

57. Dediazoniations of Arenediazonium Ions

Part 25¹⁾

Influence of Substituents on the Exchange of the Diazonio Group for External Molecular Nitrogen and on the N(α), N(β)-Rearrangement in the Diazonio Group

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The N(α), N(β)-rearrangement of the two N-atoms which can be observed in solutions of [β -¹⁵N]-labelled *p*-substituted benzenediazonium ions follows dual substituent parameter treatments. The reaction yields a negative field and a positive resonance reaction constant ($\rho_F = -3.35$, $\rho_R = 2.47$). The magnitude of these constants is, within experimental error, the same as the respective reaction constants for solvolytic dediazoniation. The exchange of the diazonio group of ¹⁵N-labelled *p*-substituted benzenediazonium ion yields, however, field and resonance reaction constants which are close to zero. This result is attributed to cancellation of the reaction constants for the forward and reverse steps in the complex mechanism of the exchange reaction.

1. Introduction. – Molecular nitrogen (N₂) as a leaving group from organic compounds is well known in dediazoniations of arene- and alkanediazonium ions, of diazoalkanes, and of azo compounds. As early as 1940, *Hammett* [2] postulated and *Crossley et al.* [3] verified experimentally a slow unimolecular heterolytic dissociation of arenediazonium ions into aryl cations and N₂. An analogous but fast dediazoniation obviously takes place with alkanediazonium ions. The highly reactive cations formed in both cases were assumed to react very rapidly with nucleophiles (including solvent) in subsequent steps (recent review: [4]). *Lewis* and *Hinds* found in 1952 [5] that some of these dediazoniations were not only first order with respect to diazonium ions but also to nucleophiles. *Lewis et al.* [6] postulated a bimolecular process involving, as a first step, attack of the nucleophile on the diazonium ion. Such a mechanism is, however, not supported by later evidence, e.g. substituent effects and kinetic isotope effects [7–9].

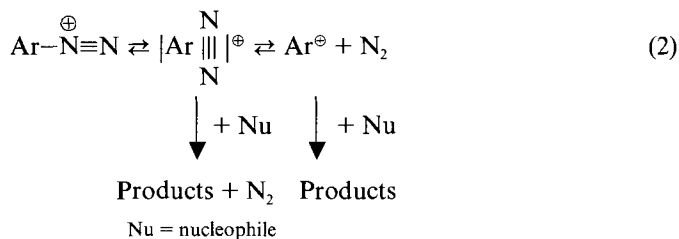
In this situation, we made the unconventional ‘anti-paradigmatic’ proposal [13] that the *reverse* of the first step in arenediazonium-ion dissociation is kinetically *not* negligible. Experimental evidence for this hypothesis came first from the observation that the N-atoms in ¹⁵N-labelled diazonium ions could exchange with unlabelled N₂ present in the solution and, second, from the detection of an N(α), N(β)-rearrangement in mono-labelled arenediazonium ions by *Insole* and *Lewis* (*Eqn. 1*) [14].



The results of careful kinetic evaluations [15], of ¹⁵N experiments (N(α), N(β)-rearrangements and exchange with external N₂), and of secondary-isotope effects with [2,4,6-

¹⁾ Part 24: see *Nakazumi et al.* [1].

$^2\text{H}_3$]benzenediazonium salt [16] are consistent with the initial formation of an ion-molecule pair from which the free (solvated) aryl cation and N_2 are formed. Both these intermediates can react with nucleophiles, the ion-molecule pair preferentially with relatively strong nucleophiles like H_2O , the aryl cation also with weaker ones like 2,2,2-trifluoroethanol (TFE) [17] (Eqn. 2).



In *Kuhn's* nomenclature [18], this is a typical example for a 'revolution' after a 'scientific crisis', followed (e.g. in [15] and [16]) by work which *Kuhn* calls 'normal science', i.e. a period which is characterized by conventional and logical (i.e. *Popperian*) verification/falsification steps (for summaries based on the theory of science, see [19]).

The dediazonation of benzenediazonium ions is furthermore characterized by an extreme inapplicability of the simple *Hammett* $\sigma\rho$ linear free energy relationship for the influence of substituents. The rates of dediazonation of substituted benzenediazonium ions do, however, correlate well with dual parameter relationships in which the contributions of resonance and field (inductive) effects are separated. This was shown originally by *Taft* [20] and subsequently also by *Swain et al.* [9]. Whereas for practically all rate constants, equilibrium constants, and other physico-chemical data of substituted benzenes, the resonance and the field reaction constants (in *Taft's* nomenclature ρ_R and ρ_F , resp.) have the same sign (and are in most cases numerically not very different), dediazonation rates yield positive resonance reaction constants and negative field reaction constants. These two effects have, therefore, an *opposing* influence on the overall dediazonation rate.

It is the purpose of this paper to measure the influence of substituents on the exchange reaction with external N_2 and on the $\text{N}(\alpha)$, $\text{N}(\beta)$ -rearrangement in order to obtain more detailed information on the mechanism of dediazonation in Eqn. 2. The dual reaction constants ρ_R and ρ_F for *m*-substituted benzenediazonium ions are difficult to interpret mechanistically [1]. We concentrated, therefore, on *p*-derivatives.

2. Results. – $^{15}\text{N}(\beta)$ -Diazonium salts were prepared, purified, and coupled with 2-naphthol as previously described [11–13]. They were reduced with $\text{Na}_2\text{S}_2\text{O}_4$ to the corresponding anilines which were analysed for ^{15}N by MS. The rate of the $\text{N}(\alpha)$, $\text{N}(\beta)$ -rearrangement (k_r) was obtained through the Eqn. 3 of *Lewis et al.* [21] on the basis of the directly determined rates of the solvolytic dediazonation (k_s) and R , the percentage of isotopic rearrangement adjusted to exactly 70% dediazonation and corrected for ^{15}N content of the starting material, i.e. substituted anilines with natural abundance of ^{15}N . D_0 and D in Eqn. 3 are diazonium-ion concentrations at 0 and at 70% dediazonation, respectively.

$$\frac{k_r}{k_s} = \log(1 - 2r) / 2 \log(D/D_0) \quad (3)$$

$r = R/100$

Table 1. *Isotopic Rearrangement of [p-XC₆H₄N≡¹⁵N]⁺BF₄⁻ in TFE at 45° (1 bar ¹⁴N₂) in the Dark*

X	Dediazoni- ation [%] ^{a)}	Rearrangement [%] ^{b)} c)	k_r/k_s ^{d)}	$10^6 k_s$ [s ⁻¹]	$10^6 k_r$ [s ⁻¹]
H	50.5	6.77 ± 0.17	0.060		96.6
	50.6	7.19 ± 0.54	0.065	1600	103.2
	52.3	6.30 ± 0.38	0.060		89.4
		7.96 ^{e)}	0.072 ^{e)}	159 ^{e)}	114 ^{e)}
MeO	49.4 ± 0.4	11.25 ± 0.68	0.106		0.014
	49.4 ± 1.5	11.09 ± 0.18	0.104	0.134	0.014
	46.5 ± 0.3	11.18 ± 0.37	0.105		0.014
		8.28 ^{f)}	0.075 ^{f)}	2.6 ^{f)}	0.19 ^{f)}
Me	55.6 ± 2.2	9.23 ± 0.07	0.085		14.7
	60.0 ± 1.2	9.34 ± 0.08	0.086	173	14.9
		8.94 ^{g)}	0.082 ^{g)}	64.7 ^{g)}	5.3 ^{g)}
Cl	53.4 ± 2.9	9.76 ± 0.11	0.090		0.239
	48.5 ± 1.4	9.79 ± 0.09	0.091	2.65	0.240
	46.9 ± 0.5	9.91 ± 0.21	0.092		0.243
	60.5 ± 0.4	9.50 ± 0.17	0.088		0.708
Br	56.3 ± 1.3	8.82 ± 0.24	0.081	8.09	0.652
	57.7 ± 1.3	9.19 ± 0.19	0.084		0.682
	58.3 ± 1.7	9.06 ± 0.18	0.083		0.672
CF ₃	48.6 ± 1.3	7.32 ± 0.23	0.066	40.0	2.64
	49.3 ± 1.1	7.04 ± 0.48	0.063		2.53
<i>t</i> -Bu	60.9 ± 0.3	13.19 ± 0.45	0.127		39.7
	52.0 ± 2.7	12.71 ± 0.58	0.122	312	28.0
	57.1 ± 2.8	12.03 ± 0.50	0.144		35.6
NMe ₂	62.3 ± 0.6	3.61 ± 0.24	0.031		0.0046
	64.6 ± 2.7	-1.48 ± 0.83 ^{h)}	–	0.147	–
	62.1 ± 0.5	2.08 ± 0.24	0.018		0.0026
	59.8 ± 0.5	1.62 ± 0.27	0.014		0.0021

a) Mean of 2 measurements (X = Br, CF₃, *t*-Bu, NMe₂) and 3 measurements (X = MeO, Me, Cl). For X = H, only 1 measurement was made. For details see *Exper. Part*.

b) 95% confidence limits.

c) Extrapolated to 70% dediazoni-ation.

d) k_r/k_s from Eqn. 3.

e) At 30° [11].

f) At 64° [11].

g) At 40° [11].

h) The 'negative' rearrangement obtained in one of these experiments is obviously wrong. It was, therefore, not included in the mean value.

The results are given in *Table 1*. It was also investigated whether the rearrangement is influenced by pressure. *Table 2* contains data obtained in rearrangements accompanying exchange with external N₂ (1000 bar N₂ of natural isotope ratio). The results of the percentage of exchange of N₂ in *p*-substituted benzene[β-¹⁵N]diazonium ions with external N₂ molecules (¹⁴N in natural isotopic abundance) at a pressure of 1000 bar N₂ corrected to 70% dediazoni-ation are given in *Table 3* together with the ¹⁵N content of the azo compound obtained by azo coupling with 2-naphthol *before* the exchange experi-

Table 2. $N(\alpha)$, $N(\beta)$ -Rearrangement Accompanying Exchange with External N_2 (1000 bar) for $[p\text{-XC}_6\text{H}_4\text{N}\equiv^{15}\text{N}]^+\text{BF}_4^-$ in TFE^{a)}

X	Temp. [°]	Dediazoniatio[n] [%] ^{b)}	Exchange [%] ^{c)}	Rearrangement [%] ^{c)}
MeO	65	48	10.10 ± 0.99	12.0 ± 0.1
		53	11.25 ± 0.25	13.6 ± 0.1
Me	45	57	5.24 ± 0.75	9.5 ± 0.2
		60	7.25 ± 0.78	10.4 ± 0.2
		57	$5.17 \pm 1.06^d)$	$10.0 \pm 0.2^d)$
Cl	65	59	7.34 ± 0.15	6.8 ± 0.1
		54	5.98 ± 0.3	7.2 ± 0.1
<i>t</i> -Bu	45	33	6.1 ± 0.6	14.0 ± 0.4

a) Errors are 95% confidence limits.
b) Based on a single measurement (see *Exper. Part*).
c) Extrapolated to 70% dediazoniatio[n].
d) 0.37M HCl in TFE.

ment. For practical reasons, the exchange experiments were not conducted at the same temperature for all the substituted diazonium salts examined (Table 3). The less reactive diazonium salts (e.g. X = MeO, Cl, CN) decompose so slowly that a higher temperature (65°) was necessary in order to avoid long reaction times. Conversely, for the more reactive diazonium salts (X = H), lower reaction temperatures were required. There was no single temperature at which it was possible to conduct all experiments. There would appear, however, to be no appreciable temperature effect on the extent of exchange with external N_2 [11].

3. Discussion. – As mentioned in *Introduction*, the rates of dediazoniatio[n] of substituted benzenediazonium ions have been successfully interpreted by various authors using dual (or triple) substituent parameters, but not with the classical *Hammett* substituent constants. In principle, all sets of dual substituent parameters can be used; they yield positive resonance reaction constants and negative reaction constants for the field effect. As we showed recently [1], the smallest standard deviations and the highest regression coefficients are generally obtained by using the dual parameter substituent constants proposed by *Ehrenson et al.* [22]. We will, therefore, use them again in this paper.

We will discuss first the $N(\alpha)$, $N(\beta)$ -rearrangement. The rate constants of solvolysis in TFE (k_s in Table 1) yield the dual-parameter Eqn. 4, and the rate constants for the corresponding $N(\alpha)$, $N(\beta)$ -rearrangement yield Eqn. 5.

$$\log(k_s^X/k_s^H) = -3.50(\pm 0.63)\sigma_F + 2.21(\pm 0.23)\sigma_R^+ \quad (4)$$

$r = 0.978 \qquad n = 8$

$$\log(k_r^X/k_r^H) = -3.35(\pm 0.20)\sigma_F + 2.47(\pm 0.07)\sigma_R^+ \quad (5)$$

$r = 0.994 \qquad n = 8$

Eqns. 4 and 5 demonstrate that, within experimental error, the respective reaction constants for both reactions, i.e. for solvolysis and rearrangement, are the same. This result demonstrates that the two reactions have the same dependence on substituent effects, which is consistent with Eqn. 2, since the transition state for rearrangement is identical to the first transition state in the mechanism of solvolytic dediazoniatio[n].

Table 3. Exchange of ^{15}N -Labelled $[\text{p-XC}_6\text{H}_4\text{N}_2]^+\text{BF}_4^-$ Salts with External N_2 in TFE

X	Conditions	Dediazoni- ation [%] ^{a)}	$^{14}\text{N}=\text{N}$ Content of azo dye ^{b)} ^{c)}	Exchange [%] ^{c)} ^{d)}
H	1 bar, air, 25°	0	99.20 ^{e)}	–
H ^{f)}	1000 bar, $^{14}\text{N}_2$, 25°	62.5	94.71 ± 0.43	5.03 ± 0.43
CN	1 bar, air, r.t.	0	100.49 ± 0.12 ^{e)}	–
	1000 bar, $^{14}\text{N}_2$, 65°	60	97.38 ± 0.10	3.64 ± 0.09
CN	1 bar, air, r.t.	0	103.10 ± 0.34 ^{e)}	–
	1000 bar, $^{14}\text{N}_2$, 65°	72	98.51 ± 0.29	4.46 ± 0.33
Cl	1 bar, air, r.t.	0	101.59 ± 0.20 ^{e)}	–
	1000 bar, $^{14}\text{N}_2$, 65°	59	98.40 ± 0.10	7.34 ± 0.15
	1000 bar, $^{14}\text{N}_2$, 65°	54	96.98 ± 0.14	5.98 ± 0.30
Me	1 bar, air, r.t.	0	99.36 ± 0.65 ^{e)}	–
	1000 bar, $^{14}\text{N}_2$, 45°	57	95.11 ± 0.22	5.24 ± 0.75
	1 bar, air, r.t.	0	98.73 ± 0.49 ^{e)}	–
	1000 bar, $^{14}\text{N}_2$, 45°	60	92.52 ± 0.41	7.25 ± 0.78
	1000 bar, $^{14}\text{N}_2$, 45° ^{g)}	57	94.53 ± 0.21	5.17 ± 1.06
MeO	1 bar, air, r.t.	0	99.50 ± 0.17 ^{e)}	–
	1000 bar, $^{14}\text{N}_2$, 65°	48	92.57 ± 0.37	10.10 ± 0.99
	1000 bar, $^{14}\text{N}_2$, 65°	53	90.98 ± 0.09	11.15 ± 0.25
Ac	1 bar, air, r.t.	0	98.61 ± 0.52 ^{e)}	–
	1000 bar, $^{14}\text{N}_2$, 45°	55	95.22 ± 0.23	4.31 ± 0.51
	1000 bar, $^{14}\text{N}_2$, 45°	59	94.38 ± 0.36	5.03 ± 0.52
<i>t</i> -Bu	1 bar, air, 25°	0	98.88 ± 0.07 ^{e)}	–
	1000 bar, $^{14}\text{N}_2$, 45°	33	95.26 ± 0.49	5.07 ± 0.75
	1000 bar, $^{14}\text{N}_2$, 45°	55	96.01 ± 0.25	6.09 ± 0.63
	1000 bar, $^{14}\text{N}_2$, 45°	57.4 ^{h)}	92.11 ± 0.13	8.26 ± 0.15
	1000 bar, $^{14}\text{N}_2$, 45°	58.8 ^{h)}	91.95 ± 0.08	8.25 ± 0.10

^{a)} Based on single determination (see *Exper. Part*).

^{b)} Determined by MS (see *Exper. Part*).

^{c)} 95% confidence limits.

^{d)} Extrapolated to 70% dediazoni-ation.

^{e)} Reference standard.

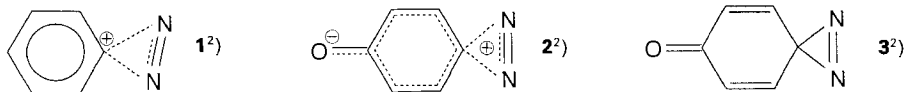
^{f)} See [11].

^{g)} In TFE containing 0.37M HCl.

^{h)} Based on 2 determinations (see *Exper. Part*).

The $\text{N}(\alpha)$, $\text{N}(\beta)$ -rearrangement has aroused considerable experimental [11–14] [16] and theoretical [23] [24] interest. The nature of the intermediate and the transition state involved is of particular importance. The current view is that in the transition state there is a weak bond between the $\text{N}(\alpha)$ atom and C(1) of the aryl ring, and very weak bonding between the latter and $\text{N}(\beta)$ (1 and Fig. 3 in [17]). The experimental results, particularly the secondary deuterium isotope effect [16], are consistent with a tight aryl cation/ N_2 molecule-ion-pair structure for the intermediate. MO calculations [24] suggest that the transition state for the rearrangement is an unsymmetrically bridged species and that the symmetrically bridged species is predicted to be the metastable intermediate, *i.e.* the ion-molecule pair mentioned. The rearrangement follows a π - rather than a σ -route [23].

The opposing signs of the reaction constants ρ_{F} and ρ_{R} indicate that the rate constants k_{r} and k_{s} are decreased by inductive electron withdrawal and by π -donation. The reso-



nance effect is, therefore, primarily a ground-state (reactant) effect. The intermediate is also stabilized by π -donors, e.g. by a *p*-MeO group or a phenolate O-atom. It is, therefore, possible that benzenediazonium ions containing such substituents in the *p*-position do not have an intermediate with a tight ion-molecule-pair structure such as **2**, but with covalent bonds such as the spirodienone-diaziridine structure **3** (see also *Grieve et al.* [25]). The results which excluded structure **2** on the basis of secondary kinetic isotope effects (see above) were obtained with [2,4,6-²H₃]benzenediazonium ions, i.e. with a compound without a π -donor substituent in the *p*-position. Increasing pressure (1000 bar) causes a significant decrease in k_s and k_r (Table 2). This result is consistent with the structure **1** for the transition state of the first step in Eqn. 2: In **1**, the C(1)–N(α) bond is considerably stretched.

The rate of the *reverse reaction* of the first two steps in Eqn. 2, i.e. the addition of N₂ to the aryl cation reforming the arenediazonium is interesting. The overall rate can be determined by measuring the decrease in the ¹⁵N-content of a labelled diazonium ion in a solution containing unlabelled molecular N₂. We have called this the *exchange reaction*. The intrinsic rate constants of these two back reaction steps are, however, very complex combinations of at least six forward and backward rate constants (see rate equation in [15]). They cannot be calculated from the available experimental data.

We are, therefore, only able to evaluate the overall (complex) percentage of exchange (E) of the addition of N₂ to substituted phenyl cations with *Taft's* dual substitution parameter treatment [22]. The result demonstrates (Eqn. 6) that the two ρ constants are close to zero.

$$\log(E^X E^H) = -0.18(\pm 0.09)\rho_F - 0.32(\pm 0.06)\rho_R \quad (6)$$

$r = 0.904 \qquad n = 7$

This result is consistent with expectations: the overall percentage of exchange, as a combination of forward and backward reaction steps, is likely to result in a complex mixture of reaction constants ρ_F and ρ_R with opposite signs. The individual ρ values will, therefore, cancel each other approximatively, yielding overall values for ρ_F and ρ_R which are close to zero. We think, therefore, that it is hardly possible to draw quantitative conclusions from the figures in Eqn. 6. As we will show in the following communication [26], information on the back reaction of the first step in Eqn. 2 can be obtained in H₂O and with CO as co-reagent with H₂O for the tight ion-molecule pair. CO is isoelectronic with N₂, but more reactive than N₂.

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²) The plane C(1)–N(α)–N(β) in **1-3** is orthogonal to the plane of the six-membered rings.

Experimental Part

1. *Materials.* The 2,2,2-trifluoroethanol (*Fluka; puriss.*) was used as received.

Substituted benzene- and benzene[β - ^{15}N]diazonium tetrafluoroborates were prepared by diazotisation of the corresponding anilines with NaNO_2 and $\text{Na}^{15}\text{NO}_2$, respectively, according to the procedure of *Starkey* [27]. Purification was effected by dissolution in MeCN and reprecipitation with Et_2O . The products were characterised by comparison of m.p. or dec. points and IR and UV spectra with literature values. Good agreement was obtained in all cases.

p-(Trifluoromethyl)benzediazonium Tetrafluoroborate (from MeOH/ Et_2O). M.p. 116–117° (dec.). UV (0.1M aq. HCl): 253 (4.06), 298 (3.31). Anal. calc. for $\text{C}_7\text{H}_4\text{BF}_7\text{N}_2$: C 32.35, H 1.55, N 10.78; found: C 32.35, H 1.55, N 10.74.

The filtrates from isolation of the diazonium salts were coupled with alkaline 2-naphthol to give the corresponding azo dyes which were purified by recrystallisation from 95% EtOH. M.p.'s were in accord with literature values.

1-[4'-(Trifluoromethyl)phenylazo]-2-naphthol. M.p. 140–147°. Anal. calc. for $\text{C}_{17}\text{H}_{11}\text{F}_3\text{N}_2\text{O}$: C 64.56, H 3.51, N 8.86; found: C 64.84, H 3.68, N 8.93.

1-[4'-(tert-Butyl)phenylazo]-2-naphthol. M.p. 86–88°. Anal. calc. for $\text{C}_{20}\text{H}_{20}\text{N}_2\text{O}$: C 78.92, H 6.62, N 9.20; found: C 78.83, H 6.84, N 9.13.

The azo dyes were converted to the corresponding aniline hydrochlorides by $\text{Na}_2\text{S}_2\text{O}_4$ [11][13]. The amine salts were purified by dissolution in MeOH and precipitation with Et_2O or by prep. TLC. All the salts were homogeneous by TLC and the R_f values identical with those of authentic samples.

2. *Exchange Reactions.* These were carried out using a glass-lined stainless-steel autoclave, as previously described [11–13]. The autoclave was pressurised to 1000 bar $^{14}\text{N}_2$ for all experiments. The temp. employed for the various diazonium salts is given in *Tables 2 and 3*.

3. *Rearrangement Reactions.* The [β - ^{15}N]diazonium salt in TFE was allowed to decompose under $^{14}\text{N}_2$ in a stoppered glass flask. The flask was wrapped in Al foil to exclude light and maintained in a water bath at 45.0° for the time required to reach ca. 70% dediazonation.

4. *Extent of Dediazonation.* Aliquots (0.20 ml) of diazonium-salt soln. were taken at 0% and at ca. 70% dediazonation and coupled with R-salt (disodium salt of 3-hydroxynaphthalene-2,7-disulfonic acid). The differences in absorbance of the resulting dyes give the extents of reaction [11–13]. For the exchange reactions, only 1 aliquot was taken at both 0 and ca. 70% reaction. For the rearrangement reactions (with the exception of X = H), 2 or 3 aliquots (see *Table 1*) were taken at both 0 and 70% reaction. For X = NMe₂, aliquots (10 ml), taken at 0 and 70% reaction, were injected into 0.1N aq. HCl (10 ml) and the absorbance (378 nm) of the diazonium salt used to directly determine the extent of reaction.

5. *Analysis of ^{15}N Content by MS.* For the exchange reactions, the extent of exchange was determined by analysing the ^{15}N content of the azo dyes formed by coupling the diazonium salt with 2-naphthol, as described previously [11–13]. For the N(α),N(β)-rearrangement, the labelled azo dyes were reduced to the corresponding substituted aniline hydrochlorides, which were then analysed for ^{15}N content by MS [11–13]. The 4-(tert-butyl) derivative was analysed as the *N*-acetanilide [28]. The molecular ion of this aniline (m/z 149) has the same mass number as that of a fragment ion of phthalate derivatives which are common MS contaminants [29]. Calculation of ^{15}N content was carried out as before [11]. The extent of exchange and rearrangement was always extrapolated linearly to 70% dediazonation.

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