 5-H), 8.71 (br. s, 1 H, 3-H). – ^{13}C NMR ($CDCl_3$): δ = 55.76 (q, 4'-OCH_3), 56.37 (q, 2'-OCH_3), 91.07 (d, C-3'), 119.93 (d, C-3), 120.12 (d, C-6), 127.40 (d, C-5), 146.16 (s, C-4), 157.85 (s, C-2'), 166.09 (s, C-4'), C-1, C-2 and C-1' not detected. – MS (70 eV): m/z (%) = 363 (3), 362 (21 [M^+], 196 (10), 195 (100), 153 (7), 152 (24), 139 (10), 137 (84), 122 (10). – $C_{15}H_{14}N_4O_7$ (362.3): calcd. C 49.73, H 3.89, N 15.47; found C 49.51, H 3.70, N 15.52.

(2-Chloro-4-nitrophenyl)(2,4,6-trimethoxyphenyl)diazene (**3ba**): According to the typical procedure **1b**-BF_4^- (1.36 g, 5.00 mmol) and **2a** (1.01 g, 6.00 mmol) were allowed to react for 30 min. Recrystallization from ethanol yielded 1.72 g (98%) of **3ba**, brown needles, m.p. 164–165 °C. – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.83 (s, 3 H, 4'-OCH_3), 3.87 (s, 6 H, 2'-OCH_3), 6.13 (s, 2 H, 3'-H), 7.61 (d, J = 8.7 Hz, 1 H, 6-H), 8.07 (dd, J = 1.8, 8.7 Hz, 1 H, 5-H), 8.30 (d, J = 1.8 Hz, 1 H, 3-H). – ^{13}C NMR ($CDCl_3$): δ = 55.61 (q, 4'-OCH_3), 56.45 (q, 2'-OCH_3), 91.13 (d, C-3'), 118.06 (d, C-6), 122.64 (d, C-5), 125.73 (d, C-3), 127.65 (s, C-1'), 133.68 (s, C-2), 147.31 (s, C-4), 154.55 (s, C-1), 157.10 (s, C-2'), 164.98 (s, C-4'). – MS (70 eV): m/z (%) = 354, 352, 353, 351 (28) [M^+], 196 (10), 195 (100), 167 (21), 166 (24), 139 (13), 137 (69), 122 (12). – $C_{15}H_{14}ClN_3O_5$ (351.8): calcd. C 51.22, H 4.01, N 11.95; found C 51.03, H 3.93, N 12.02.

(4-Nitrophenyl)(2,4,6-trimethoxyphenyl)diazene (**3da**): Compounds **1d**-BF_4^- (1.18 g, 5.00 mmol) and **2a** (1.01 g, 6.00 mmol) were allowed to react for 30 min. Recrystallization from ethanol gave 850 mg (54%) of **3da**, red needles, m.p. 140 °C. – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.83 (s, 3 H, 4'-OCH_3), 3.84 (s, 6 H, 2'-OCH_3), 6.15 (s, 2 H, 3'-H), 7.82, 8.23 (AA'BB'-system with J_{AB} = 9.0 Hz). – ^{13}C NMR ($CDCl_3$): δ = 55.54 (q, 4'-OCH_3), 56.36 (q, 2'-OCH_3), 91.18 (d, C-3'), 122.54, 124.51 (2 d, C-2, C-3), 127.31 (s, C-1'), 147.56 (s, C-4), 156.30 (s, C-2'), 157.76 (s, C-1), 164.09 (s, C-4'). – MS (70 eV): m/z (%) = 318 (9), 317 (49) [M^+], 196 (9), 195 (79), 167 (12), 166 (18), 152 (100), 137 (63), 122 (16). – $C_{15}H_{15}N_3O_5$ (317.3): calcd. C 56.78, H 4.76, N 13.24; found C 56.59, H 4.57, N 13.45.

Reactions of Arenediazonium Ions with 1,3-Dimethoxybenzene (**2b**)

(2,4-Dimethoxyphenyl)(2,4-dinitrophenyl)diazene (**3ab**): According to the typical procedure for 1,3,5-trimethoxybenzene (**2a**), **1a**-BF_4^- (564 mg, 2.00 mmol) and **2b** (415 mg, 3.00 mmol) were allowed to react for 60 min. Recrystallization from ethanol gave 530 mg (80%) of **3ab**, brown needles, m.p. 158–160 °C. – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.91 (br. s, 3 H, OCH_3), 4.02 (br. s, 3 H, OCH_3), 6.54 (br. s, 2 H, 3'- and 5'-H), 7.79 (br. s, 2 H, 6- and 6'-H), 8.43 (br. s, 1 H, 5-H), 8.73 (br. s, 1 H, 3-H). – ^{13}C NMR ($CDCl_3$): δ = 55.91, 56.32 (2 q, 2 OCH_3), 98.61 (d, C-3'), 106.77 (d, C-5'), 119.40, 120.04, 120.36, 127.62 (4 d, C-3, C-5, C-6, C-6'), 137.24 (s, C-1'), 146.26, 146.59, 149.71 (3 s, C-1, C-2 and C-4), 160.82 (s, C-2'), 166.61 (s, C-4'). – $C_{14}H_{12}N_4O_6$ (332.3): calcd. C 50.60, H 3.64, N 16.86; found C 50.57, H 3.45, N 16.80.

(2-Chloro-4-nitrophenyl)(2,4-dimethoxyphenyl)diazene (**3bb**): According to the typical procedure for 1,3,5-trimethoxybenzene (**2a**), **1b**-BF_4^- (1.36 g, 5.00 mmol) and **2b** (829 mg, 6.00 mmol) were allowed to react for 60 min. Recrystallization from ethanol gave 1.20 g (75%) of **3bb**, red needles, m.p. 174–174.5 °C. – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.93 (s, 3 H, OCH_3), 4.04 (s, 3 H, OCH_3), 6.56–6.60 (m, 2 H, 3'- and 5'-H), 7.74 (d, J = 8.9 Hz, 1 H, 6-H), 7.88 (d, J = 9.6 Hz, 1 H, 6'-H), 8.16 (dd, J = 2.3, 8.9 Hz, 1 H, 5-H), 8.40 (d, J = 2.3 Hz, 1 H, 3-H). – ^{13}C NMR ($CDCl_3$): δ = 55.80, 56.32 (2 q, 2 OCH_3), 98.69 (d, C-3'), 106.46 (d, C-5'), 118.71, 119.00, 122.67, 125.95 (4 d, C-3, C-5, C-6, C-6'), 134.31, 137.34 (2 s, C-2 and C-1'), 147.76 (s, C-4), 153.17 (s, C-1), 160.28 (s, C-2'), 165.79 (s, C-4'). – $C_{14}H_{12}ClN_3O_4$ (321.7): calcd. C 52.27, H 3.76, N 13.06; found C 51.41, H 3.67, N 13.04.

Reaction of Arenediazonium Ions with Alkenes

General Procedure. – (**1a**–**1n**)-BF_4^- was suspended in dry methanol/acetonitrile (5 ml/2 ml). After addition of two equivalents of alkene the reaction mixture was stirred at room temp. Water (40 ml) was added, and the mixture was extracted with two 10-ml-portions of CH_2Cl_2. The combined organic fractions were dried with $MgSO_4$ and the solvent was evaporated in vacuo. Azo products were purified by chromatography on silica gel (CH_2Cl_2/pentane, 7:3, v/v), while hydrazones were recrystallized from methanol.

(2,4-Dinitrophenyl)(1,1,2-trimethylallyl)diazene (**6aa**) *and (2,4-Dinitrophenyl)(2-methoxy-1,1,2-trimethylpropyl)diazene* (**7aa**): **1a**-BF_4^- (1.00 g, 3.55 mmol) and **4a** (595 mg, 7.07 mmol) were allowed to react for 5 min. Chromatographic separation (see General procedure) yielded 423 mg (43%) of **6aa** and 132 mg (12%) of **7aa**. – **6aa**: m.p. 55–56 °C. – ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 1.48 (s, 6 H, 1-CH_3), 1.83 (br. s, 3 H, 2-CH_3), 5.06 (s, 2 H, 3-H), 7.36 (d, J = 8.6 Hz, 1 H, arom. 6-H), 8.51 (dd, J = 2.4, 8.6 Hz, 1 H, arom. 5-H), 8.87 (d, J = 2.4 Hz, 1 H, arom. 3-H). – ^{13}C NMR: δ = 19.64 (q, 2-CH_3), 24.07 (q, 1-CH_3), 76.81 (s, C-1), 112.76 (t, C-3), 120.26 (d, arom. C-3), 120.79 (d, arom. C-6), 128.39 (d, arom. C-5), 144.75 (s, arom. C-2), 147.10 (s, arom. C-4), 150.13 (s, arom. C-1). – MS (70 eV): m/z (%) = 277 (0.1) [M^+ – 1], 83 (100), 55 (75). – IR (KBr): $\tilde{\nu}$ = 3015 cm^{-1}, 2968, 2922, 2856, 1600, 1521, 1445, 1434, 1340, 901, 829. – $C_{12}H_{14}N_4O_4$ (278.3): calcd. C 51.80, H 5.07, N 20.13; found C 51.88, H 5.00, N 20.07. – **7aa**: m.p. 70–72 °C. – ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 1.29 (s, 6 H, $(CH_3)_2C{-}N$), 1.36 (s, 6 H, $OC(CH_3)_2$), 3.29 (s, 3 H, OCH_3), 7.34 (d, J = 8.7 Hz, 1 H, arom. 6-H), 8.51 (dd, J = 2.4, 8.7 Hz, 1 H, arom. 5-H), 8.85 (d, J = 2.4 Hz, 1 H, arom. 3-H). – ^{13}C NMR: δ = 20.27, 20.51 [2 q, $(\mathit{C}H_3)_2CN$, $(\mathit{C}H_3)_2CO$], 49.61 (q, OCH_3), 79.04 [s, $N\mathit{C}(CH_3)_2$], 79.63 [s, $O\mathit{C}(CH_3)_2$], 120.22 (d, arom. C-3), 121.10 (d, arom. C-6), 128.39 (d, arom. C-5), 144.47 (s, arom. C-2), 147.05 (s, arom. C-4), 150.63 (s, arom. C-1). – IR (KBr): $\tilde{\nu}$ = 3095 cm^{-1}, 2970, 2929, 1596, 1527, 1339, 1139, 1061, 900, 826. – MS (70 eV): m/z (%) = 295 (0.3) [M^+ – CH_3], 195 (10), 115 (92), 83 (77), 73 (100), 55 (46), 43 (26), 41 (37).

(4-Nitrophenyl)(1,1,2-trimethylallyl)diazene (**6da**): **1d**-BF_4^- (1.00 g, 4.22 mmol) and **4a** (595 mg, 7.07 mmol) were allowed to react for 15 min. By filtration over silica gel, 590 mg (60%) of **6da** were obtained. – ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 1.47 (s, 6 H, CH_3), 1.80 (br. s, 3 H, 2-CH_3), 5.02 (s, 2 H, $=CH_2$), 7.79, 8.34 (AA'BB'-system with J = 9.1 Hz, 4 H, arom. H). – ^{13}C NMR: δ = 19.64 (q, 2-CH_3), 24.34 (q, 1-CH_3), 75.04 (s, C-1), 112.04 (t, C-3), 122.76, 124.61 (2 d, arom. C-2 and C-3), 148.04 (s, arom. C-4), 155.38 (s, arom. C-1). – IR ($CHCl_3$): $\tilde{\nu}$ = 3100 cm^{-1}, 2969, 2941, 2867, 1608, 1592, 1520, 1447, 1373, 1344, 897, 854. – MS (70 eV): m/z (%) = 234 (12) [M^+ + 1], 206 (11), 150 (15), 83 (100), 55 (27).

N-(1,2-Dimethyl-2-propenylidene)-N'-(2,4-dinitrophenyl)-hydrazine (**8ab**): **1a**-BF_4^- (1.00 g, 3.55 mmol) and **4b** (0.700 ml, 6.59 mmol) were allowed to react for 24 h. Recrystallization of the crude material from methanol yielded 187 mg (20%) of red crystals (**8ab**), m.p. 189–190 °C (Lit.[39] 191 °C). – ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 2.12 (s, 3 H, $CH_3C=$), 2.22 (s, 3 H, $N{=}CCH_3$), 5.50 (s, 1 H, vinyl-H), 5.58 (s, 1 H, vinyl-H), 8.02 (d, J = 9.6 Hz, 1 H, arom. 6-

H), 8.36 (dd, *J* = 2.6, 9.6 Hz, 1 H, arom. 5-H), 9.17 (d, *J* = 2.6 Hz, 1 H, arom. 3-H), 11.23 (br. s, 1 H, NH).

N-(Cyclopent-1-enylmethylene)-N'-(2,4-dinitrophenyl)hydrazine (**8ac**): **1a**-BF_4^- (1.00 g, 3.55 mmol) and **4c** (0.750 ml, 7.13 mmol) were allowed to react for 24 h. Recrystallization of the product from methanol yielded 205 mg (21%) of red crystals (**8ac**), m.p. 203–205 °C (Lit.[40] 227–227.5 °C). – ^1H NMR ($CDCl_3$, 200 MHz): δ = 2.00 (m, 2 H, $=CHCH_2CH_2$), 2.54–2.74 (m, 4 H, $=CHCH_2CH_2CH_2-$), 6.34 (br. s, 1 H, C=CH), 7.95 (d, *J* = 9.5 Hz, 1 H, arom. 6-H), 8.32 (dd, *J* = 2.5, 9.5 Hz, 1 H, arom. 5-H), 9.14 (d, *J* = 2.5 Hz, 1 H, arom. 3-H), 11.15 (br. s, 1 H, NH).

N-(2,4-Dinitrophenyl)-N'-(2-methylcyclohex-2-enylidene)-hydrazine (**8ad**): **1a**-BF_4^- (1.00 g, 3.55 mmol) and **4d** (0.840 ml, 7.10 mmol) reacted for 24 h to give a product, which was recrystallized from methanol: 164 mg (16%) of red crystals (**8ad**), m.p. 192–194 °C (Lit.[41] 202–204 °C). – ^1H NMR ($CDCl_3$, 200 MHz): δ = 1.56–2.62 (m, 6 H, ring protons and CH_3-group), 6.30 (br. s, 1 H, =CH), 8.02 (d, *J* = 9.5 Hz, 1 H, arom. 6-H), 8.33 (dd, *J* = 2.5, 9.5 Hz, 1 H, arom. 5-H), 9.15 (d, *J* = 2.5 Hz, 1 H, arom. 3-H), 11.29 (br. s, 1 H, NH).

N-(2,4-Dinitrophenyl)-N'-(2-phenylcyclohex-2-enylidene)-hydrazine (**8ae**): **1a**-BF_4^- (1.00 g, 3.55 mmol) and **4e** (1.16 g, 7.33 mmol) were allowed to react for 15 min to give crude **8ae**. Recrystallization from methanol yielded 730 mg (58%) of red crystals, m.p. 164–165 °C (Lit.[39] 165 °C). – ^1H NMR ($CDCl_3$, 200 MHz): δ = 2.06 (m, 2 H, $=CHCH_2CH_2$), 2.47 (br. q, 2 H, $=CHCH_2-$), 2.74 (t, *J* = 6.6 Hz, 2 H, $N=CCH_2-$), 6.49 (t, *J* = 4.6 Hz, 1 H, $=CHCH_2-$), 7.39 (s, 5 H, phenyl-H), 7.60 (d, *J* = 9.7 Hz, 1 H, arom. 6-H), 8.20 (dd, *J* = 2.7, 9.7 Hz, 1 H, arom. 5-H), 9.11 (d, *J* = 2.7 Hz, 1 H, arom. 3-H), 11.32 (br. s, 1 H, NH).

N-(2,4-Dinitrophenyl)-N'-(2-methoxy-2-phenylethylidene)-hydrazine (**9af**): **1a**-BF_4^- (1.00 g, 3.55 mmol) and **4f** (0.810 ml, 7.07 mmol) were allowed to react for 24 h. Recrystallization of the crude product from methanol yielded 152 mg (13%) of red crystals (**9af**), m.p. 100–102 °C (Lit.[42] 100–101.5 °C). – ^1H NMR ($CDCl_3$, 200 MHz): δ = 3.47 (s, 3 H, OCH_3), 4.97 (d, *J* = 6.7 Hz, 1 H, $CHOCH_3$), 7.42 (br. s, 5 H, phenyl-H), 7.48 (d, *J* = 6.7 Hz, 1 H, N=CH), 7.98 (d, *J* = 9.5 Hz, 1 H, arom. 6-H), 8.35 (dd, *J* = 2.5, 9.3 Hz, 1 H, arom. 5-H), 9.13 (d, *J* = 2.5 Hz, 1 H, arom. 3-H), 11.05 (br. s, 1 H, NH).

N-(2,4-Dinitrophenyl)-N'-(2-methoxy-2-phenylpropylidene)-hydrazine (**9ag**): **1a**-BF_4^- (1.00 g, 3.55 mmol) and **4g** (0.920 ml, 7.08 mmol) were allowed to react for 1 h. Recrystallization of the product from methanol yielded 633 mg (52%) of yellow crystals (**9ag**), m.p. 155–157 °C. – ^1H NMR ($CDCl_3$, 200 MHz): δ = 1.85 (s, 3 H, CH_3), 3.34 (s, 3 H, OCH_3), 7.32–7.50 (m, 5 H, phenyl-H), 7.54 (s, 1 H, N=CH), 7.97 (d, *J* = 9.6 Hz, 1 H, arom. 6-H), 8.35 (dd, *J* = 2.5, 9.6 Hz, 1 H, arom. 5-H), 9.14 (d, *J* = 2.5 Hz, 1 H, arom. 3-H), 11.06 (br. s, 1 H, NH). – ^{13}C NMR: δ = 21.33 (q, CH_3C), 51.17 (q, OCH_3), 79.55 (s, $OCCH_3$), 116.61 (d, arom. C-3), 123.33 (d, arom. C-6), 125.96 (d, arom. C-2'), 127.90 (d, arom. C-4'), 128.64 (d, arom. C-3'), 129.34 (s, arom. C-4), 129.99 (d, arom. C-5), 138.22 (s, arom. C-2), 141.76 (s, arom. C-1), 145.06 (s, arom. C-1'), 153.57 (d, N=CH). – IR (KBr): $\tilde{\nu}$ = 3426 cm^{-1}, 3254, 3106, 2951, 1690, 1586, 1330, 1067, 917, 828, 737. – MS (70 eV): *m/z* (%) = 344 (1.4) [M^+], 312 (12), 265 (24), 218 (27), 210 (13), 135 (42), 91 (45), 78 (53), 77 (100).

Reactions of Arenediazonium Ions with Allylsilanes

General Procedure: (**1a**–**d**)-BF_4^- (0.500 g) was suspended in dry acetonitrile (4 ml). After addition of 1.5 equiv. of **10** the reaction mixture was stirred until the diazonium salt had dissolved. Water (10 ml) was added, and the mixture was extracted with two 10-ml portions of CH_2Cl_2. The combined organic fractions were dried with $MgSO_4$ and the solvent was evaporated in vacuo. The residue was filtered over silica gel (CH_2Cl_2/pentane 7:3, v/v). Crystalline azo compounds were recrystallized from pentane, hydrazones from methanol or ethanol.

N-(2,4-Dinitrophenyl)-N'-(propenylidene)hydrazine (**14aa**): 243 mg (58%), orange crystals, m.p. 166–167 °C (Lit.[43] 166 °C). – ^1H NMR ($CDCl_3$, 200 MHz): δ = 5.78 (d, *J* = 10.4 Hz, 1 H, 3-H), 5.77 (d, *J* = 17.4 Hz, 1 H, 3-H), 6.55–6.73 (m, 1 H, 2-H), 7.81 (d, *J* = 9.2 Hz, 1 H, 1-H), 7.97 (d, *J* = 9.7 Hz, 1 H, arom. 6-H), 8.34 (dd, *J* = 2.6, 9.7 Hz, 1 H, arom. 5-H), 9.15 (d, *J* = 2.6 Hz, 1 H, arom. 3-H), 11.15 (br. s, 1 H, NH).

N-(2,4-Dinitrophenyl)-N'-(2-methyl-2-propenylidene)hydrazine (**14ab**): 320 mg (72%), red crystals, m.p. 204–206 °C (Lit.[44] 207 °C). – ^1H NMR ($CDCl_3/CF_3CO_2H$, 200 MHz): δ = 2.07 (t, *J* = 1.1. Hz, 3 H, CH_3), 5.49, 5.63 (2 m_c, 2 H, 3-H), 7.85 (s, 1 H, 1-H), 8.00 (d, *J* =9.6 Hz, 1 H, arom. 6-H), 8.34 (dd, *J* = 2.6, 9.6 Hz, 1 H, arom. 5-H), 9.16 (d, *J* = 2.6 Hz, 1 H, arom. 3-H), 11.18 (br. s, 1 H, NH).

N-(2-Methyl-2-propenylidene)-N'-(4-nitrophenyl)hydrazine (**14db**): 215 mg (50%), orange crystals, m.p. 156–158 °C (Lit.[45] 157–158 °C). – ^1H NMR ($CDCl_3$, 200 MHz): δ = 2.03 (t, *J* = 1.1 Hz, 3 H, CH_3), 5.26, 5.41 (2 m_c, 2 H, 3-H), 7.06, 8.17 (AA'BB'-system with *J* = 9.1 Hz), 7.54 (s, 1 H, 1-H), 7.88 (br. s, 1 H, NH).

(1,1-Dimethylallyl)(2,4-dinitrophenyl)diazene (**13ac**): 393 mg (84%), red oil, b.p. 145–150 °C (10^{-3} mbar). – ^1H NMR ($CDCl_3$, 300 MHz): δ = 1.50 (s, 6 H, CH_3), 5.26 (dd, *J* = 0.7, 10.7 Hz, 1 H, 3-H), 5.28 (dd, *J* = 0.7, 17.4 Hz, 1 H, 3-H), 6.15 (dd, *J* = 10.7, 17.4 Hz, 1 H, 2-H), 7.38 (d, *J* = 8.7 Hz, 1 H, arom. 6-H), 8.50 (dd, *J* = 2.4, 8.7 Hz, 1 H, arom. 5-H), 8.84 (d, *J* = 2.3 Hz, 1 H, arom. 3-H). – ^{13}C NMR: δ = 24.40 (q, CH_3), 74.67 (s, C-1), 114.93 (t, C-3), 120.23 (d, arom. C-3), 120.83 (d, arom. C-6), 128.36 (d, arom. C-5), 141.29 (d, C-2), 144.46 (s, arom. C-2), 147.17 (s, arom. C-4), 150.23 (s, arom. C-1).

(1,1-Dimethylallyl)(4-nitrophenyl)diazene (**13dc**): 333 mg (72%), orange oil, b.p. 69–72 °C (10^{-3} mbar). – ^1H NMR ($CDCl_3$, 300 MHz): δ = 1.47 [s, 6 H, $(CH_3)_2C$], 5.21 (dd, *J* = 0.9, 10.8 Hz, 1 H, 3-H), 5.23 (dd, *J* = 0.9, 17.6 Hz, 1 H, 3-H), 6.15 (dd, *J* = 10.8, 17.6 Hz, 1 H, 2-H), 7.77, 8.32 (AA'BB'-system with J_{AB} = 9.0 Hz). – ^{13}C NMR: δ = 24.73 (q, CH_3), 72.97 (s, C-1), 114.03 (t, C-3), 122.71 (d, arom. C-2), 124.54 (d, arom. C-3), 142.36 (d, C-2), 148.43 (s, arom. C-4), 155.41 (s, arom. C-1).

N-(Cyclopent-2-enylidene)-N'-(2,4-dinitrophenyl)hydrazine (**14ae**): 312 mg (67%), orange crystals, m.p. 165 °C (Lit.[46] 170–171 °C). – ^1H NMR ($CDCl_3$, 200 MHz): δ = 2.69–2.86 (m, 4 H, 4- and 5-H), 6.45 (td, *J* = 2.1, 5.7 Hz, 1 H, 2-H), 6.86–6.91 (m, 1 H, 3-H), 7.93 (d, *J* = 9.6 Hz, 1 H, arom. 6-H), 8.30 (dd, *J* = 2.6, 9.6 Hz, 1 H, arom. 5-H), 9.12 (d, *J* = 2.6 Hz, 1 H, arom. 3-H), 10.86 (br. s, 1 H, NH).

Reactions of Arenediazonium Ions with Allylstannanes (**11**)

General Procedure: (**1a**–**n**)-BF_4^- (5 mmol) was suspended in dry acetonitrile (20 ml). After addition of 1.5 equiv. of **11** in dry CH_2Cl_2 (5 ml) the reaction mixture was stirred for 10 min. Water (20 ml) was added, and the mixture was extracted with two 20-ml-portions of CH_2Cl_2. The combined organic fractions were dried with $MgSO_4$ and the solvent was evaporated in vacuo. The residue was filtered over silica gel (CH_2Cl_2/pentane 7:3, v/v, or hexane/ethyl acetate 10:1, v/v) to yield the (1,1-dimethylallyl)aryldiazenes **13**.

N-(2,4-Dinitrophenyl)-N'-(propenylidene)hydrazine (**14aa**): 763 mg (65%), orange crystals, m.p. 163–164°C (Lit.[43] 166°C). – For further characterization see above.

(1,1-Dimethylallyl)(2,4-dinitrophenyl)diazene (**13ac**): 750 mg (57%) of **13ac** was isolated from the reaction of **1a**-BF_4^- with **11c** as red oil, b.p. 145–150°C (10^{-3} mbar). – For further characterization see above.

(1,1-Dimethylallyl)(2-chloro-4-nitrophenyl)diazene (**13bc**): 1.13 g (89%), red oil, b.p. 105–110°C (10^{-3} mbar). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.50 (s, 6H, CH_3), 5.23 (dd, J = 0.9, 10.8 Hz, 1H, 3-H), 5.26 (dd, J = 0.9, 17.5 Hz, 1H, 3-H), 6.17 (dd, J = 10.8, 17.5 Hz, 1H, 2-H), 7.36 (d, J = 8.7 Hz, 1H, arom. 6-H), 8.13 (dd, J = 2.3, 8.7 Hz, 1H, arom. 5-H), 8.35 (d, J = 2.3 Hz, 1H, arom. 3-H). – ^{13}C NMR: δ = 24.78 (q, CH_3), 74.17 (s, C-1), 114.37 (t, C-3), 118.75 (d, arom. C-6), 122.65 (d, arom. C-5), 125.73 (d, arom. C-3), 133.17 (s, arom. C-2), 142.02 (d, C-2), 148.30 (s, arom. C-4), 152.54 (s, arom. C-1). Signal assignments are based on ^{13}C-^{1}H correlations.

(1,1-Dimethylallyl)(4-nitrophenyl)diazene (**13dc**): 600 mg (55%), orange oil, b.p. 69–72°C (10^{-3} mbar). – For further characterization see above.

4-(1,1-Dimethylallylazo)benzonitrile (**13fc**): 640 mg (64%), orange oil, b.p. 85–100°C (10^{-3} mbar). – ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.46 (s, 6H, CH_3), 5.20 (dd, J = 1.0, 10.8 Hz, 1H, 3-H), 5.22 (dd, J = 1.0, 17.5 Hz, 1H, 3-H), 6.14 (dd, J = 10.8, 17.5 Hz, 1H, 2-H), 7.71–7.77 (m, 4H, arom. H). – ^{13}C NMR: δ = 24.75 (q, CH_3), 72.73 (s, C-1), 113.49 (s, arom. C-4), 113.97 (t, C-3), 118.40 (s, CN), 122.66 (d, arom. C-2), 133.08 (d, arom. C-3), 142.47 (d, C-2), 154.22 (s, arom. C-1). – IR ($CHCl_3$): ṽ = 3010 cm^{-1}, 2970, 2920, 2220, 1210, 920, 840, 750, 660, 600. – MS (70 eV): m/z (%) = 171 (3), 130 (8) [$M^+ - C_5H_9$], 102 (20), 69 (96), 41 (100), 39 (17). – $C_{12}H_{13}N_3$ (199.3): calcd. C 72.33, H 6.58, N 21.09; found C 72.00, H 6.47, N 20.93.

(1,1-Dimethylallyl)(4-trifluoromethylphenyl)diazene (**13gc**): 471 mg (39%), yellow oil. – ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 1.46 (s, 6H, CH_3), 5.20 (dd, J = 1.1, 10.8 Hz, 1H, 3-H), 5.22 (dd, J = 1.1, 17.6 Hz, 1H, 3-H), 6.16 (dd, J = 10.8, 17.6 Hz, 1H, 2-H), 7.73 (m_c, 4H, arom. H). – ^{13}C NMR: δ = 24.79 (q, CH_3), 72.38 (s, C-1), 113.78 (t, C-3), 122.28 (d, arom. C-2), 126.12 (q, J_{CF} = 3 Hz, arom. C-3), 123.91 (q, J_{CF} = 272 Hz, CF_3), 131.70 (q, J_{CF} = 33 Hz, arom. C-4), 142.73 (d, C-2), 154.17 (s, arom. C-1). – IR ($CHCl_3$): ṽ = 3086 cm^{-1}, 2973, 2928, 2865, 1613, 1593, 1459, 1443, 1411, 1374, 1162, 1146, 1123, 1098, 1062, 920, 842. – MS (70 eV): m/z (%) = 243 (0.12) [$M^+ + 1$], 173 (27), 145 (52), 69 (100), 41 (99).

Methyl-4-(1,1-dimethylallylazo)benzoate (**13ic**): 650 mg (56%), yellow oil. – ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.37 (s, 6H, CH_3), 3.85 (s, 3H, OCH_3), 5.10 (dd, J = 1.0, 10.8 Hz, 1H, 3-H), 5.14 (dd, J = 1.0, 17.6 Hz, 1H, 3-H), 6.07 (dd, J = 10.8, 17.6 Hz, 1H, 2-H), 7.60, 8.04 (AA'BB'-system with J_{AB} = 8.6 Hz, 4H, arom. H). – ^{13}C NMR: δ = 24.74 (q, CH_3), 52.18 (q, OCH_3), 72.27 (s, C-1), 113.63 (t, C-3), 121.79 (d, arom. C-2), 130.42 (d, arom. C-3), 131.18 (s, arom. C-4), 142.74 (d, C-2), 154.80 (s, arom. C-1), 166.45 (C=O). – IR ($CHCl_3$): ṽ = 3020 cm^{-1}, 2975, 1715, 1605, 1435, 1280, 1215, 1110, 920, 855, 750, 665, 600. – $C_{13}H_{16}N_2O_2$ (232.3): calcd. C 67.22, H 6.94, N 12.06; found C 66.94, H 6.97, N 12.02.

(1,1-Dimethylallyl)(4-chlorophenyl)diazene (**13jc**): 532 mg (51%), orange oil. – ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 1.43 (s, 6H, CH_3), 5.17 (dd, J = 1.0, 10.8 Hz, 1H, 3-H), 5.20 (dd, J = 1.0, 17.6 Hz, 1H, 3-H), 6.15 (dd, J = 10.8, 17.6 Hz, 1H, 2-H), 7.41, 7.63 (AA'BB'-system with J_{AB} = 8.6 Hz, 4H, arom. H). – ^{13}C NMR: δ = 24.83 (q, CH_3), 71.74 (s, C-1), 113.49 (t, C-3), 123.40 (d, arom. C-2), 129.06 (s, arom. C-3), 135.07 (s, arom. C-4), 143.02 (d, C-2), 150.50 (s, arom. C-1). – IR ($CHCl_3$): ṽ = 3078 cm^{-1}, 2966, 2922, 2861, 1638, 1589, 1516, 1472, 1400, 1371, 1084, 1007, 917, 827. – MS (70 eV): m/z (%) = 209 (0.24) [$M^+ + 1$], 113 (28), 111 (85), 75 (14), 69 (81), 41 (100).

(1,1-Dimethylallyl)(4-bromophenyl)diazene (**13kc**): 900 mg (71%), orange oil, b.p. 72°C (10^{-3} mbar). – ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.43 (s, 6H, CH_3), 5.17 (dd, J = 0.8, 10.7 Hz, 1H, 3-H), 5.20 (dd, J = 0.8, 17.6 Hz, 1H, 3-H), 6.14 (dd, J = 10.7, 17.6 Hz, 1H, 2-H), 7.56 (s, 4H, arom. H). – ^{13}C NMR: δ = 24.82 (q, CH_3), 71.80 (s, C-1), 113.52 (t, C-3), 123.66 (d, arom. C-2), 124.45 (s, arom. C-4), 132.05 (d, arom. C-3), 143.00 (d, C-2), 150.90 (s, arom. C-1). – IR ($CHCl_3$): ṽ = 3010 cm^{-1}, 2970, 2930, 2870, 1640, 1580, 1520, 1470, 1410, 1395, 1375, 1360, 1295, 1215, 1140, 1060, 1005, 920, 830, 750, 690, 665, 600. – MS (70 eV): m/z (%) = 185 (42), 183 (40) [$M^+ - C_5H_9$], 157 (46), 155 (47), 76 (26), 75 (25), 69 (94), 50 (22), 41 (100), 39 (26). – $C_{11}H_{13}BrN_2$ (253.1): calcd. C 52.19, H 5.18, N 11.07; found C 51.79, H 5.34, N 10.27.

(1,1-Dimethylallyl)phenyldiazene (**13lc**): 580 mg (67%), orange oil, b.p. 50°C (10^{-3} mbar). – ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.44 (s, 6H, CH_3), 5.17 (dd, J = 1.2, 10.8 Hz, 1H, 3-H), 5.21 (dd, J = 1.2, 17.6 Hz, 1H, 3-H), 6.16 (dd, J = 10.8, 17.6 Hz, 1H, 2-H), 7.36–7.46 (m, 3H, arom. 3- and 4-H), 7.64–7.68 (m, 2H, arom. 2-H). – ^{13}C NMR: δ = 24.89 (q, CH_3), 71.54 (s, C-1), 113.32 (t, C-3), 122.01 (d, arom. C-2), 128.86 (d, arom. C-3), 130.12 (d, arom. C-4), 143.29 (d, C-2), 152.29 (s, arom. C-1).

(1,1-Dimethylallyl)(4-methylphenyl)diazene (**13mc**): 790 mg (84%), yellow oil, b.p. 45°C (10^{-3} mbar). – ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.42 (s, 6H, CH_3), 2.36 (s, 3H, CH_3), 5.14 (dd, J = 1.1, 10.8 Hz, 1H, 3-H), 5.21 (dd, J = 1.1, 17.7 Hz, 1H, 3-H), 6.16 (dd, J = 10.8, 17.7 Hz, 1H, 2-H), 7.20, 7.58 (AA'BB'-system with J_{AB} = 8.2 Hz). – ^{13}C NMR: δ = 21.24 (q, arom. CH_3), 24.92 (q, CH_3), 71.14 (s, C-1), 113.11 (t, C-3), 122.02 (d, arom. C-2), 129.43 (d, arom. C-3), 140.32 (s, arom. C-4), 143.52 (d, C-2), 150.36 (s, arom. C-1). – IR ($CHCl_3$): ṽ = 3010 cm^{-1}, 2980, 2930, 2400, 1640, 1605, 1520, 1410, 1375, 1360, 1310, 1215, 1140, 1100, 995, 920, 820, 745, 665, 600. – MS (70 eV): m/z (%) = 120 (4), 119 (39) [$M^+ - C_5H_9$], 92 (11), 91 (100), 69 (28), 65 (17), 42 (17), 41 (44), 39 (14). – $C_{12}H_{16}N_2$ (188.3): calcd. C 76.55, H 8.57, N 14.88; found C 76.08, H 8.61, N 14.62.

(1,1-Dimethylallyl)(4-methoxyphenyl)diazene (**13nc**): 600 mg (59%), yellow oil, b.p. 60–70°C (10^{-3} mbar). – ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.42 (s, 6H, CH_3), 3.83 (s, 3H, OCH_3), 5.15 (dd, J = 1.1, 10.8 Hz, 1H, 3-H), 5.19 (dd, J = 1.1, 17.6 Hz, 1H, 3-H), 6.15 (dd, J = 10.8, 17.6 Hz, 1H, 2-H), 6.93, 7.68 (AA'BB'-system with J_{AB} = 9.0 Hz). – ^{13}C NMR: δ = 24.93 (q, CH_3), 55.44 (q, OCH_3), 70.81 (s, C-1), 113.04 (t, C-3), 113.85 (d, arom. C-3), 123.76 (d, arom. C-2), 143.59 (d, C-2), 146.34 (s, arom. C-1), 161.25 (s, arom. C-4). – IR ($CHCl_3$): ṽ = 3010 cm^{-1}, 2980, 2940, 2840, 2400, 1640, 1605, 1590, 1515, 1495, 1460, 1440, 1410, 1375, 1360, 1310, 1295, 1250, 1215, 1180, 1135, 1100, 1030, 920, 835, 750, 665, 600. – MS (70 eV): m/z (%) = 136 (4), 135 (72) [$M^+ - C_5H_9$], 108 (19), 107 (100), 92 (25), 78 (12), 77 (58), 69 (34), 42 (24), 41 (40), 39 (15). – $C_{12}H_{16}N_2O$ (204.3): calcd. C 70.56, H 7.89, N 13.71; found C 69.49, H 8.05, N 12.91.

Reactions of the Arenediazonium Ions **1n**- *and* **1o**-BF_4^- *with 1-Methoxy-2-methyl-1-trimethylsiloxypropene* (**15a**)

General Procedure: (**1n–o**)-BF_4^- (5 mmol) was suspended in dry acetonitrile (20 ml). After addition of 1.05 g (6.00 mmol) of **15a** the reaction mixture was stirred for 20 min. Water (20 ml) was added, and the mixture was extracted with two 20-ml portions of

Table 9. Kinetics of the reactions of diazonium tetrafluoroborates with π-nucleophiles in acetonitrile

Ar-N$_2^+$	T/°C	[**1**]/ mol l^{-1}	[**Nuc**]/ mol l^{-1}	Method[a], Conversion/ %	k_2/ l mol^{-1} s^{-1}
*1,3,5-Trimethoxy-benzene (**2a**)*					
1a	20	5.34×10^{-5}	2.68×10^{-4}	B, 75	1.27×10^{1}
1a	20	5.39×10^{-5}	5.19×10^{-4}	B, 59	1.34×10^{1}
1a	20	3.37×10^{-5}	4.87×10^{-4}	B, 46	1.35×10^{1}
1b	20	6.13×10^{-5}	1.83×10^{-3}	B, 84	2.47×10^{0}
1b	20	4.84×10^{-5}	9.35×10^{-4}	B, 89	2.40×10^{0}
1d	20	7.29×10^{-5}	2.92×10^{-3}	B 42	9.35×10^{-2}
1d	20	1.30×10^{-4}	1.04×10^{-2}	B, 89	9.43×10^{-2}
1d	20	1.35×10^{-4}	8.13×10^{-3}	B, 83	9.47×10^{-2}
*1,3,-Dimethoxy-benzene (**2b**)*					
1a	20	4.15×10^{-4}	3.08×10^{-3}	A, 59	2.94×10^{-1}
1a	20	4.68×10^{-4}	6.16×10^{-3}	A, 76	2.91×10^{-1}
1b	20	1.71×10^{-4}	3.44×10^{-2}	B, 66	5.01×10^{-2}
1b	20	1.45×10^{-4}	1.46×10^{-2}	B, 64	5.57×10^{-2}
1d	20	4.42×10^{-4}	3.67×10^{-1}	A, 62	3.00×10^{-4}
1d	20	5.03×10^{-4}	6.36×10^{-1}	A, 65	3.12×10^{-4}
*1-Methoxy-3-methyl-benzene (**2c**)*					
1a	20	3.50×10^{-4}	2.69×10^{-2}	A, 47	3.94×10^{-3}
1a	20	3.75×10^{-4}	3.06×10^{-1}	A, 80	4.22×10^{-3}
*Anisole (**2d**)*					
1a	20	3.55×10^{-4}	6.82×10^{-1}	A, 55	4.57×10^{-5}
1a	20	4.48×10^{-4}	6.02×10^{-1}	A, 50	4.16×10^{-5}
*2,3-Dimethyl-but-2-ene (**4a**)*					
1a	20	2.13×10^{-4}	4.73×10^{-4}	B, 83	9.95×10^{0}
1a	20	2.04×10^{-4}	2.27×10^{-4}	B, 83	1.25×10^{1}
1d	20	4.20×10^{-4}	5.03×10^{-2}	A, 89	3.22×10^{-2}
1d	20	5.55×10^{-4}	3.36×10^{-2}	A, 89	3.24×10^{-2}
1g	20	4.73×10^{-4}	1.65×10^{-1}	A, 75	6.85×10^{-3}
1g	20	5.58×10^{-4}	2.45×10^{-1}	A, 73	7.10×10^{-3}
1j	20	4.39×10^{-4}	6.97×10^{-1}	A, 78	5.31×10^{-4}
1j	20	2.48×10^{-4}	5.51×10^{-1}	A, 77	5.57×10^{-4}
1l	20	7.63×10^{-4}	6.97×10^{-1}	A, 54	9.97×10^{-5}
1l	20	6.40×10^{-4}	5.51×10^{-1}	A, 59	9.62×10^{-5}
*2-Methyl-but-2-ene (**4b**)*					
1a	20	3.58×10^{-4}	3.76×10^{-2}	A, 78	2.59×10^{-2}
1a	20	3.55×10^{-4}	1.88×10^{-2}	A, 71	2.57×10^{-2}
*Methylene-cyclopentane (**4c**)*					
1a	20	3.14×10^{-4}	5.67×10^{-2}	A, 83	9.72×10^{-3}
1a	20	5.89×10^{-4}	1.68×10^{-1}	A, 92	9.06×10^{-3}
*1-Methyl-cyclohexene (**4d**)*					
1a	20	3.93×10^{-4}	1.66×10^{-1}	A, 89	3.59×10^{-2}
1a	20	5.09×10^{-4}	1.37×10^{-2}	A, 75	3.46×10^{-2}
*1-Phenyl-cyclohexene (**4e**)*					
1a	20	7.20×10^{-4}	3.14×10^{-3}	A, 67	3.13×10^{-1}
1a	20	4.65×10^{-4}	3.14×10^{-3}	A, 71	3.34×10^{-1}
*Allyl-trimethyl-silane (**10a**)*					
1a	20	3.37×10^{-4}	2.50×10^{-2}	A, 80	3.06×10^{-2}
1a	20	4.04×10^{-4}	2.31×10^{-2}	A, 82	3.47×10^{-2}
1a	20	5.63×10^{-4}	3.13×10^{-2}	A, 69	3.18×10^{-2}
1a	20	5.96×10^{-4}	5.21×10^{-2}	A, 86	3.24×10^{-2}
1a	20	4.01×10^{-4}	4.97×10^{-2}	A, 81	3.16×10^{-2}
1a	0	1.81×10^{-4}	1.26×10^{-1}	A, 41	8.34×10^{-3}
1a	10	2.17×10^{-4}	6.28×10^{-2}	A, 53	1.63×10^{-2}
1a	31.5	2.71×10^{-4}	1.23×10^{-2}	A, 65	7.08×10^{-2}
*Trimethyl-(2-methyl-allyl)-silane (**10b**)*					
1a	20	4.61×10^{-4}	5.70×10^{-4}	A, 53	1.03×10^{1}
1a	20	3.29×10^{-4}	6.84×10^{-4}	A, 63	1.04×10^{1}
1a	20	3.16×10^{-4}	5.70×10^{-4}	A, 51	9.83×10^{0}
1d	20	7.09×10^{-4}	1.94×10^{-2}	A, 45	1.33×10^{-2}
1d	20	6.67×10^{-4}	2.62×10^{-2}	A, 57	1.20×10^{-2}
1g	20	4.13×10^{-4}	4.12×10^{-2}	A, 36	3.57×10^{-3}
1g	20	8.84×10^{-4}	6.01×10^{-2}	A, 69	3.66×10^{-3}
1j	20	5.53×10^{-4}	3.44×10^{-1}	A, 45	3.00×10^{-4}
1j	20	6.43×10^{-4}	2.65×10^{-1}	A, 55	2.63×10^{-4}
1l	20	6.84×10^{-4}	1.77×10^{-1}	A, 56	1.70×10^{-4}
1l	20	5.35×10^{-4}	2.56×10^{-1}	A, 40	1.67×10^{-4}
*(3-Methyl-but-2-enyl)-trimethyl-silane (**10c**)*					
1a	20	5.14×10^{-4}	1.06×10^{-3}	A, 81	1.87×10^{0}
1a	20	4.79×10^{-4}	1.16×10^{-3}	A, 77	2.07×10^{0}
1d	20	6.33×10^{-4}	7.30×10^{-2}	A, 70	6.71×10^{-3}
1d	20	5.91×10^{-4}	5.24×10^{-2}	A, 68	6.34×10^{-3}
*Allyl-dimethyl-tert-butyl-silane (**10d**)*					
1a	20	4.29×10^{-4}	2.39×10^{-2}	A, 76	3.24×10^{-2}
1a	20	4.04×10^{-4}	1.49×10^{-2}	A, 69	3.31×10^{-2}
*1-Cyclopent-2-enyl-trimethyl-silane (**10e**)*					
1a	20	4.12×10^{-4}	1.73×10^{-3}	A, 70	1.00×10^{0}
1a	20	3.58×10^{-4}	1.15×10^{-3}	A, 36	9.60×10^{-1}
*Allyl-tributyl-stannane (**11a**)*					
1d	20	1.55×10^{-4}	2.92×10^{-3}	B, 96	1.06×10^{1}
1d	20	1.17×10^{-4}	3.41×10^{-3}	B, 79	1.22×10^{1}
1e	20	2.32×10^{-4}	7.00×10^{-3}	B, 94	1.01×10^{1}
1e	20	2.41×10^{-4}	3.25×10^{-3}	B, 80	9.95×10^{0}
1f	20	1.66×10^{-4}	7.20×10^{-3}	B, 97	6.25×10^{0}
1f	20	1.59×10^{-4}	3.44×10^{-3}	B, 61	6.31×10^{0}
1h	20	2.55×10^{-4}	1.02×10^{-2}	B, 91	1.57×10^{0}
1h	20	2.69×10^{-4}	5.25×10^{-3}	B, 94	1.61×10^{0}
1i	20	3.32×10^{-4}	1.33×10^{-2}	B, 94	1.05×10^{1}
1i	20	3.15×10^{-4}	6.31×10^{-3}	B, 91	1.17×10^{1}
1k	20	1.31×10^{-4}	5.26×10^{-3}	B, 75	3.95×10^{-1}
1k	20	1.35×10^{-4}	1.08×10^{-3}	B, 99	4.20×10^{-1}
1l	20	2.22×10^{-4}	3.38×10^{-3}	B, 88	1.00×10^{-1}
1l	20	1.95×10^{-4}	3.45×10^{-3}	B, 98	1.09×10^{-1}

[a] A: Indirect Method (Coupling with 2-naphthylamine); B: Direct Method (Diazonium ion absorbance).

CH_2Cl_2. The combined organic fractions were dried with $MgSO_4$ and the solvent was evaporated in vacuo. The residue was filtered over silica gel (hexane/ethyl acetate 3:1, v/v) to yield the methyl-2-methyl-2-arylazopropionate (**16**).

Table 9 *(continued)*

$Ar\text{-}N_2^+$	*T*/°C	[**1**]/ mol l^{-1}	[**Nuc**]/ mol l^{-1}	Method[a)], Conversion/ %	k_2/ l mol^{-1} s^{-1}
*Tributyl-(3-methyl-2-but-enyl)-stannane (**11c**)*					
1d	-29.9	$4.71\text{x}10^{-5}$	$4.48\text{x}10^{-4}$	B, 35	$2.29\text{x}10^{1}$
1d	-14.7	$3.85\text{x}10^{-5}$	$2.82\text{x}10^{-4}$	B, 49	$5.59\text{x}10^{1}$
1d	-0.3	$4.59\text{x}10^{-5}$	$2.18\text{x}10^{-4}$	B, 60	$1.31\text{x}10^{2}$
1d	20.1	$4.33\text{x}10^{-5}$	$1.27\text{x}10^{-4}$	B, 85	$3.30\text{x}10^{2}$
1f	-29.2	$9.51\text{x}10^{-5}$	$1.31\text{x}10^{-3}$	B, 67	$1.28\text{x}10^{1}$
1f	-15.5	$9.20\text{x}10^{-5}$	$6.75\text{x}10^{-4}$	B, 58	$3.12\text{x}10^{1}$
1f	-0.9	$7.38\text{x}10^{-5}$	$3.52\text{x}10^{-4}$	B, 63	$8.15\text{x}10^{1}$
1f	20.2	$7.11\text{x}10^{-5}$	$2.09\text{x}10^{-4}$	B, 64	$2.10\text{x}10^{2}$
1f	20.5	$7.00\text{x}10^{-5}$	$2.11\text{x}10^{-4}$	B, 69	$2.11\text{x}10^{2}$
1k	20	$1.02\text{x}10^{-4}$	$2.04\text{x}10^{-3}$	B, 36	$1.88\text{x}10^{1}$
1k	20.	$1.03\text{x}10^{-4}$	$1.05\text{x}10^{-3}$	B, 90	$1.76\text{x}10^{1}$
1k	20	$8.49\text{x}10^{-5}$	$2.55\text{x}10^{-3}$	B, 89	$1.83\text{x}10^{1}$
1l	20	$1.59\text{x}10^{-4}$	$1.65\text{x}10^{-3}$	B, 69	$3.73\text{x}10^{0}$
1l	20	$1.67\text{x}10^{-4}$	$3.36\text{x}10^{-3}$	B, 95	$3.58\text{x}10^{0}$
1l	20	$1.88\text{x}10^{-4}$	$1.95\text{x}10^{-3}$	B, 92	$3.69\text{x}10^{0}$
1m	20	$1.27\text{x}10^{-4}$	$3.78\text{x}10^{-3}$	B, 83	$1.11\text{x}10^{0}$
1m	20	$1.25\text{x}10^{-4}$	$7.45\text{x}10^{-3}$	B, 88	$1.12\text{x}10^{0}$
1n	20	$8.90\text{x}10^{-5}$	$8.96\text{x}10^{-3}$	B, 75	$2.04\text{x}10^{-1}$
1n	20	$4.50\text{x}10^{-5}$	$4.50\text{x}10^{-3}$	B, 59	$2.10\text{x}10^{-1}$
1n-$ZnCl_4$	19.9	$5.31\text{x}10^{-5}$	$5.44\text{x}10^{-3}$	B, 64	$1.87\text{x}10^{-1}$
1n-$ZnCl_4$	20	$6.28\text{x}10^{-5}$	$3.14\text{x}10^{-3}$	B, 86	$1.75\text{x}10^{-1}$
*1-Methoxy-2-methyl-1-trimethylsiloxy-propene (**15a**)*					
1n	-20.1	$7.94\text{x}10^{-5}$	$4.94\text{x}10^{-4}$	B, 78	$6.73\text{x}10^{0}$
1n	-11.7	$7.08\text{x}10^{-5}$	$1.10\text{x}10^{-3}$	B, 79	$1.53\text{x}10^{1}$
1n	-1.8	$7.25\text{x}10^{-5}$	$4.51\text{x}10^{-4}$	B, 78	$2.35\text{x}10^{1}$
1n	8.0	$7.01\text{x}10^{-5}$	$3.27\text{x}10^{-4}$	B, 96	$3.70\text{x}10^{1}$
1n	20.1	$7.93\text{x}10^{-5}$	$4.93\text{x}10^{-4}$	B, 78	$7.76\text{x}10^{1}$
1o	20.0	$6.66\text{x}10^{-5}$	$9.58\text{x}10^{-4}$	B, 93	$7.77\text{x}10^{-1}$
1o	19.9	$8.03\text{x}10^{-5}$	$1.85\text{x}10^{-3}$	B, 72	$7.90\text{x}10^{-1}$
1o	19.9	$8.11\text{x}10^{-5}$	$4.18\text{x}10^{-3}$	B, 87	$8.64\text{x}10^{-1}$

[a)] A: Indirect Method (Coupling with 2-naphthylamine); B: Direct Method (Diazonium ion absorbance).

Table 10. Solvent dependence of the reactions of diazonium tetrafluoroborates with allylstannane **11c** and *N,N*-dimethyl-aniline

Solvent	*T*/°C	[**1n**]/ mol l^{-1}	[**11c**]/ mol l^{-1}	Method, Conversion/ %	k_2/ l mol^{-1} s^{-1}
*4-Methoxybenzenediazonium ion (**1n**) and Tributyl-(3-methyl-2-but-enyl)-stannane (**11c**)*					
CH_2Cl_2	20.0	$8.87\text{x}10^{-5}$	$3.37\text{x}10^{-3}$	B, 90	$1.58\text{x}10^{1}$
CH_2Cl_2	-0.4	$8.14\text{x}10^{-5}$	$2.47\text{x}10^{-3}$	B, 83	$5.57\text{x}10^{0}$
CH_2Cl_2	-39.9	$9.16\text{x}10^{-5}$	$7.37\text{x}10^{-3}$	B, 18	$4.21\text{x}10^{-1}$
CH_2Cl_2	-30.3	$8.62\text{x}10^{-5}$	$6.13\text{x}10^{-3}$	B, 54	$7.51\text{x}10^{-1}$
CH_2Cl_2	-19.2	$9.24\text{x}10^{-5}$	$3.46\text{x}10^{-3}$	B, 57	$1.65\text{x}10^{0}$
CH_2Cl_2	20.0	$7.04\text{x}10^{-5}$	$3.29\text{x}10^{-4}$	B, 59	$1.53\text{x}10^{1}$
EtOAc	20.1	$7.61\text{x}10^{-5}$	$3.65\text{x}10^{-3}$	B, 21	$1.08\text{x}10^{-2}$
EtOAc	20.0	$1.54\text{x}10^{-4}$	$1.66\text{x}10^{-2}$	B, 68	$1.17\text{x}10^{-2}$
DMSO	20.1	$1.04\text{x}10^{-4}$	$1.05\text{x}10^{-2}$	B, 80	$3.79\text{x}10^{-2}$
DMSO	20.1	$1.08\text{x}10^{-4}$	$1.63\text{x}10^{-2}$	B, 78	$3.37\text{x}10^{-2}$
C_2H_5CN	20.0	$7.53\text{x}10^{-5}$	$3.78\text{x}10^{-3}$	B, 97	$1.72\text{x}10^{-1}$
C_2H_5CN	20.0	$7.38\text{x}10^{-5}$	$7.40\text{x}10^{-3}$	B, 83	$1.71\text{x}10^{-1}$
DMF	20.0	$9.80\text{x}10^{-5}$	$9.89\text{x}10^{-3}$	B, 88	$6.78\text{x}10^{-2}$
DMF	19.9	$9.37\text{x}10^{-5}$	$1.38\text{x}10^{-2}$	B, 75	$7.23\text{x}10^{-2}$
THF	20.0	$5.87\text{x}10^{-5}$	$1.73\text{x}10^{-2}$	B, 80	$9.63\text{x}10^{-2}$
THF	20.0	$1.31\text{x}10^{-4}$	$1.34\text{x}10^{-2}$	B, 68	$1.04\text{x}10^{-1}$
THF	20.0	$6.43\text{x}10^{-5}$	$4.76\text{x}10^{-3}$	B, 80	$1.14\text{x}10^{-1}$

Solvent	*T*/°C	[**1k**]/ mol l^{-1}	[**Nuc**]/ mol l^{-1}	Method, Conversion/ %	k_2/ l mol^{-1} s^{-1}
*4-Bromobenzenediazonium ion (**1k**) and N,N-Dimethyl-aniline*					
CH_2Cl_2	-67.3	$7.98\text{x}10^{-5}$	$2.34\text{x}10^{-3}$	B, 48	$2.51\text{x}10^{0}$
CH_2Cl_2	-58.3	$5.62\text{x}10^{-5}$	$3.54\text{x}10^{-3}$	B, 93	$4.41\text{x}10^{0}$
CH_2Cl_2	-47.3	$6.56\text{x}10^{-5}$	$3.03\text{x}10^{-3}$	B, 70	$1.64\text{x}10^{1}$
CH_2Cl_2	-39.2	$5.99\text{x}10^{-5}$	$7.85\text{x}10^{-4}$	B, 59	$2.85\text{x}10^{1}$
CH_2Cl_2	-20.5	$2.85\text{x}10^{-5}$	$4.48\text{x}10^{-4}$	B, 98	$8.20\text{x}10^{1}$
EtOAc	20.1	$6.81\text{x}10^{-5}$	$3.26\text{x}10^{-3}$	B, 85	$2.56\text{x}10^{-1}$
EtOAc	20.0	$5.52\text{x}10^{-5}$	$5.56\text{x}10^{-3}$	B, 86	$2.52\text{x}10^{-1}$
CH_3CN	20.0	$7.64\text{x}10^{-5}$	$8.52\text{x}10^{-4}$	B, 70	$2.14\text{x}10^{0}$
CH_3CN	20.0	$7.65\text{x}10^{-5}$	$1.60\text{x}10^{-3}$	B, 98	$2.26\text{x}10^{0}$
C_2H_5CN	20.0	$8.83\text{x}10^{-5}$	$1.43\text{x}10^{-3}$	B, 83	$2.97\text{x}10^{0}$
C_2H_5CN	20.0	$7.62\text{x}10^{-5}$	$2.28\text{x}10^{-3}$	B, 82	$3.11\text{x}10^{0}$
DMSO	20.1	$1.14\text{x}10^{-4}$	$5.80\text{x}10^{-3}$	B, 85	$2.83\text{x}10^{-1}$
DMSO	20.1	$9.66\text{x}10^{-5}$	$1.02\text{x}10^{-2}$	B, 37	$2.64\text{x}10^{-1}$
THF	20.0	$6.51\text{x}10^{-5}$	$2.08\text{x}10^{-3}$	B, 84	$6.30\text{x}10^{-1}$
THF	19.9	$4.72\text{x}10^{-5}$	$2.43\text{x}10^{-3}$	B, 84	$6.29\text{x}10^{-1}$
THF	20.0	$5.05\text{x}10^{-5}$	$1.30\text{x}10^{-3}$	B, 91	$6.11\text{x}10^{-1}$

Methyl-2-methyl-2-p-anisylazopropionate (**16na**): 590 mg (100%), yellow oil. – ^1H NMR ($CDCl_3$, 300 MHz): δ = 1.56 (s, 6H, CH_3), 3.72 (s, 3H, OCH_3), 3.81 (s, 3H, OCH_3), 6.92, 7.68 (AA'BB system with J_{AB} = 9.0 Hz). – ^{13}C NMR: δ = 23.11 (q, CH_3), 51.98 (q, OCH_3), 55.36 (q, OCH_3), 74.81 (s, C-2), 113.83 (d, arom. C-3), 124.09 (d, arom. C-2), 145.66 (s, arom. C-1), 161.71 (s, arom. C-4), 174.04 (s, C-1). – MS (70 eV): *m/z* (%) = 236 (1.5) [M^+], 177 (7), 136 (9), 135 (63), 108 (9), 107 (100), 92 (21), 77 (34). – $C_{12}H_{16}N_2O_3$ (236.3): calcd. C 61.00, H 6.83, N 11.86; found C 61.07, H 6.87, N 11.46.

Methyl-2-(4-dimethylaminophenylazo)-2-methylpropionate (**16oa**): 1.00 g (80%), yellow crystals, m.p. 72–73 °C (pentane). – ^1H NMR ($CDCl_3$, 300 MHz): δ = 1.56 [s, 6H, $C(CH_3)_2$], 3.01 [s, 6H, $N(CH_3)_2$], 3.72 (s, 3H, OCH_3), 6.67, 7.65 (AA'BB' system with J_{AB} = 9.1 Hz). – ^{13}C NMR: δ = 23.32 [q, $(CH_3)_2C$], 40.19

(q, NCH_3), 51.92 (q, OCH_3), 74.16 (s, C-2), 111.18 (d, arom. C-3), 124.13 (d, arom. C-2), 142.18 (s, arom. C-1), 152.15 (s, arom. C-4), 174.57 (s, C-1). – MS (70 eV): *m/z* (%) = 250 (1.5), 249 (7) $[M^+]$, 190 (6), 149 (7), 148 (49), 121 (10), 120 (100), 105 (16), 79 (12), 77 (15), 42 (36). – $C_{13}H_{19}N_3O_2$ (249.3): calcd. C 62.63, H 7.68, N 16.85; found C 62.72, H 7.80, N 17.07.

N-(1-Phenyl)-N'-(2-phenyl-2-oxo-1-ethylidene)hydrazine (**18**)

1l-BF_4^- (480 mg, 2.50 mmol) was suspended in dry acetonitrile (10 ml). After addition of 1-phenyl-1-trimethylsiloxyethene (**17**) (481 mg, 2.50 mmol) the mixture was stirred for 2.5 h at 0 °C. Water was added (20 ml), and the mixture was extracted with two 20-ml-protions of CH_2Cl_2. The combined organic fractions were dried with $MgSO_4$ and the solvent was evaporated in vacuo. The residue was filtered over neutral Al_2O_3 (pentane/ethyl acetate 3:1, v/v). Recrystallization from methanol yielded 50 mg (9%) of **18** with m.p. 106–106.5 °C (ref.[47] 114–117 °C).

Kinetic Investigations: The consumption of the diazonium ions was determined photometrically following a procedure described in the literature[11] using a Kontron Uvikon 860 instrument or by directly following the diazonium or the azo dye (arenes) absorbance using a Zeiss CLD 300 deuterium lamp, a Zeiss TS 5 A/180 immersion probe and a Zeiss MCS 220-spectrometer in a work station as described in ref.[15]. Details of the kinetic experiments are given in Tables 9 and 10.

☆ This and the succeeding article are dedicated to Professor *Jürgen Sauer* on the occasion of his 65th birthday.

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