151. Reactivity of Carbenes and Related Compounds towards Molecular Nitrogen¹)

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The thermal N_2 exchange of a number of ^{15}N-labelled diazo compounds was studied in solution. The compounds involved were 3-diazo-1-methylindolin-2-one (**1**), 9-diazofluorene (**2**), 5-diazo-1,3-cyclopentadiene-1,2,3,4-tetracarbonitrile (**3**), 2-diazo-2*H*-imidazole-4,5-dicarbonitrile (**4**), 4-diazocyclohexa-2,5-dienone (**5**), and the conjugate acids of **4** and **5**, namely 4,5-dicyano-1*H*-imidazole-2-diazonium ion (**6**) and 4-hydroxybenzenediazonium ion (**7**). Only **1**, **4**, **6**, and **7** exchange their diazo group with 'external' molecular N_2. The results are explained on the hypothesis that only organic species which have an empty σ orbital and which are effective in π electron back-donation are able to react with N_2. Thus, reaction with carbenes is likely to occur only if the carbene is in the $^1A_2$ singlet state and if its electrophilicity is high.

1. Introduction. – Since 1965 it has been known that certain organometallic complexes are able to react with N_2. With purely (*i.e.* non-metal-containing) organic compounds, however, no reactions with N_2 have been reported, except the photolytic N_2 exchange of diazomethane in an N_2 matrix, *i.e.* in the solid state [2], and in the gas phase [3] [4], *i.e.* in the absence of other molecules (*e.g.* solvent) which may compete with N_2.

Our detailed investigations of the mechanism of the heterolytic dediazoniation of arenediazonium ions [5–7] are consistent with the initial formation of an ion-molecule pair from which the free (solvated) aryl cation and N_2 are formed *(Eqn. 1)*. The back reaction $Ar^+ + N_2 \rightarrow\rightarrow Ar{-}N_2^+$ is a process in which molecular N_2 reacts with a 'simple' organic species. To the best of our knowledge this is the first report of a reaction of a non-metallated organic moiety with N_2 in solution.

$$\begin{tikzcd}
Ar{-}N^{\oplus}{\equiv}N \arrow[r, phantom, "\rightleftharpoons"] & {|Ar\,N_2|^{\oplus}} \arrow[r, phantom, "\rightleftharpoons"] \arrow[d, "+\,Nu"] & Ar^{\oplus} + N_2 \arrow[d, "+\,Nu"] \\
 & \text{Products} + N_2 & \text{Products}
\end{tikzcd} \qquad (1)$$

Nu = Nucleophile(s)

This paper is concerned with the question of whether there are other highly reactive organic species which may react with N_2. We considered that carbenes might be suitable candidates. Both singlet and triplet carbenes add to the double bond of alkenes to form

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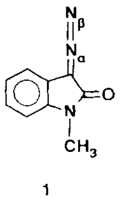
cyclopropanes. As postulated by *Skell* and *Woodworth* and corroborated among others by *Jones et al.* [8], singlet states of carbenes such as fluorenylidene formed by photolysis of diazofluorene add to *cis*-butene stereospecifically in a concerted reaction. The respective triplet states add non-stereospecifically. The correlation diagram for the simplest reaction of this type, namely $:CH_2 + CH_2{=}CH_2$, can also be used for the reaction of $:CH_2$ with N_2. The latter reaction, however, which leads to diazirine as the primary product, is significantly less favourable. A detailed theoretical study of the bonding nature of N_2 with singlet $:CH_2$ was made by *Yamabe, Fukui et al.* [9]. They compared the C,N-bond character of diazomethane and diazirine with that of N,metal bonds in end-on and side-on complexes of organometallic compounds with N_2. For both the metal complexes and the reaction of $:CH_2$ with N_2, the linear (end-on) product is calculated to be more stable, but not by so much that the formation of side-on complexes would not be feasible. This result is, therefore, similar to our experimental and theoretical results [7] which show the end-on arenediazonium ion to be more stable than the side-on ion-molecule pair of an aryl cation with N_2.

The kinetics of flash photolysis of diazomethane in the presence of N_2 in the gas phase [4] show that the rate of reaction of singlet $:CH_2$ with N_2 ($^1{:}CH_2 + N_2 \rightarrow CH_2N_2^* \rightarrow CH_2N_2$) is quite high and similar to the reaction rates with CH_4 and with H_2. The main reaction of triplet $:CH_2$ is dimerisation ($^3{:}CH_2 + {^3}{:}CH_2 \rightarrow CH{\equiv}CH + H_2$). It is unreactive towards H_2 and CH_4 and probably towards N_2.

At the time this investigation was started, little was known about relative energies of singlet and triplet states of the carbenes we considered suitable for study. In order to obtain high concentrations of N_2, it was necessary to run the reactions under pressure. This condition, for experimental reasons, required thermal carbene generation. Consequently, we originally selected 3-diazo-1-methylindolin-2-one (**1**) and 9-diazofluorene (**2**), two diazo compounds for which detailed information was available on the products of the carbenes generated by thermal reactions. In a similar way to our investigations of arenediazonium ions, ^{15}N-labelled **1** and **2** were decomposed in the presence of unlabelled N_2. In **1**, N(α) (→(α-^{15}N)-**1**) and in **2** both N-atoms (→(α,β-N_2)-**2**) were labelled. The diazo compounds remaining after 30 to 80% dediazoniation were examined for any decrease in ^{15}N-content.



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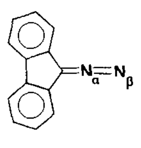

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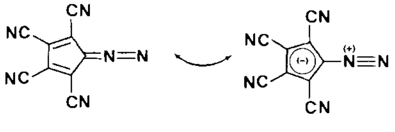
^{15}N(β)-Labelled derivatives of 5-diazo-1,3-cyclopentadiene-1,2,3,4-tetracarbonitrile (**3**) and 2-diazo-2*H*-imidazole-4,5-dicarbonitrile (**4**) were included in our investigation since their chemical reactivity (*e.g.* formation of azo compounds in electrophilic aromatic substitution reactions corresponding to the conventional azo-coupling reaction of arenediazonium ions) indicated a very close resemblance to diazonium ions, *i.e.* structures close to the zwitterionic diazonium-type resonance structures **3b** and **4b**, respectively [10] [11]. These zwitterionic structures are also indicated by the ^{15}N- and ^{13}C-NMR chemical shifts of their $\rangle C{=}N{=}N$ groups [12]. In this context, we also studied the $^{15}N(\beta)$-labelled derivative of 4-diazocyclohexa-2,5-dienone (**5**)[3]) which can be represented by the structures **5a** and **5b**, but according to the ^{15}N- and ^{13}C-NMR chemical shifts [12] (see below, *Fig.*), **5** falls together with **2** in the group of diazo compounds. For comparison with **4** and **5**, their conjugate acids 4,5-dicyano-1*H*-imidazole-2-diazonium ion (**6**) and 4-hydroxybenzenediazonium ion (**7**) have also been studied[4]).



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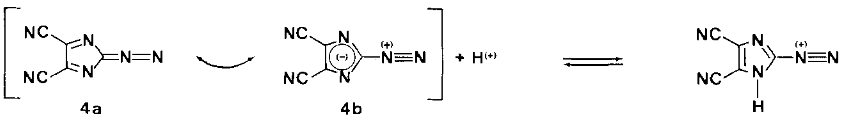
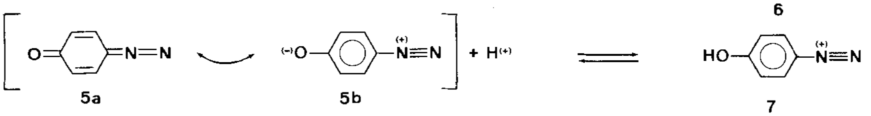
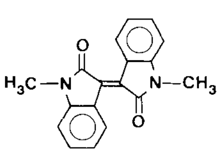


4a 4b 6 (2)



5a 5b 7 (3)

2. Results. – 2.1. *3-Diazo-1-methylindolin-2-one* (**1**). The products of thermolysis of **1** are well known from a detailed investigation by *Moriconi* and *Murray* [17]. We studied the thermal N_2 exchange of (α-^{15}N)-**1** in hexafluoroisopropyl alcohol (HFIP) at 54 ± 2° in a glass-lined autoclave under 800 and 1000 atm N_2, corresponding to concentrations of dissolved N_2 of more than 5M [6]. The following products were obtained: *N,N'*-dimethylisoindigo (**8**), *N,N'*-dimethylisatinazine (**9**), 3-(hexafluoroisopropoxy)-1-methylindolin-2-one (**10**), 1-methylisatin (**11**), and some unknown product which was difficult to separate from **9** (see *Exper. Part, Table 8*).



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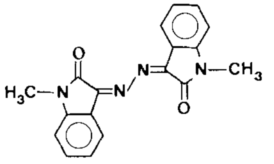

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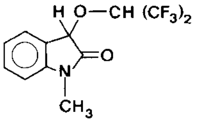

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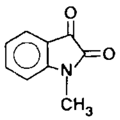

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The dediazoniation reactions were stopped after periods of 2 to 18 days, corresponding to 39 to 70% reaction. The remaining diazo compound **1** was analyzed by MS after reduction to the hydrazone with $NaBH_4$. Direct MS analysis of **1** did not give reliable results. The MS results were evaluated by two methods (see *Exper. Part*) and extrapo-

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[3]) The name 4-diazocyclohexa-2,5-dienone will be used for compound **5**. The name 4-diazoniophenolate should be used according to IUPAC rules *C-87* [13] for its zwitterionic structure. Other names encountered in the literature are: 1,4-diazoquinone, 1,4-quinonediazide, and 4-diazophenol. See also [14].

[4]) The pK_a values of 4,5-unsubstituted **6** and of **7** in H_2O are 2.6 [15] and 3.40 [16], respectively.

Table 1. *N_2-Exchange Experiments with 3-(α-^{15}N)Diazo-1-methylindolin-2-one ((α-^{15}N)-***1***) under Pressure of N_2 in HFIP at 54 ± 2°*

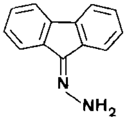
Run	Pressure [atm]	Reaction time [h]	Dediazoniation [%]	Exchange [%]
1	1000	96	56	[a])
2	1000	67	48	< 0.3
3	1000	96	70	[a])
4	800	72	54	0.83 ± 0.27
5	1000	96	53	1.94 ± 0.21
6	800	72	54	1.30 ± 0.11
7	1000	144	42	< 0.3
8	1000	264	48	< 0.3
9	1000	432	39	< 0.3

[a]) Not measured.

lated to 70% dediazoniation as described before [6]. They are given together with the reaction conditions in *Table 1*: No exchange was detected in *Runs 2* and *7–9*, but exchange was found in *Runs 4–6*. Concerning the significance of these results, it is interesting to note that in spite of doubling the reaction time in *Run 7* (relative to *Run 6*) the percentage of conversion decreased by almost a quarter. In *Runs 8* and *9*, further substantial increases of reaction times did not give correspondingly higher conversions, *i.e.* the reaction rates decreased further. Since the same new glass-insert in the autoclave was used for all runs, this is likely to be due to surface effects which seem to occur frequently in dediazoniation reactions of diazo compounds [18]. We suppose that the intermediate which reacts with N_2 and which is highly reactive in general, is converted into another intermediate which reacts more slowly in the usual reactions of diazoketones, but does not react at all with N_2[5]). In conclusion, it seems therefore that 3-diazo-1-methylindolin-2-one (**1**) is able to exchange its diazo group with molecular N_2, but to a small degree only.

2.2. *9-Diazofluorene* (**2**). As 9-diazofluorene is insoluble in HFIP but somewhat soluble in trifluoroethanol (TFE) and slightly more so in mixtures of TFE and CH_3CN and in mixtures of fluorinated hydrocarbons, these solvent systems were chosen for studying the N_2 exchange with (α,β-$^{15}N_2$)-**2**.

A 3.8×10^{-2}M solution of (α,β-$^{15}N_2$)-**2** in TFE/CH_3CN 58:42 *(v/v)* was heated to 85° and quenched after 75 min, corresponding to 35% dediazoniation, and 62% of the remaining diazofluorene was recovered as the hydrazone **12** by reduction with $NaBH_4$. The dediazoniation products were 9,9′-bifluorenylidene (**13**) and 9-fluorenone azine (**14**) in about equal amounts. The formation of bifluorenylidene **13** is strongly dependent on



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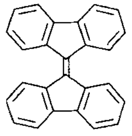

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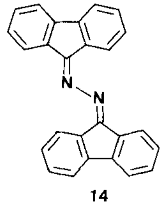

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[5]) The first and second intermediate may be the singlet and triplet carbene, respectively. Inter-system-crossing of singlet carbenes to the triplet ground state by collision with other molecules is well known [19].

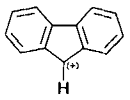
Table 2. *Influence of Concentration of 9-Diazofluorene* (**2**) *and of Solvent on Formation of Bifluorenylidene* **13**

Concentration of **2** [mol/l]	Solvent[a])	Reaction conditions[b])	Yield of **13** [%]
5.6×10^{-5}	TFE/CH_3CN 58:42	85°, 20 h	8.6
7.6×10^{-4}		85°, 25 h	21
5.0×10^{-3}		85°, 22 h	21
5.0×10^{-2}		85°, 6 d	62
6.0×10^{-5}	BTF	103°, 27 h	49
2.4×10^{-3}		103°, 22 h	60
2.5×10^{-2}		103°, 22 h	93
2.8×10^{-3}	FC-75/BTF 70:30	110°, 4 h (60% dediaz.)	85
2.8×10^{-3}	FC-43/BTF 70:30	110°, 4 h	83
2.8×10^{-3}	FC-75/FB 70:30	110°, 8 h (90% dediaz.)	86

[a]) TFE = 2,2,2-trifluoroethanol, BTF = (trifluoromethyl)benzene, FC-75 = mixture of perfluoro-2-butyl-tetrahydrofurane ($C_8F_{16}O$) and perfluorooctane, FC-43 = perfluoro-tributylamine, FB = perfluorobenzene.

[b]) > 97% Dediazoniation, unless otherwise stated.

the concentration of **2** and on the solvent. Examples are given in *Table 2* together with data obtained for the other fluorinated solvents. In contrast to TFE, these solvents do not contain acidic H-atoms which may cause an acid-catalyzed dediazoniation of **2** with subsequent formation of the fluorenyl cation **15** rather than the carbene **16**. Since, however, 9-(trifluoroethoxy)fluorene was not found, we assume that the cation **15** is unlikely to be formed under the described experimental conditions.



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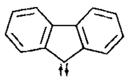
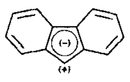
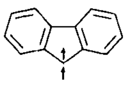


16a



16b



16c

We also measured the kinetics of this dediazoniation spectrophotometrically by monitoring both the increase in the absorption of bifluorenylidene (450 nm) and the decrease of the absorption of 9-diazofluorene at 345 nm. Spectra taken at various times show well defined isosbestic points and the first-order rate constants calculated from the two absorption changes are the same within experimental error *(Table 3)*. This indicates

Table 3. *Reaction-Rate Constants of Dediazoniations of 9-Diazofluorene* (**2**)

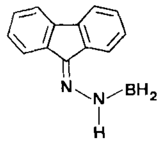
Concentration of **2** [10^{-5} mol/l]	Solvent	Temperature	k [$10^{-5}s^{-1}$]	Method[a])
4.64	TFE	23°	2.6	A
7.14		23°	2.6	A
111		23°	2.6	B
8.43		50°	31.0	A
4.70	TFE/CH_3CN 83.5:16.5	50°	4.6	A
1.57		50°	4.6	B
5.56	TFE/CH_3CN 58:42	85°	13.3	A, B

[a]) A and B = Absorption measurements at 345 and 450 nm, respectively.

that the rate-limiting step for the formation of **13** is the dediazoniation of **2**, *i.e.* the formation of the carbene.

High-pressure experiments (335–1000 atm N_2) with **2** in TFE/CH_3CN 58:42 (6 experiments) and in the mixtures of perfluorinated solvents given in *Table 2* were carried out in a glass-lined autoclave. Initial concentrations of **2** were in the range of (2.8 to 5.9) $\times 10^{-3}$M. The reactions were stopped after 30 to 83% dediazoniation (two runs with less than 30%). The temperature used for experiments in TFE/CH_3CN was 73–75°, and for those in perfluorinated solvents 109–110, 113, and 120°. Reaction times varied between 4 and 8 h (two runs with 12 and 18 h). A rough calculation of rate constants based on time and percentage dediazoniation and assuming first-order kinetics showed that under comparable conditions, rates varied in all solvents by a factor of *ca.* 2 (one run was 4 times slower). This is similar to the results of pressure experiments with 3-diazo-1-methylindolin-2-one (**1**). Dediazoniations of **2** investigated by *Bethell* and *Brown* [20] at atmospheric pressure gave very different product ratios depending on the material of the reaction vessel. This indicates again that surface effects may cause irreproducible results.

The exchange experiments were analyzed by MS of the recrystallized 9-fluorenone hydrazone (**12**) and 9-fluorenone azine (**14**). However, the MS of **12** proved to be unsuitable due to contamination of **12** with a by-product from reduction of 9-diazofluorene with $NaBH_4$. The presence of the boron compounds **17** and **18** from excess $NaBH_4$ was indicated. Fragmentation peaks of **17** and **18** correspond to the molecular ion *m/z* 194 of 9-fluorenone (^{14}N)hydrazone. In all cases where we observed an increase of the peak at m/z 194 after the exchange experiment, there was no increase of the corresponding peak in the spectrum of azine **14**. We concluded the peak at *m/z* 194 to be due to fragmentation of **17** or **18** or both. In all 12 experiments with (α,β-$^{15}N_2$)-**2**, no decrease in ^{15}N-content was found, within experimental error ($\pm$ 0.3%), by analysis of **14**. We therefore conclude that the intermediates generated in dediazoniation of **2** do not react with N_2 to a measurable extent under the described reaction conditions.



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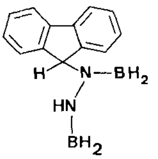

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2.3. *5-Diazo-1,3-cyclopentadiene-1,2,3,4-tetracarbonitrile* (**3**) and (β-^{15}N)-**3** were synthesized according to *Webster* [11]. The exchange experiments in HFIP as solvent were carried out under pressures of 300 to 1000 atm N_2 at temperatures of 135 to 145° in a glass-lined autoclave. Since **3** is sufficiently stable to be vaporized, the remaining diazo compound was analyzed directly by MS after evaporation of the solvent and purification of the residue (see *Exper. Part*). As shown in *Table 4*, no exchange was observed and, as for compounds **1** and **2** discussed above, the rate of dediazoniation is not reproducible.

2.4. *2-Diazo-2*H*-imidazole-4,5-dicarbonitrile* (**4**) *and 4,5-Dicyano-1*H*-imidazole-2-diazonium Ion* (**6**). Exchange experiments with 2-(β-^{15}N)diazo-2*H*-imidazole-4,5-dicarbonitrile ((β-^{15}N)-**4**) were carried out as with **3**, but using TFE as solvent at 61 and 62° and under 1100 to 1150 atm N_2. As **4** is explosive [10], 2-amino-1*H*-imidazole-4,5-dicarboni-

Table 4. *N_2-Exchange Experiments with 5-(β-^{15}N)Diazo-1,3-cyclopentadiene-1,2,3,4-tetracarbonitrile ((β-^{15}N)-**3**) in HFIP*[a])

Temp. [°]	Pressure [atm]	Reaction time [h]	Dediazoniation [%]	^{15}N [%]	Exchange[b]) [%]
135	300	24	25	99.8	< 0.3
135	300	29.5	37	99.7	< 0.3
135	300	31.5	56.2	99.4	< 0.3
140	300	4	5.1	99.8	< 0.3
135		1.8	16.1[c])		
135	1000	48	6	> 99.8	< 0.3
145	980	87	35[c])		
135	1000	33	11	> 99.8	< 0.3
115	800	3	12.5[c])		

[a]) Compound (β-^{15}N)-**3** was labelled to 99.6 and 99.7%.
[b]) Amount of exchange extrapolated to 70% dediazoniation.
[c]) Total amount of dediazoniation.

trile was diazotized in TFE with pentyl (^{15}N)nitrite and the resulting solution of (β-^{15}N)-**4** was directly subjected to the exchange experiment. MS analyses were made of the corresponding azo compound after coupling remaining **4** with 2-naphthol. The results are summarized in *Table 5*. The amount of exchange of **4** with N_2 is as high or higher than that observed for 4-hydroxybenzenediazonium ion (**7**) and fairly reproducible. The rate of dediazoniation is very reproducible.

Table 5. *N_2-Exchange Experiments with 2-(β-^{15}N)Diazo-2*H*-imidazole-4,5-dicarbonitrile ((β-^{15}N)-**4**) in TFE and 4,5-Dicyano-1*H*-imidazole-2-(β-^{15}N)diazonium Ion ((β-^{15}N)-**6**) in TFE/H_2SO_4*

Compound	Solvent	Temp.	Pressure [atm]	Reaction time [h]	Dediazoniation [%]	^{15}N[a]) [%]	Exchange[b]) [%]
(β-^{15}N)-**4**	TFE	62°	1100	15	39.5	88.4	20.0
		61°	1150	15	33.0	88.7	22.5
		62°	1140	15	38.9	90.0	17.3
(β-^{15}N)-**4**$\rightleftarrows$(β-^{15}N)-**6**	TFE/H_2SO_4 (5.2 × 10^{-3}M)	52°	1125	15.25	9.5	97.4	16.2
	TFE/H_2SO_4 (0.15M)	50°	1125	15	30.8	98.2	3.0
	TFE/H_2SO_4 (0.30M)	53°	1090	15	61.3	97.5	2.3

[a]) Compound (β-^{15}N)-**4** was labelled to 99.7, 99.3, 99.6, 99.6, 99.5, and 99.5%, respectively.
[b]) Amount of exchange extrapolated to 70% dediazoniation.

As compounds **4** and **6** are the components of an acid-base equilibrium (see *Eqn. 2*), a second set of experiments was conducted with (β-^{15}N)-**4** at 50–53°, under 1090 and 1125 atm N_2 in TFE and increasing amounts of H_2SO_4 (*Table 5*). The pK_a of **6** is unknown. However, since the pK_a of unsubstituted imidazole-2-diazonium ion is 2.6 [15], we can assume that in the third run (TFE/0.3M H_2SO_4), mainly the diazonium ion (β-^{15}N)-**6** was present. As *Table 5* shows, with increasing amounts of H_2SO_4 the amount of exchange with N_2 decreases to 2.3%.

2.5. *4-Diazocyclohexa-2,5-dienone* (**5**) *and 4-Hydroxybenzenediazonium Ion* (**7**). As compounds **5** and **7** are also the components of an acid-base equilibrium (see *Eqn. 3*), two sets of experiments were again conducted. The thermal decomposition of (β-^{15}N)-**5** was

Table 6. *N_2-Exchange Experiments with 4-(β-^{15}N)Diazocyclohexa-2,5-dienone ((β-^{15}N)-**5**) in TFE and 4-Hydroxybenzene(β-^{15}N)diazonium Ion ((β-^{15}N)-**7**) in TFE, Saturated with HCl, at 65° and 1000 atm N_2*

Run	Compound[a]	Reaction time [d]	Dediazoniation [%]	^{15}N[b] [%]	Exchange[c] [%]
1	(β-^{15}N)-**5**	3	77	98.45 ± 0.52	0.14 ± 0.61
2		3	78	98.95 ± 0.87	0.78 ± 0.83
3	(β-^{15}N)-**7**	10	86	81.03 ± 1.02	14.30 ± 0.89
4		9	81	83.31 ± 0.64	13.21 ± 0.72
5		8	53	86.07 ± 0.52	18.03 ± 2.70

[a] ^{15}N content of starting materials: *Run 1, 3* and *4* 98.60 ± 0.37%; *Run 2* 99.73 ± 0.87%; *Run 5* 99.72 ± 2.24%.
[b] Average of two MS analyses, using a total of 20 measurements of the peak heights of *m/z* 264, 265.
[c] Calculated for 70% dediazoniation.

run in both neutral TFE and TFE acidified with HCl, under 1000 atm of N_2 at 65°. The diazo compound and the diazonium ion remaining at about 70% dediazoniation were converted to the corresponding azo compound with 2-naphthol and the ^{15}N-content determined by MS. The times necessary for 70% dediazoniation were determined by rate measurements at the respective UV maxima. Rates were acceptably reproducible.

The results of the exchange experiments are given in *Table 6*. They clearly show a large extent of reaction with N_2 for the 4-hydroxyphenyl cation derived from **7**, but no significant reaction for the carbene derived from 4-diazocyclohexa-2,5-dienone (**5**).

3. Discussion. – The interpretation of the N_2-exchange results presented in this paper is based among other considerations on two points stressed in the theoretical study by *Yamabe, Fukui et al.* [9] on reactions of N_2 with transition-metal complexes and with $:CH_2$. The authors suggest firstly, that for formation of M,N and C,N bonds, σ-bond formation is important as well as π back-donation, σ-bond formation being energetically dominant. Secondly, they assumed that for $:CH_2$, the two electrons in the n_C orbital (singlet state $^1A_1$) are promoted into the p_y orbital (singlet state $^1A_2$) for reaction with N_2. From orbital correlations it follows that this is a necessary condition for both the linear end-on and the linear side-on cheletropic reaction, otherwise the diazomethane and the diazirine [21] formed would be in doubly-excited singlet states.

Accordingly, in the process of reacting end-on with N_2, the $^1A_2$ state of $:CH_2$ corresponds to the electronic ground-state configuration of the phenyl cation: Theory [22–24] has come to the conclusion that this is the 6 π singlet with an empty σ orbital in the plane of the six-membered ring[6]). Thus, the p_y orbital corresponding to the p_y orbital of the $^1A_2$ state of $:CH_2$ here is part of the aromatic 6 π electron system. Thermal dediazoniation of a diazonium ion to the aryl cation in the 6 π singlet state is a symmetry-allowed linear fragmentation of the C–N bond [23] and hence the end-on back reaction with N_2 is also symmetry-allowed and has been established experimentally *(Eqn. 1)* [5–7].

As diazomethane formed from $^1A_1$ $:CH_2$ and N_2 in an end-on reaction would be in a doubly-excited singlet state, the thermal linear fragmentation of the C=N bond in an

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[6]) It may be mentioned, however, that theory does not yet explain all experimental observations, *e.g. Castenmiller* and *Buck* [24], with MINDO/3 and STO-3G, calculated an energy barrier for dediazoniation of $C_6H_5\text{-}N_2^+$ into $C_6H_5^+ + N_2$ which is unrealistically high (356 kJ/mol). The authors consider the results to be unreliable and write 'Calculations of this kind of models appear to be beyond the scope of the present possibilities'.

aliphatic diazo compound – in contrast with diazonium ions – to the carbene and N_2 is symmetry-forbidden, since the carbene would be in the excited $^1A_2$ singlet state with the p_y orbital occupied. The $^1A_1$ singlet state carbene must be generated by bending the developing N_2 molecule out of the R_2C plane [23]. Clearly, the back reaction with N_2 must also proceed in a non-linear manner.

Summarizing this discussion, we can conclude that a carbene from thermal dediazoniation of a diazo compound may react with N_2: 1) in a non-linear end-on fashion in the $^1A_1$ state or 2) linear end-on, if the $^1A_2$ state is generated either directly or *via* promotion of two electrons into the p_y orbital.

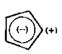
Table 7. *Properties of Phenyl Cation and of a Carbene from Thermal Dediazoniation.* For the carbene, the $^1A_1$ state is assumed to be lower in energy than the $^1A_2$ state; for the case where the $^1A_2$ singlet is of lower energy, both types of fragmentation/back reaction become allowed.

Compound	Fragmentation of respective diazo(nium) compound	Configuration	Reaction with N_2	Symmetry selection [a])
Phenyl cation	linear	6 π singlet strong electrophile	linear end-on	allowed
Carbene	linear	$^1A_2$ singlet strong electrophile	linear end-on	forbidden
Carbene	non-linear	$^1A_1$ singlet weak electrophile	non-linear end-on	allowed

[a]) A scheme of orbital energies and symmetries is found in [21].

As indicated in *Table 7*, the $^1A_1$ singlet carbene is expected to be a weaker electrophile, *i.e.* less reactive towards N_2 than the $^1A_2$ singlet (*e.g.* empty p_y orbital *versus* empty n_C orbital). Thus, the question arises whether the $^1A_2$ singlet state of a carbene can be stabilized (*i.e.* p_y or π orbital lower than n_C orbital) such that in thermal dediazoniation of the corresponding diazo compound it will be generated directly by linear fragmentation as is the case with diazonium ions.

Such stabilization of $^1A_2$ singlet carbenes has been postulated in conjugated cyclic (4n + 2) π electron systems (*e.g.* **19**) as has been destabilization in cyclic conjugated 4 n π electron systems (*e.g.* leading ot **20**) [25]. As a consequence, both the electrophilicity and the nucleophilicity of the respective conjugated $^1A_2$ and $^1A_1$ singlet carbenes have been considered and demonstrated experimentally [26–28][7]).



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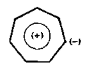

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If we assume that such a stabilization of an $^1A_2$ singlet carbene might also manifest itself in the electronic structure of the precursor, *i.e.* the diazoalkene, it is of interest to examine the NMR results of *Roberts et al.* [12]. As can be seen from the *Fig.*, there are two distinct groups of compounds: the group of diazo compounds including **1**, **2**, and **5** and the group of arenediazonium ions including **3**, **4**, and **7**. Without going into details of

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[7]) For a review, see [29].

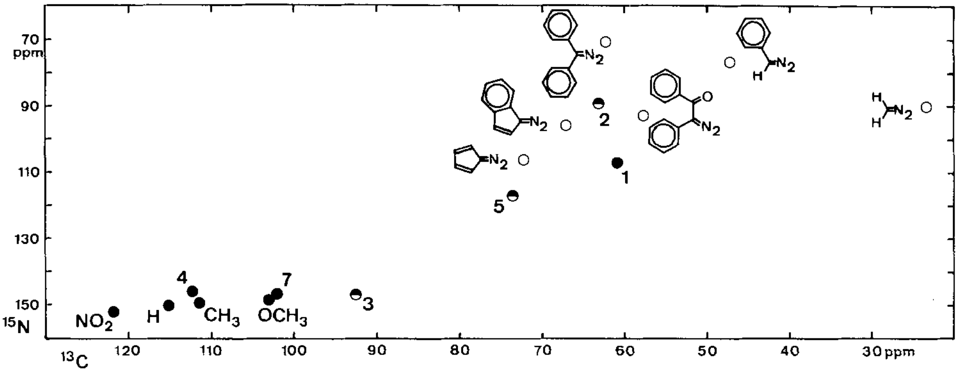

Fig. *Correlation of ^{13}C- and ^{15}N-NMR chemical shifts of C(1) and N(α) of* **1–5**, arenediazonium ions, and additional diazo compounds. Arbitrary numbering, C(1) being the C-atom to which the diazo or diazonio group is linked. H, NO$_2$, CH$_3$, and OCH$_3$ indicate the unsubstituted and 4-substituted benzenediazonium ions. Shifts are downfield from TMS (^{13}C) and upfield from external 1M HNO$_3$ (^{15}N). Data are from *Roberts et al.* [12], except **1** (this paper). ●: Exchange with N$_2$; ⊖: no exchange with N$_2$; ○: compounds not investigated.

possible correlations (*e.g.* for the 4-substituted benzenediazonium ions for which a parallel correlation has also been found [30] between the amount of exchange with external N$_2$ and substituent constants or for **2**, 1-diazoindene and diazocyclopentadiene), a qualitative conclusion seems to be justified. The ^{13}C- and ^{15}N-NMR chemical shifts of *C*=*N*=N indicate that the diazo compounds **3** and **4** have the zwitterionic resonance structures **3b** and **4b** rather than the diazo structures **3a** and **4a**. Therefore, according to the above arguments, dediazoniation of **3** and **4** might be expected to lead to ^{1}A$_2$ singlet carbenes, and hence exchange with external N$_2$ is more likely than for the diazo compounds **1**, **2**, and **5** which are expected to lead to ^{1}A$_1$ singlet carbenes. At this stage of the discussion, however, it must be stressed first of all that we have used ^{15}N- and ^{13}C-NMR chemical shifts as probes of the electronic structures of the diazo compounds, *i.e.* the precursors, to predict the electronic structures of the corresponding carbenes. Secondly, even formation of an ^{1}A$_2$ singlet carbene would make the reaction with N$_2$ only more likely, since competing reactions such as singlet-triplet conversion (and subsequent reaction of the triplet[8])) or reaction with other nucleophiles (*e.g.* solvent or anions present) might also be much faster for the ^{1}A$_2$ state.

The experimental results, namely no exchange with external N$_2$ of *9-diazofluorene* (**2**) and of *4-diazocyclohexa-2,5-dienone* (**5**) are in accord with the above considerations. Various recent MO calculations [29] [32–35] suggest that **16**, **21**, and other conjugated cycloalkene carbenes have a triplet ground state. *Halevi* and *Metcalfe* [32] with INDO and *Schleyer* and *Krogh-Jespersen* [33] with STO-3G found significant energy differences between the triplet of fluorenylidene (**16c**) and the 4 π singlet **16a** (*e.g.* [33]: 99kJ/mol). Furthermore, the 4 π singlet (^{1}A$_1$ state) was calculated to be more stable than the 6 π singlet **16b** (^{1}A$_2$ state) by 115 kJ/mol. As a very recent experimental investigation demonstrates, however, the trend in these calculations seems to be correct, but the energy

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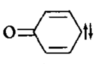
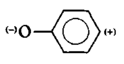
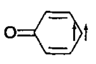
[8]) According to a remark of *Turro et al.* [31], diphenylcarbene reacts extremely rapidly with molecular O$_2$ ($k = 2 \times 10^9 \text{M}^{-1}\text{s}^{-1}$). Thus, in the N$_2$ gas used in our experiments, O$_2$ present at the ppm level would be an efficient scavenger for triplet carbenes.

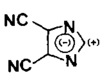
differences must be by far too large, since the electronic configurations **16a** and **16c** are rapidly interconverting and therefore nearly degenerate [36]. For 4-oxocyclohexa-2,5-dien-1-ylidene derived from **5**, the electronic configurations corresponding to **16a–c** are **21a–c.** An energy difference of 1.40 eV has been calculated [29] for **21a** and **21c.** According to *Hoffmann's* empirical rule [37], the ground state should therefore be the triplet **21c.** To our knowledge, no theoretical work comparing the two singlet configurations $^1A_1$ and $^1A_2$ (**21a** and **21b**) has been published. For 3,5-di(*tert*-butyl)-4-oxocyclohexa-2,5-dien-1-ylidene, formation of a singlet state has been demonstrated [38] [39] experimentally by conservation of stereospecificity in addition reactions. Singlet-triplet conversion has also been observed [38]. For 3,5-dichloro-4-oxocyclohexa-2,5-dien-1-ylidene, high electrophilicity has been shown [40] in substitution reactions with benzene derivatives, and this has been interpreted in terms of a $^1A_2$ singlet configuration [29] [40]. However, since a carbene in the $^1A_1$ singlet configuration can be either an electrophile or a nucleophile, depending on the relative levels of the interacting HOMO's and LUMO's, the question of whether the configuration is $^1A_1$ or $^1A_2$ still seems to be open.


21a


21b


21c

In agreement with previously reported results [5–7], exchange with N_2 has been found for *4-hydroxybenzenediazonium ion* (**7**). The high amount of exchange, *i.e.* 15.2% (average of three experiments, *Table 6)*, compared to 6.5% for the unsubstituted benzenediazonium ion [30] under comparable conditions, can be rationalized by the following argument. The 4-hydroxy group is an electron-releasing substituent which increases π back-donation and therefore increases the reactivity of the phenyl cation towards N_2, according to the postulate of *Yamabe et al.* [9].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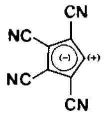
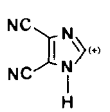
23a


23b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In accord with the expectations, *2-diazo-2*H*-imidazole-4,5-dicarbonitrile* (**4**) also exchanges with N_2. The average amount of 19.9% (first three experiments in *Table 5*) is even higher than that of **7**. The zwitterionic structure **4b** presumably leads to generation of the highly electrophilic $^1A_2$ singlet carbene **22.** Carbene **22** is expected to be particularly electrophilic because of inductive destabilization by two ring N-atoms in α-positions. Such a destabilization has been suggested for the phenyl cation [23]. The influence of the two ring N-atoms, however, is twofold, since on the other hand they stabilize⁹) the charge separation in **4b** in a 6 π electron system.

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⁹) Stabilization of a negative charge in five-membered rings by N-atoms is well known [41]. See also pK_a values of five-membered heterocyclic diazonium ions, *e.g.* [15].

In contrast to **4**, *5-diazo-1,3-cyclopentadiene-1,2,3,4-tetracarbonitrile* (**3**) does not exchange with N_2. This is in accord with observations that the parent compound does not exchange either in a N_2 matrix [42] or in the gas phase [3]. On the other hand, the electrophilicity of cyclopentadienylidene has been demonstrated experimentally and has been discussed as an indication of the $^1A_2$ configuration of the singlet [27]. In agreement with theory [35], the triplet has been observed as the ground state [43]. However, multiconfigurational SCF calculations indicate a lower energy minimum for the 4 π $^1A_1$ singlet than for the 6 π $^1A_2$ singlet with a significant energy barrier between the two states [34]. Thus, the question concerning the singlet configuration still seems to be open, since, as also pointed out for fluorenylidene **16**, both the $^1A_1$ and the $^1A_2$ configuration could exhibit electrophilicity. To our knowledge, there are no MO calculations published for the carbene **23**. According to the ^{13}C- and ^{15}N-NMR chemical shifts of C(1) and N(α), diazocyclopentadiene is in the group of diazo compounds (*Fig.*), whereas for the tetracyano derivative **3** the zwitterionic structure **3b**, stabilized by four cyano groups, is indicated rather than **3a**. Thus, we might expect the $^1A_1$ singlet carbene to be generated from the parent compound, whereas from **3** we anticipate formation of the $^1A_2$ singlet carbene **23b**. Nevertheless, any of the above reservations for a correlation between the electronic structure of a diazo compound and the reactivity of the corresponding carbene will explain our results.

The significance of the N_2-exchange results with *3-diazo-1-methylindolin-2-one* (**1**) is unclear. We have recorded the ^{13}C- and ^{15}N-NMR spectrum of **1**. The chemical shifts of 60.92 ppm for C(1) (60.0 [21]) and 107.01 ppm for N(α) place **1** in the group of diazo compounds (see *Fig.*). Dediazoniation of **1** would, therefore, be expected to lead to an $^1A_1$ singlet carbene. However, the fact that in three experiments a small amount of exchange was found indicates either a $^1A_2$ configuration of the carbene or a surprisingly electrophilic $^1A_1$ singlet state.

Finally, we consider the results with *4,5-dicyano-1*H*-imidazole-2-diazonium ion* (**6**). The following explanations seem to account for the decreasing amount of exchange with increasing amounts of H_2SO_4: First, N_2 has to compete with high concentrations of HSO_4^- and SO_4^{2-} as nucleophiles[10]) (5.2×10^{-3}M to 0.3M H_2SO_4, *Table 5*). Second, either 4,5-dicyano-1*H*-imidazolyl cation (**24**) or the carbene **22**, or both of these, are electrophilic enough to react with N_2, but to a small extent only. Since the acid-base equilibrium (see *Eqn. 2*) favors **6**, and **24** is likely to be more electrophilic than **22** (in **22** only π back-donation may be favored), we assume that **24** reacts with N_2.

The aim of this investigation was to search for carbenes which may react with N_2. Summarizing the results presented in this paper, we can conclude that among the diazo compounds studied, only 2-diazo-2*H*-imidazole-4,5-dicarbonitrile (**4**) leads to a carbene reacting to a significant extent – comparable to aryl cations – with N_2. In accordance with theory [9], the carbene is likely to react in the $^1A_2$ configuration **22** sufficiently electrophilic and capable of π back-donation[11]). The results with the diazo compounds **1** and **3**

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[10]) In a N_2-exchange experiment with (β-^{15}N)-**5** in TFE/H_2SO_4 (0.37M), the amount of exchange of (β-^{15}N)-**7** decreased from 15.2% (average of *Runs 3–5, Table 6*) to 5.3%.

[11]) Preliminary calculations (EHT, MNDO, MINDO/3) of frontier orbitals and of singlet and triplet energies of the investigated carbenes gave a picture inconsistent with the experimental results. However, the results of calculations also indicate a high sensitivity to the assumed geometries (*e.g.* EHT or MNDO for **22** and **23**).

together with the *Fig.* demonstrate that for the reservations discussed above, the NMR data can only indicate which diazo compounds are most likely to exchange with N_2.

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Experimental Part

1. General. – 1.1. *Analytical Techniques.* M.p. are uncorrected. Pre-coated plastic sheets or glass plates of (silanised) silica gel (*60 F_{254}, DC 60 F_{254}, PSC 60 F_{254}*) and (silanised) silica gel (0.063–0.2 mm, *Merck AG*, Darmstadt) were used for anal. TLC, prep. TLC, and column chromatography, respectively. Spectra were run on a *Beckman IR-33* or *Acculab 4* (IR), on a *Unicam SP 800 A* or a *Shimadzu UV-240* (UV/VIS), and on a *Bruker WH 90* or *AM 300 WB* (^{1}H-, ^{13}C-, ^{15}N-NMR). Mass spectra were recorded on a *Hitachi-Perkin Elmer RMU-6* (Organ.-Chem. Laboratorium, ETH). Unless stated otherwise, elemental analyses and spectral data of all compounds were in accord with literature and/or structures.

1.2. *Chemicals.* Solvents were purchased from *Fluka AG* (*puriss. p.a.* or *purum* grade) and *Merck AG* (*p.a.* grade) and used without further purification. The 2-naphthol was recrystallized from EtOH (m.p. 121°). The disodium salt of 2-naphthol-3,6-disulfonic acid (R-salt) was recrystallized twice from H_2O and charcoal. The 4-aminophenol *(Fluka AG, purum)* was used without further purification as were (*Z*)-2,3-diamino-2-butenedinitrile *(Fluka AG, pract.)* and cyanogen bromide *(Fluka AG, purum)*. $Na^{15}NO_2$, $^{15}NH_2OH \cdot HCl$, and $^{15}N_2H_4 \cdot H_2SO_4$ (all 99% ^{15}N) were obtained from *Stohler Isotope Chemicals.*

2. Syntheses. – 2.1. *3-Diazo-1-methylindolin-2-one* (**1**) was prepared according to [17] *via* the oxime and purified by column chromatography (silanised SiO_2, EtOH-free $CHCl_3$). This method was found to be superior to that of [17]. M.p. 89.5–90° ([17]: 88–90°). The 3-(α-^{15}N)diazo-1-methylindolin-2-one ((α-^{15}N)-**1**) was obtained analogously using $^{15}NH_2OH \cdot HCl$.

2.2. *1-Methylisatin 3-Hydrazone (= 1-Methylindoline-2,3-dione 3-Hydrazone).* Equimolar quantities of purified **1** (*e.g.* 50 mg) and $NaBH_4$ (12 mg) were stirred overnight (18 h) at r.t. in abs. CH_3OH (30 ml) under N_2. Et_2O (50 ml) was then added, followed by H_2O (50 ml). After shaking, the Et_2O layer was drawn off and the H_2O/CH_3OH washed with 3 similar quantities of Et_2O. The combined Et_2O extracts were dried (anh. K_2CO_3), and the solvent was evaporated. The resulting yellow residue was chromatographed on silanised silica plates (EtOH-free $CHCl_3$), and the top yellow band was rechromatographed on a second plate with AcOEt/hexane 1:1. Upon standing of the $CHCl_3$ soln. at r.t. for *ca.* 3 h, some isomerisation occurs, as detected by TLC. The stable isomer has R_f 0.6–0.7 ($CHCl_3$) and the other isomer R_f 0.3–0.4. M.p. 105–108° ([17] 104–106°).

1-Methylisatin 3-(α-^{15}N)hydrazone was obtained in the same way from (α-^{15}N)- **1**.

2.3. *9-Diazofluorene* (**2**). *9-Fluorenone Hydrazone* (**12**). For the conventional synthesis [44], an excess of hydrazine sulfate is necessary. The following method allows synthesis of labelled hydrazone without excess of the costly (^{15}N)hydrazine: A soln. of hydrazine (prepared from 1.04 g (8 mmol) of hydrazine sulfate and 2.18 g (16 mmol) of NaOAc in CH_3OH/H_2O 1:1) was added to a boiling soln. of 1.44 g (8 mmol) of 9-fluorenone in 5 ml of CH_3OH, and the mixture was refluxed for 30 min. Formation of the azine **14** (brilliant red needles) was observed. The red solid was filtered from the hot soln. and the filtrate cooled in ice. Pale yellow needles precipitated (1.147 g, 74%), m.p. 148–149°. Recrystallization from EtOH afforded 0.836 g (54%) of **12**. M.p. 150–151° ([45]: 149°).

9-Fluorenone ($^{15}N_2$)hydrazone was synthesized analogously from 1.37 g (10.5 mmol) $^{15}N_2H_4 \cdot H_2SO_4$ and 1.897 g (10.5 mmol) of 9-fluorenone. Crude yield 1.348 g and an additional 0.104 g from the filtrate. Recrystallization from EtOH gave 0.957 g of colorless needles, m.p. 147.0–148.5°. For MS, a sample was recrystallized from benzene (m.p. 148–149°).

9-Diazofluorene (**2**) was obtained from **12** according to [44]. TLC (SiO_2/C_6H_6, R_f of **2** 0.55–0.58) demonstrated the presence of small amounts of **14** (R_f 0.45), 9-fluorenone (R_f 0.30), and **12** (R_f 0.05). Recrystallization of the crude sample (3.18 g) from anh. Et_2O (20 ml) gave 1.30 g (34% from 20 mmol **12**) of **2**, m.p. 98.5–99.5° ([46]: 94–95°). Repeated recrystallization of the residue from the mother liquor gave 3 further fractions of pure **2** (total 0.68 g, m.p. 97.5–99.5°) and an unidentified red solid (0.617 g).

9-(α,β-$^{15}N_2$)Diazofluorene ((α,β-$^{15}N_2$)-**2**) from 9-fluorene ($^{15}N_2$)hydrazone (1.765 g, 8.99 mmol) was synthesized in the same way. Recrystallization from Et_2O gave 0.733 g (42%), m.p. 98–99°.

2.4. *5-Diazo-1,3-cyclopentadiene-1,2,3,4-tetracarbonitrile* (**3**) *and (β-^{15}N)-***3** (from $Na^{15}NO_2$) were synthesized according to [11] from disodium hexacyanobutenediide without isolation of intermediates. On 2-mmol scales, the yields of crude **3** varied between 53 and 69% ([11]: 61%) depending on the purity of the butenediide. Column chromatography (30 g of SiO_2, AcOEt), *e.g.* of 250 mg of crude **3**, adsorbed on 1 g of SiO_2 from CH_3CN soln., yielded 182 mg (47%) of pure **3**, which was identified by the usual techniques.

2.5. *2-Diazo-2*H*-imidazole-4,5-dicarbonitrile* (**4**) *and 4,5-Dicyano-1*H*-imidazole-2-diazonium Ion* (**6**). They were not isolated, but obtained by diazotization of 2-amino-1*H*-imidazole-4,5-dicarbonitrile in TFE and TFE/H_2SO_4 soln., respectively. The 2-amino-1*H*-imidazole-4,5-dicarbonitrile was synthesized by modification of a published procedure [47]. Equimolar amounts (2 mmol) of cyanogen bromide (212 mg) and (*Z*)-2,3-diamino-2-butenedinitrile (216 mg) were refluxed in 8 ml of CH_3OH/H_2O 1:1 for 39 h to give 116 mg (44%) of crude product, which was recrystallized from 5 ml of CH_3CN and a small amount of charcoal to give 55 mg of pure product. M.p. 272° (dec.; [47]: 270° (dec.)).

2.6. *4-Diazocyclohexa-2,5-dienone* (**5**). *4-Hydroxybenzenediazonium ion* (**7**) was obtained as the chloride by diazotization of 4-aminophenol with pentyl nitrite and HCl in abs. EtOH [48].

4-Diazocyclohexa-2,4-dienone (**5**) was prepared by stirring (with a glasscoated magnet [49]) **7** with freshly prepared moist AgO [50]. M.p. 98–99° (dec.; [50]: > 100° (dec.)). (β-^{15}N)-**5** and (β-^{15}N)-**7** were prepared in the same way as the unlabelled compounds.

2.7. *N,N'-Dimethylisoindigo* (= *N,N'-Dimethyl-[3,3'-biindolinylidene]-2,2'-dione;* **8**) *and N,N'-Dimethylisatinazine* (= *N,N'-Dimethyl-3,3'-azinodi-2-indolinone;* **9**) required for TLC comparison with thermolysis products from experiments in HFIP were obtained by thermolysis of **1** in EtOH according to [17].

2.8. *3-(Hexafluoroisopropoxy)-1-methylindolin-2-one* (**10**) was obtained from dediazoniation experiments of **1** in HFIP. Column chromatography of the thermolysis mixture gave a fraction containing **10** as well as **8**. Pure **10** was obtained as a white crystalline solid by prep. TLC on silanised SiO_2 plates with dioxan/hexane 15:85 (R_f 0.42–0.43). M.p. 114–115°. ^{1}H-NMR (90 MHz, $CDCl_3$): 3.18 (*s*, CH_3N); 5.07 (*s*, H–C(3)); 5.48 (*sept.*, $J = 5.4$, $(CF_3)_2CH$); ~ 6.8–7.5 (*m*, 4 arom. H). MS: 313 (M^+), 298, 294, 162, 146, 134, 118, 106, 91, 77.

2.9. *9,9'-Bifluorenylidene* (**13**) was synthesized from fluorene by bromination to 9-bromofluorene [51] followed by formation of **13** with Na(*t*-BuO)/*t*-BuOH under reflux [52]. Yield 51%. M.p. after recrystallization from CCl_4/EtOH 185.0–185.5° ([52]:187–189°).

2.10. *Attempted Preparation of 9-(Fluoroalkoxy)fluorenes from 9-Bromofluorene.* Following the method described [53] for the synthesis of 9-alkoxyfluorenes from 9-bromofluorene and silver salts in alcoholic soln., the preparation of 9-(hexafluoroisopropoxy)fluorene and 9-(trifluoroethoxy)fluorene was examined in analogous reactions in HFIP and TFE, respectively. A soln. of 9-bromofluorene (2.45 g, 10 mmol) in 7 ml of hot benzene was added dropwise to a suspension of 3.75 g (12 mmol) of Ag_2SO_4 in 10 ml of HFIP. The Ag_2SO_4 disappeared during stirring at r.t. (3 days). Another white solid was formed slowly and the soln. became dark blue. The soln. was decolorized by addition of EtOH. After separation of the white precipitate and evaporation of the solvents (EtOH/HFIP), an oily mixture was obtained. Distillation and spectroscopic investigation (^{1}H- and ^{13}C-NMR, MS) gave no indication of the presence of 9-(hexafluoroisopropoxy)fluorene. Similar results were obtained with TFE.

3. Kinetics, Thermolyses, and High Pressure Exchange Experiments.

– All high pressure exchange experiments were run in a steel autoclave with glass vessel inset as described before [5].

Table 8. *Products of Thermolyses of 3-(α-^{15}N)Diazo-1-methylindolin-2-one* (**1**) *in HFIP at 54 ± 2° under* N_2

Run	Quantity of **1**	Pressure	Reaction time	Products [mg]				
	[mg]	[atm]	[h]	**8**[a])	**9**	**10**	**11**	**1**[c])
1	150	1000	96	(40.0)	5.6	[b])	6.3	48.6
2	150	1000	67	(30.8)	13.6	[b])	5.0	61.5
3	150	1000	96	(15.2)	8.6	[b])	2.7	16.7
4	150	800	72	(31.7)	39.0	[b])	3.0	67.0
5	150	1000	96	(38.7)	14.9	[b])	2.0	58.1
6	100	800	72	(17.6)	18.0	[b])	1.7	37.4
7	100	1000	144	12.6	4.5	12.7	2.0	40.8
8	100	1000	264	19.6	2.6	21.0	5.4	48.0
9	100	1000	432	3.6	1.7	16.7	2.3	33.1

[a]) Values in brackets include amount of **10**.

[b]) Amount included in **8**.

[c]) Recovered starting material.

3.1. *Thermolyses of (α-^{15}N)-1 under High Pressure in HFIP.* Details of the experiments including product analyses are summarized in *Table 8*. For all runs, the same new glass-vessel inset was used. Concentration of **1** in HFIP was *ca.* 5 × 10^{-2}M. After thermolysis, the solvent was evaporated and the components of the mixtures separated by column chromatography (50 g of silanised SiO_2 per 100 mg, EtOH-free $CHCl_3$). R_f (silanised SiO_2, EtOH-free $CHCl_3$): **1** 0.47, **8** *ca.* 0.6, **9** 0.2–0.4, **10** *ca.* 0.6, **11** 0.51–0.53, and by-products < 0.2 (depending on the purity of the $CHCl_3$). MS analysis was carried out both on **1** directly (after chromatography) and after $NaBH_4$ reduction of **1** to the hydrazone (see *Exper. 3.4*).

3.2. *Kinetics of Dediazoniations of* **2**. The changes in UV/VIS spectra of **2** in TFE were followed at 23.0 ± 0.5° and 7.14 × 10^{-5}M, 4.64 × 10^{-5}M, and 1.11 × 10^{-3}M. In the two dilute solns., isosbestic points were observed at 252, 276, and 375 nm. At 1.11 × 10^{-3}M, an additional isosbestic point was detectable at 512 nm. The changes in optical density at 345 nm and 450 nm were plotted in the usual way against time. Good first-order constants were obtained over 90% conversion.

3.3. *Preparative Dediazoniation of* **2**. A soln. of **2** (576 mg, 3 mmol) in 78.65 ml of TFE/CH_3CN 58:42, after having bubbled N_2 through for 30 min, was heated at 60° under N_2 for 5 days. Cooling to –30° gave yellowish-red crystals of **13** (309 mg, m.p. 184.0–185.5°). On concentration, an additional 7 mg of **13** were isolated. Prep. TLC (SiO_2/toluene) of the residue of the mother liquor (247 mg) gave a colourless unidentified oil (70 mg), the azine **14** (6 mg), and an orange mixture of **13** and some additional unidentified by-products.

3.4. *Reduction of* **2** *to* **12** *after Dediazoniation.* A soln. of 192 mg (1 mmol) of **2** in 26 ml of TFE/CH_3CN 58:42 was refluxed for 75 min (85°) under N_2. After filtration from **13** (11 mg), the solvent was evaporated. Then, 24.6 mg (0.65 mmol) of $NaBH_4$ and 10 ml of anh. THF were added and the mixture stirred overnight at r.t. The solvent was removed, the mixture extracted with Et_2O, washed with H_2O, and dried over Na_2SO_4. Prep. TLC on SiO_2 with toluene gave 22 mg of **13** (total yield 33 mg (20%)), 42 mg (24%) of **14** and 78 mg (40%) of **12**. In preliminary experiments of this type, it was shown that **2** alone gives **12** in 62% yield and that the azine **14** is not reduced under these conditions.

3.5. *High Pressure Exchange Experiments with* (α,β-^{15}N)-**2** (2.8 to 5.0 × 10^{-3}M) in various solvent mixtures *(Table 2)* at temperatures between 73 and 120° were carried out as described for (α-^{15}N)-**1**. After 30 to 83% of dediazoniation, **12** and **14** for MS analysis were obtained as described for the reduction of **2** to **12**.

3.6. *High Pressure Exchange Experiments with (β-^{15}N)-***3**. The solns. of (β-^{15}N)-**3** (50 to 70 mg) in HFIP (25 to 30 ml) were *ca.* 10^{-2}M. After dediazoniation in the autoclave (conditions, see *Table 4*) the remaining **3** was purified for MS analysis by column chromatography (*ca.* 20 g SiO_2, AcOEt) or prep. TLC (SiO_2, AcOEt) and precipitation of **3** with Et_2O from solns. in CH_3CN.

The half-lives of **3** at the respective temp. *(Table 4)* were estimated by following the decrease of **3** by azo coupling with 2-naphthol [11] and monitoring the absorption maximum at 488 nm (ε = 21,400, CH_3CN, 3 to 7 measurements per temp.). The amount of dediazoniation was determined analogously assuming 100% azo coupling of the remaining **3**.

3.7. *High Pressure Exchange Experiments with (β-^{15}N)-***4** *and (β-^{15}N)-***6**. Since **4** is explosive [10], the known procedure [54] of diazotization of 2-amino-1*H*-imidazole-4,5-dicarbonitrile in H_2O was modified. A suspension of 213 mg (1.6 mmol) of 2-amino-1*H*-imidazole-4,5-dicarbonitrile in 8 ml of TFE (neutralized over Na_2CO_3) and a soln. of 214 mg (1.6 mmol) of pentyl nitrite in 4 ml of neutralized TFE were slowly mixed and stirred for 3 h at 35°. After filtration, a yellow soln. of **4** was obtained.

The yield of **4**, the half-lives at the respective temp. *(Table 5)*, and the amounts of dediazoniation were determined by azo coupling of aliquots of the respective solns. with an excess of 2-naphthol. The stock soln. for azo coupling was obtained from 577 mg (4 mmol) of 2-naphthol, 210 mg (1 mmol) of tetraethylammonium bromide and 50 mg of KOAc in 10 ml of H_2O and 220 ml of CH_3CN. The concentration of 2-(2-hydroxy-1-naphthylazo)-1*H*-imidazole-4,5-dicarbonitrile was determined spectrophotometrically at 476 nm (ε = 14,100).

The azo compound for MS analysis was obtained by coupling of the remaining **4** with an equivalent amount of 2-naphthol, *e.g.* 87 mg (0.6 mmol) and 10 mg of NaOAc in 2.5 ml of CH_3OH, filtration, and drying *in vacuo*. (β-^{15}N)-**4** was obtained from pentyl (^{15}N)nitrite (from $Na^{15}NO_2$ according to [55]).

Experiments with (β-^{15}N)-**6** were performed in an analogous way, by acidifying the TFE solns. of (β-^{15}N)-**4** with the necessary amount of H_2SO_4 *(Table 5)*.

3.8. *Kinetics of Dediazoniations of* **5** *and* **7**. The rates of thermal dediazoniation of **5** in TFE and **7** in TFE acidified with dry HCl were determined by monitoring the decrease in absorption maxima of **5** (λ_{max} 347 nm) and **7** (λ_{max} 312 nm) at 65.0°. The reactions were followed for at least two half-lives, during which time first-order kinetics were obeyed.

3.9. *High-pressure Exchange Experiments with (β-^{15}N)-***5** *and (β-^{15}N)-***7**. The autoclave was pressurized with 1000 atm $^{14}N_2$ and shaken in an oil bath at 65° for all exchange experiments. For reactions with (β-^{15}N)-**7**, dry HCl gas was bubbled through the TFE before use. For MS analysis, 1-(4-hydroxyphenylazo)-2-naphthol was prepared by reaction of **5** or **7** with alkaline 2-naphthol. M.p. 190 – 2° ([56]: 194°).

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