2-Alkyl-1,2,3,4-benzotetrazinium Tetrafluoroborates: Their Reaction with Nucleophiles

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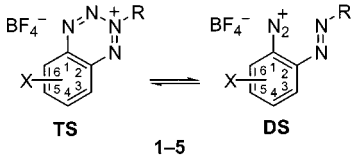
Treatment of 2-alkyl-1,2,3,4-benzotetrazinium tetrafluoroborates with a nucleophile ($AlkO^-$, ArO^-, AcO^-, Hal^-, CN^-, NCO^-, $ArNH_2$, $AlkNH_2$, Alk_2NH), at room temperature, results in elimination of an N_2 molecule to afford *ortho*-substituted azobenzenes. This reaction could be suitable for mild phenylation of carboxylic acids and other compounds containing active hydrogen. A plausible reaction pathway for the reaction is discussed.

Introduction

Aromatic 1,2,3,4-tetrazines are represented in the literature only by annulated compounds,[1] especially triazolo-annulated 1,2,3,4-tetrazine[2] and benzo-annulated 1,2,3,4-tetrazine N^1-oxides.[3] The question of ring-chain tautomerism is of considerable importance in the chemistry of these compounds.[4] It has been disclosed recently that diazonium salts **DS**, which were synthesized by diazotization of *ortho*-(2-alkylazo)anilines, exist in equilibrium with 2-alkyl-1,2,3,4-benzotetrazinium salts **TS** (Table 1).[5]

Table 1. The percentage ratio of the ring-chain tautomers **TS/DS** at 297 K



Compound	R	X	TS/DS
1[a]	*t*Bu	H	50:50
2[a]	*t*Bu	4,6-Br_2	100:0
3[b]	Me	H	ca. 60:40
4[b]	Me	4,6-Br_2	ca. 95:5
5[a]	*t*Bu	5-Br	85:15

[a] In acetone solution. [b] In acetonitrile solution.

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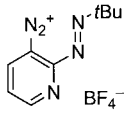
NMR spectroscopic studies demonstrated that this equilibrium is fast on the NMR timescale, and only one set of signals is observed in the ^1H and ^{13}C NMR spectra even at low temperatures (220 K). The equilibrium depends on the nitrogen substituents R and the benzene-ring substituents X. Herein, the reactions of nucleophiles with five typical salts **1**−**5** have been investigated. The **TS/DS** ratios of these salts are shown in Table 1. The salts **6**[5] and **7**,[6] both of which exist only in the open-ring form, were also studied in order to underline the difference in reactivity between the **DS** and **TS** forms.



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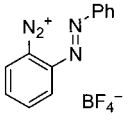

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Results and Discussion

The reaction of salts **1**−**5** with nucleophiles could, a priori, proceed in two main directions: a nucleophile could attack the open-chain form of the salt at the terminal nitrogen atom of the diazonium ion, or the cyclic form could be attacked at the carbon atom of the benzene ring.

O-Nucleophiles

Regardless of the **TS/DS** ratio, salts **1**, **2**, and **5** readily react at room temperature with water, sodium methoxide, sodium acetate, or sodium phenoxide, with evolution of nitrogen, to afford compounds **8a**−**h** (Table 2). The open-ring diazonium salts **6** and **7** do not give the products of N_2 replacement upon reaction with the above-mentioned nucleophiles under the same conditions.[7] Such a high reactivity

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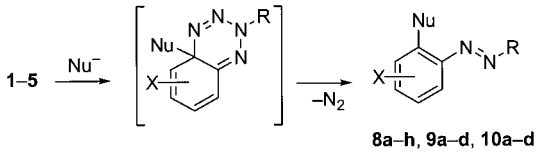
of salts **1**−**5** as compared with ordinary aryldiazonium salts[8] could be due to the fact that the electrophilicity of the C-1 atom in benzotetrazinium salts **TS** is much higher than that of the C-1 atom in aryldiazonium salts **DS**.

Table 2. Reaction of salts **1**−**5** with O-nucleophiles, halogen anions, and the cyanide ion



Starting salt	Reagent[a]	Time [min]	Product	Nu	Yield (%)
1	H_2O[b]	30	**8a**	OH	72
2	H_2O[b]	10	**8b**	OH	79
5	H_2O[b]	15	**8c**	OH	80
1	MeON[c] [d]	5	**8d**	OMe	73
2	MeON[c] [d]	5	**8e**	OMe	92
1	AcONa[c] [e]	15	**8f**	OAc	84
2	AcONa[c] [e]	5	**8g**	OAc	82
2	PhONa[c] [e]	5	**8h**	OPh	89
1	Bu_4NBr[e] [f]	40	**9a**	Br	40
2	NaCl[f] [g]	60	**9b**	Cl	43
2	NaBr[f] [g]	30	**9c**	Br	52
2	Bu_4NBr[e] [f]	10	**9c**	Br	64
2	Bu_4NF[e] [f]	30	**9d**	F	89
1	NaCN[e] [f]	45	**10a**	CN	62
2	NaCN[e] [f]	10	**10b**	CN	65
3	NaCN[e] [f]	30	**10c**	CN	68
4	NaCN[e] [f]	10	**10d**	CN	70

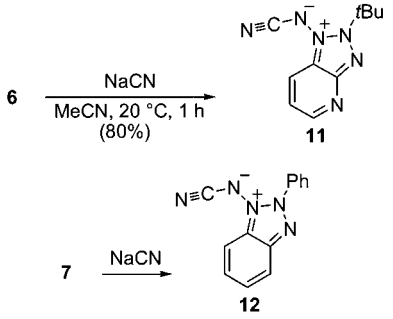
[a] At 20 °C. [b] 20 % H_2O in MeCN. [c] 1 equiv. of reagent. [d] Solvent: MeOH. [e] Solvent: MeCN. [f] 5 equiv. of reagent. [g] Solvent: acetone.

Halogen Anions (F^-, Cl^-, Br^-)

The reaction of salts **1** and **2** with halogen anions also proceeded with evolution of nitrogen. The reaction of salt **1** with NaBr proceeded very slowly in acetone or acetonitrile solution to give **9a**, whereas the more reactive salt **2** easily afforded compounds **9b** and **9c** upon reaction with NaCl and NaBr, respectively (Table 2). The reactions of salts **1** and **2** with Bu_4NBr are faster than with NaBr. The reaction of salt **2** with NaF failed due to the low solubility of the latter. However, with Bu_4NF the replacement of nitrogen proceeded easily to afford **9d**. The diazonium salts **6** and **7**, as well as the ordinary aryldiazonium salts,[9,10] failed to react with Bu_4NBr or with Bu_4NF under these reaction conditions.

Cyanide Ion

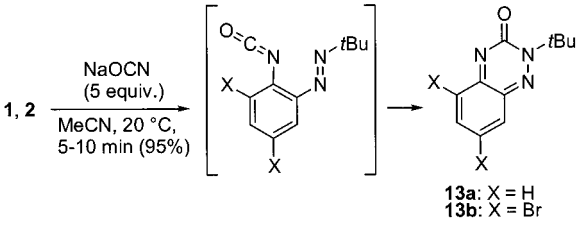
The reaction of salts **1**−**4** with NaCN also proceeded with the evolution of nitrogen to give products **10a**−**d** (Table 2). The diazonium salts **6** and **7** react as ordinary aryldiazonium salts — the cyanide ion attacks the terminal atoms of the diazonium ions, and subsequent cyclizations afford the triazole derivatives **11** and **12**, respectively (Scheme 1). For the salt **7**, this reaction was described by Katritzky and coworkers already in 1964.[6]



Scheme 1

Isocyanate Anion

The reaction of salts **1** and **2** with NaOCN resulted in 1,2,4-triazine derivatives **13a**,**b** by the intermediate formation of the aryl isocyanates (Scheme 2).[11] Ordinary aryldiazonium salts afforded aryl isocyanates only when the reaction with NaOCN was performed in the presence of copper or copper salts.[12]

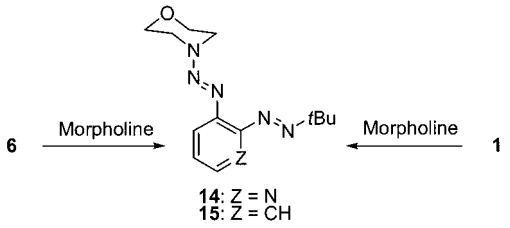


Scheme 2

The cyclic structure of 1,2,4-triazolones **13a**,**b** was confirmed by the lack of an absorption band due to the isocyanate group in the 2000−2200 cm^{-1} region of the IR spectra, the typical high-field signal of the nitrogen atom connected to a *tert*-butyl group in the ^{15}N NMR spectrum (**13a**: $\delta_N = -138.0$ ppm for N-2),[13] and the low-field signal of the *tert*-butyl group in the ^1H and ^{13}C NMR spectra [**13a**: $\delta_H = 1.81$ and $\delta_C = 69.1$ (CMe_3)].

Amines

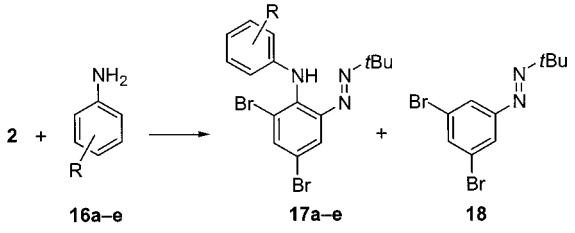
The reactions of salts **1**−**5** with amines depend on the nature of the salt and the amine. The open-chain pyridodiazonium salt **6** reacts with morpholine, as expected, to afford triazene **14**. Salt **1**, containing about 50 % of the ring form, reacts similarly to afford only triazene **15** (Scheme 3). Evolution of N_2 was not observed in this case.



Scheme 3

Interaction of the more reactive salt **2** with amines was more complicated. Aromatic amines **16a**–**e** replaced the N_2 molecule to afford compounds **17a**–**e** (Table 3). The reaction took place not only with the parent aniline, but also with substituted anilines bearing electron-withdrawing groups. For example, 4-chloroaniline (**16b**) and 2,4-dichloroaniline (**16c**) gave compounds **17b** and **17c**, respectively.

Table 3. Reaction of salt **2** with anilines



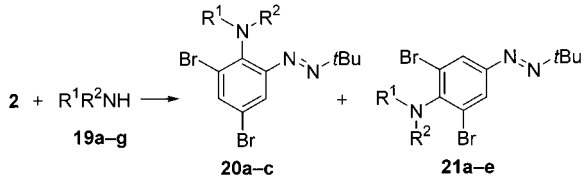
Aniline[a]	R	Time [min]	Yield of **17a**–**e** (%)	Yield of **18** (%)
16a	H	10	**17a**: 97	0
16b[b]	4-Cl	15	**17b**: 66	0
16c	2,4-Cl_2	30	**17c**: 49	0
16d	4-Me	10	**17d**: 42	11
16e	4-OMe	5	**17e**: 0	65

[a] 5 equiv. of anilines **16**, CH_2Cl_2, 20 °C. [b] 2 equiv. of aniline **16b**.

With anilines bearing electron-releasing substituents, for example *p*-toluidine (**16d**), the reaction of salt **2** proceeds in two directions. The first one is reduction to give compound **18** and the second one is substitution to give **17d**. With *p*-anisidine (**16e**), only reduction took place. It is likely that the first stage of the reduction involves electron transfer from the amine to the tetrazinium salt, followed by elimination of N_2.

The reaction of salt **2** with aliphatic sterically hindered secondary amines such as Pr_2NH and iPr_2NH resulted in the substitution of N_2 to give products **20a** and **20b**, respectively (Table 4). The reaction with primary amines ($MeNH_2$, $iPrNH_2$) and secondary amines (Me_2NH, morpholine) afforded products of type **21**. The latter were readily distinguished from isomers **20** by NMR spectroscopy due to their symmetrical structure. The reaction with sterically hindered $tBuNH_2$ resulted in the products of both types, with a **20c**/**21a** ratio of about 3:4.

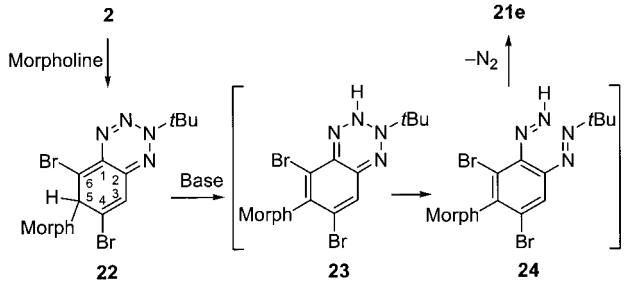
Table 4. Reaction of **2** with aliphatic amines



Amine[a]	R^1 and R^2	Time [min]	Product	Yield (%)
19a	$R^1 = R^2 =$ Pr	30	**20a**	65
19b	$R^1 = R^2 = i$Pr	30	**20b**	75
19c	$R^1 = t$Bu, R^2 = H	30	**20c**	35
			21a	44
19d	R^1 = Me, R^2 = H	10	**21b**	60
19e	$R^1 = i$Pr, R^2 = H	20	**21c**	81
19f	$R^1 = R^2$ = Me	15	**21d**	75
19g	R^1R^2N = morpholino	15	**21e**	76

[a] Reagents and conditions: 5 equiv. of amine, CH_2Cl_2, 20 °C.

The formation of compounds of type **21** can be rationalized by proposing that the amine initially attacks salt **2** at the C-5 position of the benzene ring to give intermediate **22** (Scheme 4). This compound was observed in solution when salt **2** was treated with 2 equiv. of morpholine; its structure was confirmed by NMR spectroscopy. The C-5 signal of **22** appears in the aliphatic region at δ_C = 73.3 ppm [$^1J(^1H,^{13}C)$ = 144.3 Hz], and the signal of the nitrogen atom connected to the *tert*-butyl group appears at δ_N = −135.4 ppm in the ^{15}N NMR spectrum, as expected. Unfortunately, we failed to isolate **22** in a pure state due to its decomposition upon concentrating the solution.



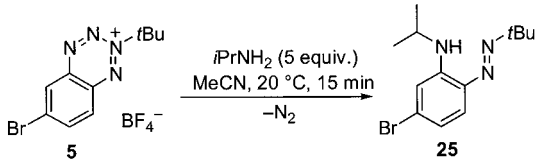
Scheme 4

When a CCl_4 solution of **22** (0.023 mmol/mL) was allowed to stand at 20 °C for 30 min, **21e** was obtained in 44 % yield (Scheme 4) along with other, tarry products.

The conversion of **22** to **21e** proceeded rapidly, with high yield, when an excess of morpholine or another organic base was added (e.g., Et_3N or $tBuNH_2$). It is likely that a base is required for transfer of the proton from C-5 to nitrogen to give the intermediate **23**, which could readily ring-

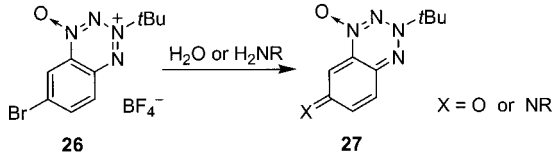
open to afford the azo compound **24**, followed by evolution of nitrogen.[14]

It is interesting to note that salt **5**, bearing a bromine atom in the 5-position of the benzene ring, reacts with isopropylamine, with the evolution of nitrogen, to give **25**, but the bromine atom is not replaced (Scheme 5). The hydrolysis of salt **5** also proceeds with the evolution of nitrogen to afford **8c** (see Table 2).



Scheme 5

The closely related 1,2,3,4-benzotetrazinium N^4-oxide **26** reacts with water[3] or primary amines[15] in another way — replacement of bromine to give the quinoid structures **27** (Scheme 6).



Scheme 6

It is possible that such a great difference in the reactivities of the related compounds **5** and **26** is due to the higher thermodynamic stability of the N_2 molecule, which is liberated in the course of the reaction, as compared with the N_2O molecule; this results in a lower activation barrier in case of salt **5**.

In conclusion, we propose that the reaction of 2-alkyl-1,2,3,4-benzotetrazinium salts with nucleophiles could be suitable for mild phenylation of carboxylic acids and other compounds containing active hydrogen. The products of this reaction could also serve as precursors for annulated heterocycles.

Experimental Section

General Remarks: Mass spectra were recorded at 70 eV using the electron-impact technique. Melting points were determined with a Kofler apparatus and are uncorrected. NMR spectra were recorded with an AM 300 Bruker spectrometer (300.13 MHz for ^{1}H, 75.47 MHz for ^{13}C, 21.69 MHz for ^{14}N, and 30.42 MHz for ^{15}N); chemical shifts are quoted in δ units downfield from internal TMS (^{1}H, ^{13}C) or external CH_3NO_2 (^{14}N, ^{15}N). Negative values of δ_N correspond to upfield shifts. The assignments of the ^{1}H and ^{13}C NMR signals were made by experiments without proton decoupling (for **8a**, **8e**, **8**, **18**, **21e**, **22**) and CH COSY (**8a**, **8c**, **8d**, **8f**, **8h**, **13a**, **17a**), HH COSY (**8f**), SPT (**8d**, **8f**, **8**, **9a**, **9c**, **9d**, **10a**, **10b**, **21b**), NOE-difference (**8d**), and selective decoupling experiments (**8e**, **8**, **13b**).

4,6-Dibromo-2-(*tert*-butylazo)benzenediazonium Tetrafluoroborate (2):[5,16] ^{1}H NMR at 297 K ([D$_6$]acetone): δ = 2.16 (s, 9 H, 3 CH_3, *t*Bu), 9.44 (d, *J* = 2.1 Hz, 1 H, 3-H), 9.56 (d, *J* = 2.1 Hz, 1 H, 5-H) ppm. ^{13}C NMR at 297 K ([D$_6$]acetone): δ = 29.4 (CH_3), 82.9 (*C*Me$_3$), 126.4 (C-2), 132.8 (C-3), 135.0 (C-6), 139.6 (C-4), 141.1 (C-1), 152.0 (C-5) ppm. The ^{1}H and ^{13}C signals remained unchanged when cooling the sample to 263 K.

4,6-Dibromo-2-(methylazo)benzenediazonium Tetrafluoroborate (4):[5,16] ^{1}H NMR at 297 K (at, 273 K in parentheses) (CD_3CN): δ = 5.25 (5.30) (s, 3 H, CH_3), 9.01 (9.05) (d, *J* = 1.5 Hz, 1 H, 3-H), 9.25 (9.29) (d, *J* = 1.5 Hz, 1 H, 5-H) ppm. ^{13}C NMR at 297 K (at 263 K in parentheses) (CD_3CN): δ = 56.1 (56.0) (CH_3), 127.0 (126.8) (C-2), 132.4 (132.5) (C-3), 140.8 (141.0) (C-4), 152.8 (153.3) (C-5) ppm. The ^{13}C NMR signals remained unchanged when cooling the sample from 263 to 253 K.

2-[(*tert*-Butyl)azo]phenol (8a): A solution of salt **1** (200 mg, 0.73 mmol) in 10 mL of CH_3CN and 2 mL of H_2O was stirred at room temperature for 30 min. The solvents were then removed in vacuo. The residue was purified by chromatography (silica gel; benzene) to yield 93 mg (72 %) of **8a** as a yellow oil. IR (KBr): $\tilde{\nu}$ = 3590 (OH) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.35 (s, 9 H, 3 CH_3, *t*Bu), 6.96 (m, 2 H, 4-H and 6-H), 7.23 (dt, *J* = 7.2, 1.7 Hz, 1 H, 5-H), 7.82 (dd, *J* = 8.0, 1.7 Hz, 1 H, 3-H), 12.7 (s, 1 H, OH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 27.1 (CH_3), 66.8 (*C*Me$_3$), 117.9 (ddd, *J* = 158.3, 11.8, 4.6 Hz, C-6), 119.1 (dddd, *J* = 161.1, 11.1, 5.1, 4.2 Hz, C-4), 132.1 (dddd, *J* = 160.3, 10.0, 6.0, 4.8 Hz, C-5), 132.4 (ddd, *J* = 156.1, 10.4, 6.6 Hz, C-3), 135.9 (br.s, C-2), 152.5 (dd, *J* = 11.2, 5.6 Hz, C-1) ppm. MS (70 eV), *m*/*z*: 178 [M$^+$]. $C_{10}H_{14}N_2O$ (178.23): calcd. C 67.39, H 7.92, N 15.72; found C 67.45, H 7.93, N 15.60.

2,4-Dibromo-6-[(*tert*-butyl)azo]phenol (8b): The reaction of salt **2** (50 mg, 0.12 mmol) with water (5 mL MeCN and 1 mL of H_2O) was carried out as described above to give, after 10 min of stirring, 32 mg (79 %) of **8b** as a yellow oil. IR (KBr): $\tilde{\nu}$ = 3600 (OH) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.40 (s, 9 H, 3 CH_3, *t*Bu), 7.63 (d, *J* = 2.7 Hz, 1 H), 7.95 (d, *J* = 2.7 Hz, 1 H), 13.65 (s, 1 H, OH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 27.1 (CH_3), 67.6 (*C*Me$_3$), 110.3 (C-2 or C-4), 112.0 (C-4 or C-2), 134.0 (C-3 or C-5), 136.0 (C-6), 137.0 (C-5 or C-3), 149.2 (C-1) ppm. ^{15}N NMR/INEPT (30 MHz, $CDCl_3$): δ = 116.0 (N*t*Bu) ppm. MS (70 eV), *m*/*z* (rel. intensities): 334, 336, 338 (1:2:1) [M$^+$]. $C_{10}H_{12}Br_2N_2O$ (336.02): calcd. C 35.74, H 3.60, Br 47.56, N 8.34; found C 35.78, H 3.59, Br 47.42, N 8.28.

5-Bromo-2-[(*tert*-butyl)azo]phenol (8c): The reaction of salt **5** (43 mg, 0.12 mmol) with water (5 mL MeCN and 1 mL of H_2O) was carried out as described above to give, after 15 min of stirring and chromatographic purification (silica gel; $CHCl_3$), 25 mg (80 %) of **8c** as an orange oil. IR (KBr): $\tilde{\nu}$ = 3610 (OH) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.35 (s, 9 H, 3 CH_3, *t*Bu), 7.14 (dd, *J* = 8.2, 1.8 Hz, 1 H, 4-H), 7.18 (d, *J* = 1.8 Hz, 1 H, 6-H), 7.75 (d, *J* = 8.2 Hz, 1 H, 3-H), 12.4 (s, 1 H, OH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 26.8 (CH_3), 67.8 (*C*Me$_3$), 121.1 (C-6), 122.7 (C-4), 126.0 (C-5), 134.6 (C-3), 135.1 (C-2), 155.8 (C-1) ppm. MS (70 eV), *m*/*z* (rel. intensities): 256, 258 (1:1) [M$^+$]. $C_{10}H_{13}BrN_2O$ (257.13): calcd. C 46.71, H 5.10, Br 31.08, N 10.89; found C 46.63, H 5.09, Br 31.01, N 10.79.

1-(*tert*-Butyl)-2-(2-methoxyphenyl)diazene (8d): A solution of sodium methoxide in CH_3OH (1.0 mL of 1.15 mmol/mL solution, 1.15 mmol) was added to a stirred solution of salt **1** (300 mg, 1.08 mmol) in 5 mL of dry CH_3OH. After 5 min of stirring at room temperature, the solvent was evaporated in vacuo and the residue

chromatographed (silica gel; $CHCl_3$) to yield 150 mg (73 %) of **8d** as an orange oil. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.36 (s, 9 H, 3 CH_3, *t*Bu), 3.69 (s, 3 H, CH_3), 6.92 (d, *J* = 7.9 Hz, 3-H), 6.95 (t, *J* = 7.9 Hz, 5-H), 7.23 (dd, *J* = 7.9, 1.7 Hz, 6-H), 7.30 (dt, *J* = 7.9, 1.7 Hz, 4-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 26.7 (CH_3), 56.2 (OMe), 68.0 (*C*Me_3), 112.5 (C-3), 117.2 (C-6), 120.6 (C-5), 130.7 (C-4), 142.3 (C-1), 155.3 (C-2) ppm. ^{15}N NMR/INEPT (30 MHz, $CDCl_3$): δ = 120.3 (NAr), 168.4 (N*t*Bu) ppm. MS (70 eV), *m*/*z*: 192 [M^+]. $C_{11}H_{16}N_2O$ (192.26): calcd. C 68.72, H 8.39, N 14.57; found C 68.56, H 8.36, N 14.62.

1-(*tert*-Butyl)-2-(3,5-dibromo-2-methoxyphenyl)diazene (8e): The reaction of salt **2** (50 mg, 0.12 mmol) with sodium methoxide was carried out as described above to give, after chromatographic purification (silica gel; benzene), 39 mg (92 %) of **8e** as an orange oil. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.36 (s, 9 H, 3 CH_3, *t*Bu), 4.01 (s, 3 H, OMe), 7.43 (d, *J* = 2.3 Hz, 1 H, 6-H), 7.79 (d, *J* = 2.3 Hz, 1 H, 4-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 63.4 (OCH_3), 69.6 (*C*Me_3), 116.9 (t, *J* = 4.3 Hz, C-5), 119.4 (dd, *J* = 4.3, 1.5 Hz, C-3), 120.6 (dd, *J* = 170.3, 6.4 Hz, C-6), 136.7 (dd, *J* = 172.8, 6.8 Hz, C-4), 146.9 (t, *J* = 2.2 Hz, C-1), 154.0 (m, C-2) ppm. ^{15}N NMR/INEPT (30 MHz, $CDCl_3$): δ = 186.0 (N*t*Bu) ppm. MS (70 eV), *m*/*z* (rel. intensities): 348, 350, 352 (1:2:1) [M^+]. $C_{11}H_{14}Br_2N_2O$ (350.05): calcd. C 37.74, H 4.03, Br 45.65, N 8.00; found C 37.79, H 4.01, Br 45.72, N 7.94.

General Procedure for the Reaction of Salts 1 and 2 with NaOAc: NaOAc was added at room temperature to a stirred solution of 0.54 mmol of salt **1** or **2** in 5 mL of dry CH_3CN, (45 mg, 0.54 mmol). After the reaction had reached completion (TLC control), the solution was concentrated to dryness and extracted with hexane. The solvent was removed in vacuo and the residue was purified by chromatography (silica gel, $CHCl_3$).

2-[(*tert*-Butyl)azo]phenyl Acetate (8f): According to the general procedure salt **1**, after 15 min of stirring, gave 110 mg (84 %) of **8f** as an orange oil. IR (KBr): $\tilde{\nu}$ = 1760 (C=O) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.31 (s, 9 H, 3 CH_3, *t*Bu), 2.29 (s, 3 H, $COCH_3$), 7.15 (dd, *J* = 8.0, 1.7 Hz, 1 H, 6-H), 7.25 (dt, *J* = 7.8, 1.7 Hz, 1 H, 5-H), 7.38 (dt, *J* = 8.0, 1.7 Hz, 1 H, 4-H), 7.48 (dd, *J* = 7.8, 1.7 Hz, 1 H, 3-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.5 (CO*CH*$_3$), 26.9 (CH_3), 68.5 (*C*Me_3), 117.6 (C-3), 122.8 (C-6), 126.5 (C-5), 131.0 (C-4), 143.3 (C-2), 147.9 (C-1), 169.2 (*C*OCH_3) ppm. ^{15}N NMR/INEPT (30 MHz, $CDCl_3$): δ = 116.0 (NAr), 174.0 (N*t*Bu) ppm. MS (70 eV), *m*/*z*: 220 [M^+]. $C_{12}H_{16}N_2O_2$ (220.27): calcd. C 65.43, H 7.32, N 12.72; found C 65.48, H 7.34, N 12.59.

2,4-Dibromo-6-[(*tert*-butyl)azo]phenyl Acetate (8): According to the general procedure salt **2**, after 5 min of stirring, gave 180 mg (82 %) of **8** as a yellow oil. IR (KBr): $\tilde{\nu}$ = 1750 (C=O) cm^{-1}. ^1H NMR (300 MHz, [D_6]acetone): δ = 1.30 (s, 9 H, 3 CH_3, *t*Bu), 2.35 (s, 3 H, $COCH_3$), 7.56 (d, *J* = 2.3 Hz, 1 H, 5-H), 7.90 (d, *J* = 2.3 Hz, 1 H, 3-H) ppm. ^{13}C NMR (75 MHz, [D_6]acetone): δ = 20.1 (CO*CH*$_3$), 26.6 (CH_3), 69.7 (*C*Me_3), 118.8 (dd, *J* = 4.0, 1.5 Hz, C-2), 119.9 (t, *J* = 4.4 Hz, C-4), 120.3 (dd, *J* = 172.0, 6.5 Hz, C-5), 136.6 (dd, *J* = 174.0, 6.8 Hz, C-3), 145.7 (s, C-6), 145.8 (t, *J* = 8.0 Hz, C-1), 167.7 (q, *J* = 7.0 Hz, *C*OCH_3) ppm. ^{15}N NMR/INEPT (30 MHz, [D_6]acetone): δ = 113.2 (NAr), 185.6 (N*t*Bu) ppm. MS (70 eV), *m*/*z* (rel. intensities): 376, 378, 380 (1:2:1) [M^+]. $C_{12}H_{14}Br_2N_2O_2$ (378.06): calcd. C 38.12, H 3.73, Br 42.27, N 7.41; found C 38.05, H 3.74, Br 42.37, N 7.29.

1-(*tert*-Butyl)-2-(3,5-dibromo-2-phenoxyphenyl)diazene (8h): NaOPh (14 mg, 0.12 mmol) was added to a stirred solution of salt **2** (50 mg, 0.12 mmol) in 5 mL of dry CH_3CN. After 5 min of stirring at room temperature, the solvent was evaporated and the residue purified by chromatography (silica gel; benzene) to yield 45 mg (89 %) of **8h** as a yellow oil. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.05 (s, 9 H, 3 CH_3, *t*Bu), 6.79 (d, *J* = 8.1 Hz, 2 H, H_o, C_6H_5), 6.96 (t, *J* = 8.2 Hz, 1 H, H_p, C_6H_5), 7.20 (t, *J* = 7.4 Hz, 2 H, H_m, C_6H_5), 7.40 (d, *J* = 2.1 Hz, 1 H, 6-H), 7.81 (d, *J* = 2.1 Hz, 1 H, 4-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 26.5 (CH_3), 69.4 (*C*Me_3), 115.7 (C_o, Ph), 118.6 (C-3), 119.2 (C-5), 120.2 (C-6), 122.2 (C_p, Ph), 129.4 (C_m, Ph), 136.4 (C-4), 158.9 ppm. MS (70 eV), *m*/*z* (rel. intensities): 410, 412, 414 (1:2:1) [M^+]. $C_{16}H_{16}Br_2N_2O$ (412.12): calcd. C 46.63, H 3.91, Br 38.78, N 6.80; found C 46.68, H 3.91, Br 38.71, N 6.75.

Attempt to Hydrolyse 2-(Phenylazo)phenyldiazonium Tetrafluoroborate 7. Experiment 1: A solution of salt **7** (50 mg, 0.17 mmol) in 7 mL of CH_3CN and 1.5 mL of H_2O was stirred at room temperature for 24 h. The solvent was evaporated and the residue washed with Et_2O to give 48 mg (96 %) of unchanged salt **7**. **Experiment 2:** A solution of NaOH (34 mg, 0.85 mmol) in 1.5 mL of H_2O was added to a solution of salt **7** (50 mg, 0.17 mmol) in 7 mL of CH_3CN. After 30 min of reflux, the solvent was evaporated. The residue was purified by chromatography (silica gel; benzene) to give 30 mg (90 %) of 2-(phenylazo)phenol as an orange solid, m.p. 82−84 °C (ref.[17] m.p. 82.5−83 °C).

Reactions of 2-Alkyl-1,2,3,4-benzotetrazinium Tetrafluoroborates 1−4 with Halide and Cyanide Ions. General Procedure: The appropriate reagent (0.6 mmol) was added to a stirred solution containing 0.12 mmol of salts **1**−**4** in 5 mL of dry CH_3CN or acetone (see Table 2). After the reaction had reached completion (TLC control), the precipitate of inorganic salts was filtered off and the solvent evaporated. The residue was purified by chromatography [silica gel; hexane (for **10d**: hexane/EtOAc, 7:1)] to afford **9a**−**d** and **10a**−**d** (see Table 2).

1-(2-Bromophenyl)-2-(*tert*-butyl)diazene (9a): Orange oil. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.39 (s, 9 H, 3 CH_3, *t*Bu), 7.24 (m, 2 H, 3-H and 5-H), 7.31 (dt, *J* = 6.8, 1.6 Hz, 1 H, 4-H), 7.66 (dd, *J* = 6.7, 1.6 Hz, 1 H, 6-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 27.0 (CH_3), 69.1 (*C*Me_3), 118.0 (C-6), 123.8 (C-2), 127.6 (C-5), 130.7 (C-4), 133.2 (C-3), 149.8 (C-1) ppm. MS (70 eV), *m*/*z* (rel. intensities): 240, 242 (1:1) [M^+]. $C_{10}H_{13}BrN_2$ (241.13): calcd. C 49.81, H 5.43, Br 33.14, N 11.62; found C 49.75, H 5.43, Br 33.22, N 11.67.

1-(3,5-Dibromo-2-chlorophenyl)-2-(*tert*-butyl)diazene (9b): Orange oil. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.34 (s, 9 H, 3 CH_3, *t*Bu), 7.34 (d, *J* = 2.1 Hz, 1 H, 6-H), 7.81 (d, *J* = 2.1 Hz, 1 H, 4-H) ppm. MS (70 eV), *m*/*z* (rel. intensities): 352, 354, 356, 358 (2:5:4:1) [M^+]. $C_{10}H_{11}Br_2ClN_2$ (354.47): calcd. C 33.88, H 3.13, Br 45.08, Cl 10.00, N 7.90; found C 33.93, H 3.13, Br+Cl 55.16, N 7.79.

1-(2,3,5-Tribromophenyl)-2-(*tert*-butyl)diazene (9c): Orange oil. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.38 (s, 9 H, 3 CH_3, *t*Bu), 7.28 (d, *J* = 2.2 Hz, 1 H, 6-H), 7.80 (d, *J* = 2.2 Hz, 1 H, 4-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 29.7 (CH_3), 69.8 (*C*Me_3), 120.0 (C-6), 124.3 (C-2), 126.9 (C-5), 135.9 (C-4), 137.2 (C-3), 158.6 (C-1) ppm. MS (70 eV), *m*/*z* (rel. intensities): 395, 397, 399, 401, 403 (1:3:5:3:1) [M^+]. $C_{10}H_{11}Br_3N_2$ (398.92): calcd. C 30.11, H 2.78, Br 60.09, N 7.02; found C 30.01, H 2.77, Br 60.01, N 6.99.

1-(3,5-Dibromo-2-fluorophenyl)-2-(*tert*-butyl)diazene (9d): Orange oil. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.36 (s, 9 H, 3 CH_3, *t*Bu), 7.48 (d, *J* = 6.4, 2.1 Hz, 1 H, 6-H), 7.73 (d, *J* = 5.9, 2.1 Hz, 1 H, 4-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 28.9 (CH_3), 69.8 (*C*Me_3), 111.2 (C-3, $J_{^{13}C^{19}F}$ = 21.1 Hz), 117.1 (C-5, $J_{^{13}C^{19}F}$ = 4.7 Hz), 120.1 (C-6, $J_{^{13}C^{19}F}$ = 7.1 Hz), 136.3 (C-4, $J_{^{13}C^{19}F}$ = 7.2 Hz), 141.1 (C-1, $J_{^{13}C^{19}F}$ = 10.5 Hz), 154.9 (C-2, $J_{^{13}C^{19}F}$ = 256.8 Hz) ppm. MS (70 eV), *m*/*z* (rel. intensities): 336, 338, 340 (1:2:1) [M^+].

$C_{10}H_{11}Br_2FN_2$ (338.01): calcd. C 35.53, H 3.28, Br 47.28, F 5.62, N 8.29; found C 35.59, H 3.27, Br + F 52.76, N 8.32.

2-[(*tert*-Butyl)azo]benzonitrile (10a): Orange oil. IR (KBr): $\tilde{\nu}$ = 2270 (CN) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.39 (s, 9 H, 3 CH_3, *t*Bu), 7.36−7.46 (m, 2 H, 4-H and 6-H), 7.80 (t, *J* = 8.2 Hz, 1 H, 5-H), 8.04 (d, *J* = 8.7 Hz, 1 H, 3-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 26.6 (CH_3), 69.8 (*C*Me_3), 114.0 (CN), 115.3 (C-1), 116.8 (C-3), 118.5 (C-6), 130.0 (C-5), 131.6 (C-4), 143.7 (C-2) ppm. MS (70 eV), *m*/*z*: 187 [M^+]. $C_{11}H_{13}N_3$ (187.24): calcd. C 70.56, H 7.00, N 22.44; found C 70.62, H 6.98, N 22.16.

2,4-Dibromo-6-[(*tert*-butyl)azo]benzonitrile (10b): Yellow oil. IR (KBr): $\tilde{\nu}$ = 2240 (CN) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.41 (s, 9 H, 3 CH_3, *t*Bu), 7.62 (d, *J* = 2.0 Hz, 1 H, 5-H), 7.89 (d, *J* = 2.0 Hz, 1 H, 3-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 26.8 (CH_3), 70.7 (*C*Me_3), 113.8 (CN), 114.1 (C-1), 119.6 (C-5), 125.4 (C-2), 126.6 (C-4), 136.1 (C-3), 155.0 (C-6) ppm. MS (70 eV), *m*/*z* (rel. intensities): 343, 345, 347 (1:2:1) [M^+]. $C_{11}H_{11}Br_2N_3$ (345.03): calcd. C 38.29, H 3.21, Br 46.32, N 12.18; found C 38.34, H 3.23, Br 46.24, N 12.21.

2-(Methylazo)benzonitrile (10c): Orange oil. IR (KBr): $\tilde{\nu}$ = 2240 (CN) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 4.12 (s, 3 H, CH_3), 7.45 (m, 2 H, 4-H and 6-H), 7.78 (d, *J* = 8.1 Hz, 1 H, 3-H), 8.07 (t, *J* = 8.6 Hz, 1 H, 5-H) ppm. MS (70 eV), *m*/*z*: 145 [M^+]. $C_8H_7N_3$ (145.16): calcd. C 66.19, H 4.86, N 28.95; found C 66.24, H 4.85, N 29.91.

2,4-Dibromo-6-(methylazo)benzonitrile (10d): Orange oil. IR (KBr): $\tilde{\nu}$ = 2260 (CN) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 4.14 (s, 3 H, CH_3), 7.63 (d, *J* = 1.9 Hz, 1 H, 5-H), 7.90 (d, *J* = 1.9 Hz, 1 H, 3-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 57.0 (CH_3), 120.1 (C-5), 136.2 (C-3) ppm. MS (70 eV), *m*/*z* (rel. intensities): 301, 303, 305 (1:2:1) [M^+]. $C_8H_5Br_2N_3$ (302.95): calcd. C 31.72, H 1.66, Br 52.75, N 13.87; found C 31.75, H 1.66, Br 52.66, N 13.93.

2-(*tert*-Butyl)-2*H*-[1,2,3]triazolo[4,5-*b*]pyridin-1-cyanoimide (11): NaCN (43 mg, 0.87 mmol) was added to a solution of **6** (50 mg, 0.175 mmol) in 5 mL of dry CH_3CN. After stirring for 20 min at room temperature, the precipitate of inorganic salts was filtered off and the solvent evaporated. The residue was extracted with EtOAc, and the organic layer washed with H_2O and dried ($MgSO_4$). The solvent was evaporated and the residue purified by chromatography (silica gel; EtOAc) to give 32 mg (80 %) of **11** as a red solid, m.p. 155−158 °C (decomp.). IR (KBr): $\tilde{\nu}$ = 2210 (CN) cm^{-1}. ^1H NMR (300 MHz, [D_6]DMSO): δ = 2.11 (s, 9 H, 3 CH_3, *t*Bu), 7.33 (dd, *J* = 8.1, 4.4 Hz, 1 H, 6-H), 7.97 (dd, *J* = 4.4, 1.5 Hz, 1 H, 5-H), 8.48 (dd, *J* = 8.1, 1.5 Hz, 1 H, 7-H) ppm. MS (70 eV), *m*/*z*: 216 [M^+]. $C_{10}H_{12}N_6$ (216.24): calcd. C 55.54, H 5.59, N 38.86; found C 55.59; H 5.60; N 38.71.

General Procedure for the Reaction of Benzotetrazinium Salts 1 and 2 with Sodium Isocyanate: NaNCO (39 mg, 0.6 mmol) was added to a stirred solution of 0.12 mmol of salt **1** or **2** in 5 mL of dry CH_3CN. The stirring was continued for 5−10 min (TLC control) and then the precipitate of inorganic salts was filtered off and the solvent evaporated. The residue was purified by chromatography (silica gel; benzene) to afford **13a** or **13b**, respectively

2-(*tert*-Butyl)-1,2,4-benzotriazin-3(2*H*)-one (13a): Brown solid, m.p. 110−112 °C. IR (KBr): $\tilde{\nu}$ = 1870 (C=O) cm^{-1}. ^1H NMR (300 MHz, [D_6]acetone): δ = 1.81 (s, 9 H, 3 CH_3, *t*Bu), 7.34 (dd, *J* = 9.0, 1.3 Hz, 1 H, 5-H), 7.34 (ddd, *J* = 9.2, 6.5, 1.3 Hz, 1 H, 7-H), 7.68 (dd, *J* = 9.2, 1.3 Hz, 1 H, 8-H), 7.75 (ddd, *J* = 9.0, 6.5, 1.3 Hz, 1 H, 6-H) ppm. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.83 (s, 9 H, 3 CH_3, *t*Bu), 7.30 (ddd, *J* = 8.7, 6.4, 1.1 Hz, 1 H, 7-H), 7.43 (d, *J* = 9.0 Hz, 1 H, 5-H), 7.68 (m, 2 H, 6-H, 8-H) ppm. ^{13}C NMR (75 MHz, [D_6]acetone): δ = 27.4 (CH_3), 69.1 (*C*Me_3), 126.8 (dd, *J* = 165.0, 9.0 Hz, C-7 or C-8), 126.9 (dd, *J* = 167.3, 9.0 Hz, C-8 or C-7), 129.8 (ddt, *J* = 166.2, 7.3, 1.5 Hz, C-5), 136.1 (dd, $^3J_{7\text{-H}}$ = 10.7, $^3J_{5\text{-H}}$ = 5.5 Hz, C-8a), 139.1 (ddd, *J* = 161.0, 10.6, 2.0 Hz, C-6), 153.6 (s, C-3), 153.7 (dd, $^3J_{6\text{-H}}$ = 10.3, $^3J_{8\text{-H}}$ = 5.0 Hz, C-4a) ppm. ^{15}N NMR/INEPT (30 MHz, [D_6]acetone): δ = −138.0 (N*t*Bu) ppm. ^{15}N NMR/SPT from 5-H (30 MHz, [D_6]acetone): δ = −108.4 (d, *J* = 1.3 Hz, N-4) ppm. ^{15}N NMR (30 MHz, [D_6]acetone): δ = −138.2 (m, N-2), −108.4 (d, *J* = 1.3 Hz, N-4), 2.8 (d, *J* = 0.8 Hz, N-1) ppm. ^{14}N NMR (21 MHz, [D_6]acetone): δ = −140 ($\Delta\nu_{1/2}$ = 2000 Hz) (N-2) ppm. MS (70 eV), *m*/*z*: 203 [M^+]. $C_{11}H_{13}N_3O$ (203.24): calcd. C 65.01, H 6.45, N 20.68; found C 64.96, H 6.41, N 20.47.

5,7-Dibromo-2-(*tert*-butyl)-1,2,4-benzotriazin-3(2*H*)-one (13b): Brown solid, m.p. 133−134 °C. IR (KBr): $\tilde{\nu}$ = 1850 (C=O) cm^{-1}. ^1H NMR (300 MHz, [D_6]acetone): δ = 1.80 (s, 9 H, 3 CH_3, *t*Bu), 8.10 (d, *J* = 2.0 Hz, 1 H, 8-H), 8.25 (d, *J* = 2.0 Hz, 1 H, 6-H) ppm. ^{13}C NMR (75 MHz, [D_6]acetone): δ = 27.1 (CH_3), 70.2 (*C*Me_3), 118.2 (t, *J* = 4.7 Hz, C-7), 121.7 (dd, *J* = 5.3, 2.1 Hz, C-5), 131.5 (dd, *J* = 174.3, 5.3 Hz, C-8), 136.0 (s, C-8a), 143.5 (dd, *J* = 173.5, 7.2 Hz, C-6), 149.7 (dd, $^3J_{6\text{-H}}$ = 7.7, $^3J_{8\text{-H}}$ = 4.7 Hz, C-4a), 153.2 (s, C-3) ppm. ^{15}N NMR/INEPT (30 MHz, [D_6]acetone): δ = −132.5 (N-2) ppm. MS (70 eV), *m*/*z* (rel. intensities): 359, 361, 363 (1:2:1) [M^+]. $C_{11}H_{11}Br_2N_3O$ (361.03): calcd. C 36.59, H 3.07, Br 44.26, N 11.64; found C 36.68, H 3.07, Br 44.31, N 11.52.

General Procedure for the Reaction of Benzotetrazinium Salts 1 and 6 with Morpholine: Morpholine (190 mg, 2.16 mmol) was added to a stirred suspension of salts **1** or **6** (0.72 mmol) in 20 mL of dry CH_2Cl_2. After the reaction reached completion (TLC control), the solution was washed with H_2O and 5 % HCl. The organic layer was dried ($MgSO_4$) and the solvent evaporated. The residue was purified by chromatography (silica gel; Et_2O) to afford compounds **14** or **15**, respectively.

4-{[2-[(*tert*-Butyl)azo]-3-pyridinyl]azo}morpholine (14): According to the general procedure, salt **6**, after 15 min of stirring, gave 165 mg (92 %) of **14** as a brownish oil. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.42 (s, 9 H, 3 CH_3, *t*Bu), 3.27 (t, *J* = 5.2 Hz, 4 H, NCH_2), 3.68 (t, *J* = 5.2 Hz, 4 H, OCH_2), 7.26 (dd, *J* = 8.1, 4.4 Hz, 1 H, 5-H), 7.37 (dd, *J* = 8.1, 1.5 Hz, 1 H, 4-H), 8.20 (dd, *J* = 4.4, 1.5 Hz, 1 H, 6-H) ppm. MS (70 eV), *m*/*z*: 276 [M^+]. $C_{13}H_{20}N_6O$ (276.34): calcd. C 56.50, H 7.29, N 30.41; found C 56.41, H 7.30, N 30.37.

4-{[2-[(*tert*-Butyl)azo]phenyl]azo}morpholine (15): According to the general procedure, salt **1**, after 10 min of stirring, gave 190 mg (96 %) of **15** as a red oil. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.35 (s, 9 H, 3 CH_3, *t*Bu), 3.7 (br. s, 8 H, OCH_2, NCH_2), 7.17 (m, 2 H, 4-H, 6-H), 7.29 (dt, *J* = 8.0, 2.1 Hz, 1 H, 5-H), 7.47 (d, *J* = 8.0 Hz, 1 H, 3-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 26.6 (CH_3), 47.6 (br., NCH_2), 65.7 (br., OCH_2), 67.7 (*C*Me_3), 116.8 (C-6), 119.0 (C-3), 126.0 (C-4), 129.2 (C-5), 144.6 (C-1 or C-2), 145.9 (C-2 or C-1) ppm. ^{15}N NMR/INEPT, MS (70 eV), *m*/*z*: 275 [M^+]. $C_{14}H_{21}N_5O$ (275.35): calcd. C 61.07, H 7.69, N 25.43; found C 60.98, H 7.70, N 25.36.

General Procedure for the Reaction of Salt 2 with Amines 16a−e and 19a−g: Amine (0.6 mmol) was added dropwise to a stirred suspension of salt **2** (50 mg, 0.12 mmol) in 5 mL of dry CH_2Cl_2 at room temperature. After the reaction had reached completion (TLC control, see Tables 3 and 4), the solution was passed through a silica gel pad. The solvent was evaporated and the residue was

purified by chromatography [silica gel; benzene, or hexane, or hexane/benzene (3:1)] to afford **17a**−**e**, **18**, **20a**−**c**, and **21c**−**e**.

2,4-Dibromo-6-[(*tert*-butyl)azo]-*N*-phenylaniline (17a): According to the general procedure, the reaction of salt **2** with aniline gave 48 mg (97 %) of **17a** as an orange oil. IR (KBr): $\tilde{\nu}$ = 3420 (NH) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.08 (s, 9 H, 3 CH_3, *t*Bu), 6.66 (s, 1 H, NH), 6.74 (d, *J* = 8.0 Hz, 2 H, H_o, Ph), 6.89 (t, *J* = 7.4 Hz, 1 H, H_p, Ph), 7.16 (dd, *J* = 7.4, 8.0 Hz, 2 H, H_m, Ph), 7.43 (d, *J* = 2.0 Hz, 1 H, 5-H), 7.75 (d, *J* = 2.0 Hz, 1 H, 3-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 26.5 (CH_3), 68.9 (CMe_3), 115.6 (C-4), 118.5 (C_o, Ph), 118.6 (C-2), 120.9 (C-5), 121.6 (C_p, Ph), 128.9 (C_m, Ph), 136.2 (C-3), 144.4 [C-1 or C_i (Ph)], 145.1 [C_i (Ph) or C-1] ppm. MS (70 eV), *m*/*z* (rel. intensities): 409, 411, 413 (1:2:1) [M^+]. $C_{16}H_{17}Br_2N_3$ (411.13): calcd. C 46.74, H 4.17, Br 38.87, N 10.22; found C 46.65, H 4.15, Br 38.99, N 10.11.

2,4-Dibromo-6-[(*tert*-butyl)azo]-*N*-(4-chlorophenyl)aniline (17b): According to the general procedure, the reaction of salt **2** with *p*-chloroaniline gave 35 mg (66 %) of **17b** as a yellow solid, m.p. 105−107 °C. IR (KBr): $\tilde{\nu}$ = 3400 (NH) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.10 (s, 9 H, 3 CH_3, *t*Bu), 6.66 (d, *J* = 6.7 Hz, 2 H, H_o, ClC_6H_4), 6,87 (br. s, 1 H, NH), 6.86 (d, *J* = 6.7 Hz, 2 H, H_m, ClC_6H_4), 7.45 (d, *J* = 2.7 Hz, 1 H, 5-H), 7.75 (d, *J* = 2.7 Hz, 1 H, 3-H) ppm. MS (70 eV), *m*/*z* (rel. intensities): 443, 445, 447, 449 (2:5:4:1) [M^+]. $C_{16}H_{16}Br_2ClN_3$ (445.58): calcd. C 43.13, H 3.62, Br 35.87, Cl 7.96, N 9.43; found C 43.05, H 3.60, Br+Cl 43.95, N 9.49.

2,4-Dibromo-6-[(*tert*-butyl)azo]-*N*-(2,4-dichlorophenyl)benzenamine (17c): According to the general procedure, the reaction of salt **2** with 2,4-dichloroaniline gave 28 mg (49 %) of **17c** as a yellow solid, m.p. 131−133 °C. IR (KBr): $\tilde{\nu}$ = 3410 (NH) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.15 (s, 9 H, 3 CH_3, *t*Bu), 6.38 (d, *J* = 8.7 Hz, 1 H, 6′-H, $Cl_2C_6H_3$), 6.60 (d, *J* = 2.0 Hz, 1 H, 3′-H, $Cl_2C_6H_3$), 6.88 (s, 1 H, NH), 6.96 (dd, *J* = 8.7, 2.0 Hz, 1 H, 5′-H, $Cl_2C_6H_3$), 7.33 (d, *J* = 2.7 Hz, 1 H, 5-H), 7.51 (d, *J* = 2.7 Hz, 1 H, 3-H) ppm. MS (70 eV), *m*/*z* (rel. intensities): 477, 479, 481, 483, 485 (4:12:13:6:1) [M^+]. $C_{16}H_{15}Br_2Cl_2N_3$ (480.02): calcd. C 40.03, H 3.15, Br 33.29, Cl 14.77, N 8.75; found C 39.93, H 3.15, Br + Cl 48.16, N 8.66.

Reaction of Salt 2 with *p*-Toluidine (16d): According to the general procedure, the reaction of salt **2** with *p*-toluidine gave 22 mg (42 %) of **17d** as a yellow oil and 5 mg (11 %) of **18** as an orange oil.

2,4-Dibromo-6-[(*tert*-butyl)azo]-*N*-(4-methylphenyl)benzenamine (17d): IR (KBr): $\tilde{\nu}$ = 3410 (NH) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.08 (s, 9 H, 3 CH_3, *t*Bu), 2.24 (s, 3 H, CH_3), 5.90 (br. s, 1 H, NH), 6.67 (d, *J* = 8.1 Hz, 2 H, H_o, MeC_6H_4), 6.97 (d, *J* = 8.1 Hz, 2 H, H_m, MeC_6H_4), 7.42 (d, *J* = 2.1 Hz, 1 H, 5-H), 7.72 (d, *J* = 2.1 Hz, 1 H, 3-H) ppm. MS (70 eV), *m*/*z* (rel. intensities): 423, 425, 427 (1:2:1) [M^+]. $C_{17}H_{19}Br_2N_3$ (425.16): calcd. C 48.02, H 4.50, Br 37.59, N 9.88; found C 47.96, H 4.48, Br 37.73, N 9.81.

1-(*tert*-Butyl)-2-(3,5-dibromophenyl)diazene (18): ^1H NMR (300 MHz, $CDCl_3$): δ = 1.32 (s, 9 H, 3 CH_3, *t*Bu), 7.62 (t, *J* = 1.8 Hz, 1 H, 4-H), 7.72 (d, *J* = 1.8 Hz, 2 H, 2-H and 6-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 26.6 (CH_3), 68.5 (CMe_3), 123.0 (br.t, *J* ≈ 2 Hz C-3 and C-5), 124.1 (dt, *J* = 170.2, 5.6 Hz, C-2 and C-6), 134.8 (dt, *J* = 173.5, 5.8 Hz, C-4), 153.2 (t, *J* = 2.5 Hz, C-1) ppm. ^{15}N NMR/INEPT (30 MHz, [D$_6$]acetone): δ = 179.8 (N*t*Bu), 118.3 (ArN) ppm. MS (70 eV), *m*/*z* (rel. intensities): 318, 320, 322 (1:2:1) [M^+]. $C_{10}H_{12}Br_2N_2$ (320.02): calcd. C 37.53, H 3.78, Br 49.94, N 8.75 found C 37.61, H 3.79, Br 50.02, N 8.70.

Reaction of Salt 2 with Anisidine (16e): According to the general procedure, the reaction of salt **2** with **16e** gave 25 mg (65 %) of **18** identical to the sample obtained above.

2,4-Dibromo-6-[(*tert*-butyl)azo]-*N*,*N*-dipropylaniline (20a): According to the general procedure, the reaction of salt **2** with Pr_2NH gave 33 mg (65 %) of **20a** as an orange oil. ^1H NMR (300 MHz, $CDCl_3$): δ = 0.85 (t, *J* = 6.9 Hz, 6 H, 2 $CH_2CH_2CH_3$), 1.25 (s, 9 H, 3 CH_3, *t*Bu), 1.28 (m, 4 H, 2 $CH_2CH_2CH_3$), 3.11 (t, *J* = 6.8 Hz, 4 H, 2 $CH_2CH_2CH_3$), 7.32 (d, *J* = 2.7 Hz, 1 H, 5-H), 7.68 (d, *J* = 2.7 Hz, 1 H, 3-H) ppm. MS (70 eV), *m*/*z* (rel. intensities): 417, 419, 421 (1:2:1) [M^+]. $C_{16}H_{25}Br_2N_3$ (419.20): calcd. C 45.84, H 6.01, Br 38.12, N 10.02; found C 45.90, H 6.01, Br 38.01, N 10.10.

2,4-Dibromo-6-[(*tert*-butyl)azo]-*N*,*N*-diisopropylaniline (20b): According to the general procedure, the reaction of salt **2** with iPr_2NH gave 38 mg (75 %) of **20b** as an orange oil. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.29 (s, 9 H, 3 CH_3, *t*Bu), 1.37 (d, *J* = 7.1 Hz, 12 H, 4 CH_3, 2 *i*Pr), 4.03 (sept, *J* = 7.1 Hz, 2 H, 2 C*H*Me_2), 7.31 (d, *J* = 2.7 Hz, 1 H, 5-H), 7.76 (d, *J* = 2.7 Hz, 1 H, 3-H) ppm. MS (70 eV), *m*/*z* (rel. intensities): 417, 419, 421 (1:2:1) [M^+]. $C_{16}H_{25}Br_2N_3$ (419.20): calcd. C 45.84, H 6.01, Br 38.12, N 10.02; found C 45.89, H 6.02, Br 38.19, N 9.95.

Reaction of Salt 2 with *t*BuNH$_2$: According to the general procedure, the reaction of salt **2** with $tBuNH_2$ gave 16 mg (35 %) of **20c** as an orange oil and 21 mg (44 %) of **21a** as a yellow oil.

2,4-Dibromo-6-[(*tert*-butyl)azo]-*N*-(*tert*-butyl)aniline (20c): IR (KBr): $\tilde{\nu}$ = 3380 (NH) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.15 (s, 9 H, 3 CH_3, *t*Bu), 1.37 (s, 9 H, 3 CH_3, *t*BuN), 5.40 (s, 1 H, NH), 7.38 (d, *J* = 2.0 Hz, 1 H, 5-H), 7.72 (d, *J* = 2.0 Hz, 1 H, 3-H) ppm. MS (70 eV), *m*/*z* (rel. intensities): 389, 391, 393 (1:2:1) [M^+]. $C_{14}H_{21}Br_2N_3$ (391.14): calcd. C 42.99, H 5.41, Br 40.86, N 10.74; found C 43.07, H 5.39, Br 40.78, N 10.70.

2,6-Dibromo-4-[(*tert*-butyl)azo]-*N*-(*tert*-butyl)aniline (21a): IR (KBr): $\tilde{\nu}$ = 3400 (NH) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.31 (s, 9 H, 3 CH_3, *t*Bu), 1.40 (s, 9 H, 3 CH_3, *t*BuNH), 3.69 (s, 1 H, NH), 7.80 (s, 2 H, 3-H and 5-H) ppm. MS (70 eV), *m*/*z* (rel. intensities): 389, 391, 393 (1:2:1) [M^+]. $C_{14}H_{21}Br_2N_3$ (391.14): calcd. C 42.99, H 5.41, Br 40.86, N 10.74; found C 43.03, H 5.40, Br 40.94, N 10.62.

2,6-Dibromo-4-[(*tert*-butyl)azo]-*N*-methylaniline (21b): According to the general procedure, the reaction of salt **2** with $MeNH_2$ gave 25 mg (60 %) of **21b** as a yellow oil. IR (KBr): $\tilde{\nu}$ = 3380 (NH) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.28 (s, 9 H, 3 CH_3, *t*Bu), 3.07 (s, 3 H, MeNH), 4.17 (s, 1 H, NH), 7.86 (s, 2 H, 3-H and 5-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 27.0 (C*C*H_3), 34.8 (NCH_3), 67.3 (CMe_3), 114.2 (d, *J* = 5.4 Hz, C-2 and C-6), 127.0 (dd, *J* = 168.4, 6.1 Hz, C-3 and C-5), 145.7 (t, ^2J = 3.2 Hz, C-4), 146.9 (m, C-1) ppm. MS (70 eV), *m*/*z* (rel. intensities): 347, 349, 351 (1:2:1) [M^+]. $C_{11}H_{15}Br_2N_3$ (349.07): calcd. C 37.85, H 4.33, Br 45.78, N 12.04; found C 37.90, H 4.34, Br 45.75, N 11.93.

2,6-Dibromo-4-[(*tert*-butyl)azo]-*N*-isopropylaniline (21c): According to the general procedure, the reaction of salt **2** with $iPrNH_2$ gave 37 mg (81 %) of **21c** as a yellow oil. IR (KBr): $\tilde{\nu}$ = 3380 (NH) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.18 (d, *J* = 6.7 Hz, 6 H, 2 CH_3, *i*Pr), 1.28 (s, 9 H, 3 CH_3, *t*Bu), 3.87 (s, 1 H, NH), 4.10 (sept, *J* = 6.7 Hz, 1 H, C*H*Me_2), 7.84 (s, 2 H, 3-H and 5-H) ppm. MS (70 eV), *m*/*z* (rel. intensities): 375, 377, 379 (1:2:1) [M^+]. $C_{13}H_{19}Br_2N_3$ (377.12): calcd. C 41.40, H 5.08, Br 42.38, N 11.14; found C 41.40, H 5.08, Br 42.38, N 11.14.

2,6-Dibromo-4-[(*tert*-butyl)azo]-*N*,*N*-dimethylaniline (21d): According to the general procedure, the reaction of salt **2** with Me_2NH gave 33 mg (75 %) of **21d** as an orange oil. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.29 (s, 9 H, 3 CH_3, *t*Bu), 2.98 (s, 6 H, Me_2N), 7.85 (s, 2 H, 3-H and 5-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 27.1 (CH_3), 35.4 (CH_3N), 67.0 (CMe_3), 112.9 (C-2 and C-6), 127.1 (C-3 and C-5), 143.5 (C-4), 148.6 (C-1) ppm. MS (70 eV), *m*/*z* (rel. intensities): 361, 363, 365 (1:2:1) [M^+]. $C_{12}H_{17}Br_2N_3$ (363.09): calcd. C 39.69, H 4.72, Br 44.01, N 11.57; found C 39.76, H 4.73, Br 43.90, N 11.45.

4-{2,6-Dibromo-4-[(*tert*-butyl)azo]phenyl}morpholine (21e): According to the general procedure, the reaction of salt **2** with morpholine gave 37 mg (76 %) of **21e** as an orange oil. ^1H NMR (300 MHz, [D_6]acetone): δ = 1.33 (s, 9 H, 3 CH_3, *t*Bu), 3.22 (m, 4 H, CH_2N), 3.79 (m, 4 H, CH_2O), 7.86 (s, 2 H, 3-H and 5-H) ppm. ^{13}C NMR (75 MHz, [D_6]acetone): δ = 27.0 (CH_3), 50.1 (CH_2N), 67.8 (CH_2O), 68.9 (CMe_3), 126.2 (d, *J* = 5.0 Hz, C-2 and C-6), 127.4 (dd, *J* = 169.4, 6.2 Hz, C-3 and C-5), 148.9 (m, $^3J_{3\text{-}H} = {}^3J_{5\text{-}H}$ = 7.0 Hz, C-1), 150.4 (t, ^2J = 3.1 Hz, C-4) ppm. ^{15}N NMR/INEPT (30 MHz, [D_6]acetone): δ = 182.7 (N*t*Bu) ppm. MS (70 eV), *m*/*z* (rel. intensities): 403, 405, 407 (1:2:1) [M^+]. $C_{14}H_{19}Br_2N_3O$ (405.13): calcd. C 41.51, H 4.73, Br 39.45, N 10.37; found C 41.45, H 4.71, Br 39.51, N 10.41.

5,7-Dibromo-2-(*tert*-butyl)-2,6-dihydro-6-(4-morpholinyl)-1,2,3,4-benzotetrazine (22): A solution of morpholine (80 mg, 0.92 mmol) in 10 mL of dry CCl_4 was added dropwise to a stirred suspension of salt **2** (200 mg, 0.46 mmol) in 10 mL of dry CCl_4 at 0 °C. The reaction reached completion after an additional 5 min of stirring at 0 °C, to afford a solution of **22**, which was analyzed by NMR spectroscopy. ^1H NMR at 273 K (300 MHz, $CCl_4/CDCl_3$): δ = 1.50 (s, 9 H, 3 CH_3, *t*Bu), 2.81 (m, 4 H, CH_2N), 3.65 (m, 4 H, CH_2O), 4.66 (s, 1 H, 6-H), 6.69 (s, 1 H, 8-H) ppm. ^{13}C NMR at 273 K (75.5 MHz, $CCl_4/CDCl_3$): δ = 28.1 (CH_3), 49.3 (CH_2N), 64.9 (CMe_3), 67.3 (CH_2O), 73.3 (dd, *J* = 144.3, 6.0 Hz, C-6), 106.5 (d, *J* = 11.0 Hz, C-5), 124.4 (t, *J* = 5.3 Hz, C-4a or C-7), 126.0 (dd, *J* = 171.5, 4.2 Hz,C-8), 135.9 (dd, *J* = 10.6, 5.0 Hz, C-7 or C-4a), 138.5 (d, *J* = 2.4 Hz, C-8a) ppm. ^{15}N NMR/INEPT (30 MHz, $CCl_4/CDCl_3$): δ = −135.4 (m, N-2), −89.5 (d, ^3J = 2.7 Hz, N-1).

Formation of 21g from 22. Experiment 1: A solution of **22** in CCl_4 (5 mL, 0.023 mmol/mL) was allowed to stand at 20 °C for 30 min. The solvent was evaporated and the residue purified by chromatography (silica gel; hexane/EtOAc, 7:1) to give 20.5 mg (44 %) of **21g** identical to the sample obtained above. **Experiment 2:** A solution of morpholine (20 mg, 0.23 mmol) in 5 mL of dry CCl_4 was added to a stirred solution of **22** (0.115 mmol) in 5 mL of dry CCl_4. After 5 min of stirring at room temperature, the solvent was evaporated and the residue purified by chromatography (silica gel; hexane/EtOAc, 7:1) to give 34.5 mg (76 %) of **21g**, identical to the sample obtained above. **Experiment 3:** Treatment of **22** (0.115 mmol) with *t*$BuNH_2$ (17 mg, 0.23 mmol) according to the above procedure afforded 32.6 mg (70 %) of **21g**, identical to the sample obtained above. **Experiment 4:** Treatment of **22** (0.115 mmol) with Et_3N (17 mg, 0.23 mmol) according to the above procedure afforded 25.6 mg (55 %) of **21g**, identical to the sample obtained above.

5-Bromo-2-[(*tert*-butyl)azo]-*N*-isopropylaniline (25): Isopropylamine (71 mg, 1.2 mmol) was added to a stirred suspension of salt **5** (86 mg, 0.24 mmol) in 5 mL of dry CH_3CN. After 15 min of stirring at room temperature, the solvent was evaporated and the residue was purified by chromatography (silica gel; $CHCl_3$) to give 60 mg (84 %) of **25** as a red oil. IR (KBr): $\tilde{\nu}$ = 3420 cm^{-1} (NH). ^1H NMR (300 MHz, $CDCl_3$): δ = 1.26 (d, *J* = 6.6 Hz, 6 H, 2 CH_3, *i*Pr), 1.33 (s, 9 H, 3 CH_3, *t*Bu), 3.67 (sept, 1 H, C*H*Me_2), 5.60 (br. s, 1 H, NH), 6.79 (dd, *J* = 8.1, 1.7 Hz, 1 H, 4-H), 6.88 (d, *J* = 1.7 Hz, 1 H, 6-H), 7.51 (d, *J* = 8.1 Hz, 1 H, 3-H) ppm. MS (70 eV), *m*/*z* (rel. intensities): 297, 299 (1:1) [M^+]. $C_{13}H_{20}BrN_3$ (298.22): calcd. C 52.36, H 6.76, Br 26.79, N 14.09; found C 52.39, H 6.77, Br 26.69, N 14.15.

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