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2-Methoxy-4-nitrobenzenediazonium Salt as a Practical Diazonium-Transfer Agent for Primary Arylamines via Tautomerism of 1,3-Diaryltriazenes: Deaminative Iodination and Arylation of Arylamines without Direct Diazotization

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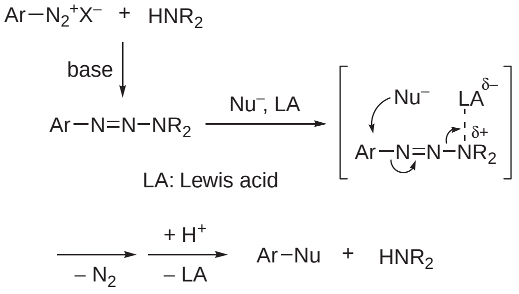
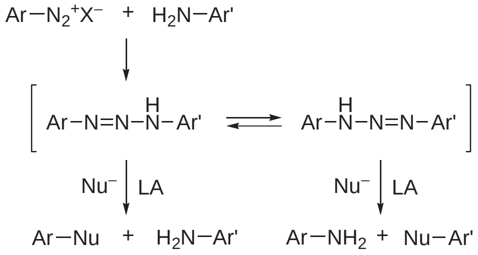
1,3-Diaryltriazenes, prepared from a 2-methoxy-4-nitrobenzenediazonium salt and primary arylamines, exist as "azo-transfer" tautomers in which the 2-methoxy-4-nitrophenyl group is present on the saturated nitrogen atom and forms a hydrogen bond between the 2-methoxy group and the N–H moiety. The synthetic utility of the diazonium salt as a practical diazonium-transfer agent for primary arylamines via tautomerism of the 1,3-diaryltriazenes has been demonstrated by the deaminative iodination and arylation of the arylamines without direct diazotization. The starting 2-methoxy-4-nitrophenylamine can be easily recovered after the reactions.

Although triazene compounds have been known for a long period since their first synthesis in the middle of the 19th century, their versatility in organic synthesis has mainly expanded in the last three decades.[1] Among the related compounds, the 1-aryl-3,3-dialkyltriazenes, derived from arenediazonium salts and secondary amines, have been extensively studied for synthetic applications such as a precursor of aryl halides,[2] a protecting group for amine derivatives,[3] and also a linker for polymer-supported materials.[3b,4] In addition, we have recently reported the palladium-catalyzed cross-coupling reactions of 1-aryltriazenes with arylboronic acids[5] and aryltrifluorosilanes[6] in the presence or absence of a Lewis acid such as boron trifluoride.[7] In these reactions, the interaction between the terminal nitrogen atom and Lewis acid is essential to enhance the cleavage of the sp^2-carbon–nitrogen bond, and, on the whole, the aryl group on the unsaturated nitrogen atom serves as an electrophile (Scheme 1).



Scheme 1.

On the other hand, the 1,3-diaryltriazenes, derived from arenediazonium salts and primary arylamines, have been much less considered so far in organic synthesis, because of the tautomerism of the three-nitrogen "allylic" system.[8–10] Thus, similar Lewis acid-induced transformations of unsymmetrical 1,3-diaryltriazenes should afford a mixture of two products derived from both of the isomers (Scheme 2). Some reports on the substituent effects have revealed that an electron-withdrawing aryl group tends to link to the saturated nitrogen atom to enhance the resonance stabilization with the unshared electron pair on it.[8] However, it has not been realized that one of the isomers can be selectively utilized for organic synthesis through control of the tautomeric equilibrium.



Scheme 2.

We found that the tautomerism of unsymmetrical 1,3-diaryltriazenes could be effectively controlled by introducing a 2-methoxy-4-nitrophenyl group as one of the two aryl substituents up to a synthetically useful level such that only the other aryl group can be selectively utilized in some transformations, as shown in Scheme 3. The 2-methoxy-4-nitrobenzenediazonium salt **2**, derived from the corresponding arylamine **1**, serves as a practically useful diazonium-transfer agent for arylamines via tautomerism of the "original" 1,3-diaryltriazenes **3-*ori*** to its "azo-transfer" tautomer **3-*at*** and thus various deaminative transformations of the arylamines can be conducted without direct diazotization under acidic conditions. The structural aspects and the deaminative iodination and palladium-catalyzed arylation of primary arylamines are reported in this paper.[11]

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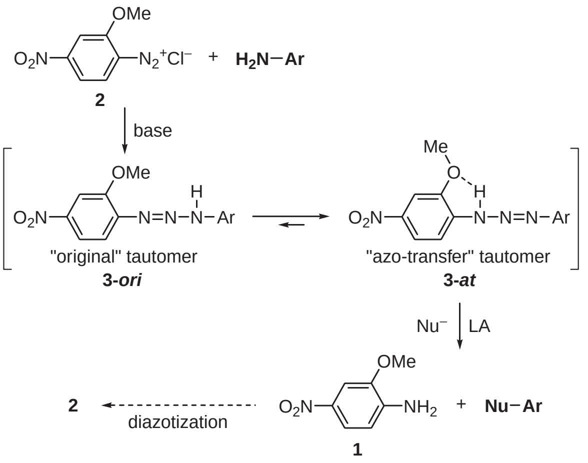
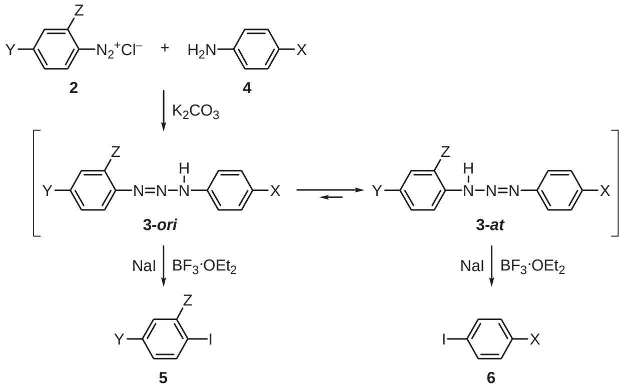


Scheme 3. A general scheme for deaminative transformation of arylamines via tautomerism of 1,3-diaryltriazenes.



Scheme 4. Iodination of 1,3-diaryltriazenes with variant substituents.

Results and Discussion

Structural Aspects. First, we estimated the extent of the tautomerization from the product distribution in the iodination as a model reaction as shown in Scheme 4. Thus, several 1,3-diaryltriazenes **3** derived from some substituted arenediazonium salts **2** and 4-methylphenylamine **4** (X = Me) were treated with sodium iodide in the presence of boron trifluoride, and these results are summarized in Table 1. Among them, only the 2-methoxy-4-nitrophenyl derivative (Entry 1) exclusively gave the 4-iodomethylbenzene **6** (X = Me) arising from the "azo-transfer" tautomer **3-*at*** in 77% GC yield, together with only a trace amount of 4-iodo-3-methoxynitrobenzene (**5**) attributable to the "original" tautomer **3-*ori***. In other cases, the latter type products were always formed in 3–13% yields. These results strongly suggest that the introduction of the 2-methoxy-4-nitrophenyl group caused the tautomerization to exclusively shift to the "azo-transfer" tautomer **3-*at***.[12]

The molecular structure of the 2-methoxy-4-nitrophenyl-substituted triazenes, namely the "azo-transfer" tautomer **3-*at***, was unambiguously confirmed by the X-ray crystallographic analysis of **3** (X = OMe), derived from 4-methoxyphenylamine **4** (X = OMe), as shown in Fig. 1. It is noted that the 2-methoxy-4-nitrophenyl group is present on the saturated nitrogen atom N1, and the hydrogen atom H1 thereon forms a hydrogen bond with the oxygen atom O1 of the 2-methoxy group with the distance of 2.28(4) Å.[13] This hydrogen bond,[14] in addition to the electronic effect, appears to fix the tautomerism on this side.

Table 1. Iodination of 1,3-Diaryltriazenes **3** (X = Me) for Estimation of the Tautomer Distribution According to Scheme 4[a)]

Entry	Y	Z	Yield/%[b)]	
			5	**6**
1	NO_2	OMe	trace	77
2	H	OMe	13	67
3	NO_2	H	3	75
4	H	NO_2	—[c)]	76
5	NO_2	Cl	10	69
6	C(O)Me	H	4	55

a) Reaction conditions: 1,3-diaryltriazene (0.30 mmol), NaI (0.60 mmol), $BF_3 \cdot OEt_2$ (0.45 mmol), MeCN (3.0 mL), 40 °C, 2 h. b) Yields determined by GC analysis with tetradecane as an internal standard. c) Not determined due to overlap with unidentified peaks.

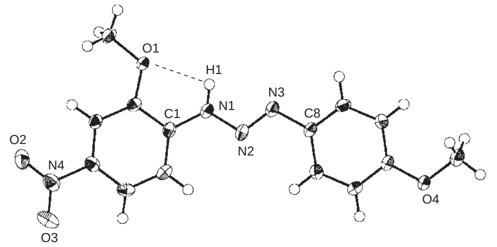
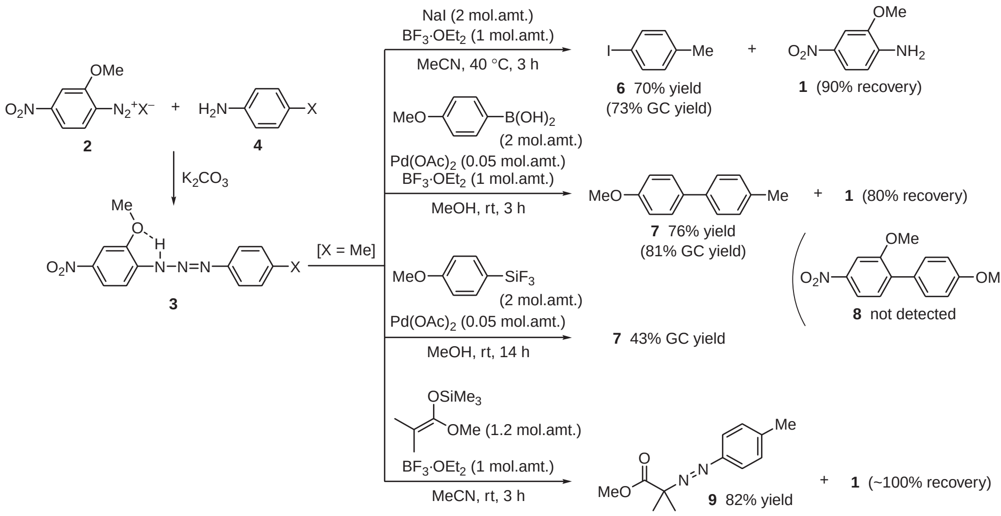


Fig. 1. X-ray crystal structure of **3** (X = OMe). Selected bond lengths [Å] and angles [deg]: C1–N1; 1.380(2), N1–N2; 1.353(2), N2=N3; 1.263(2), N3–C8; 1.428(2), H1···O1; 2.28(4), C1–N1–N2; 121.2(2), N1–N2–N3; 110.7(2), N2–N3–C8; 113.7(2).

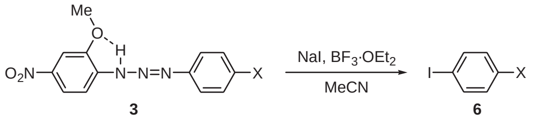
Deaminative Iodination and Arylation of Some Arylamines Using the Diazonium-Transfer Agent. The synthetic utility of the 2-methoxy-4-nitrobenzenediazonium salt **2** as a practical diazonium-transfer agent for some 4-substituted arylamines has been demonstrated in the deaminative iodination, the palladium-catalyzed cross-coupling reaction with arylboronic acids and aryltrifluorosilane, and the azo-coupling reaction with the silyl enol ether, as represented by the reactions shown in Scheme 5. Hereafter, the 1,3-diaryltriazenes **3** are depicted only as the "azo-transfer" tautomer.

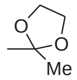
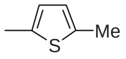
Iodination with Sodium Iodide. Typically, in the case of X = Me, treatment of the 1,3-diaryltriazene **3** (X = Me) with sodium iodide and boron trifluoride in acetonitrile at 40 °C for 3 h selectively gave 4-iodomethylbenzene **6** in 70% isolated yield (73% GC yield),[15] together with a trace amount of 4-iodo-3-methoxynitrobenzene and 90% recovery of 2-methoxy-4-nitrophenylamine **1** which can be recycled for the preparation of the reagent **2**. Some other results are summarized in Table 2. The electron-donating and neutral substituents produced good yields ranging from 70% to 87% (Entries 1, 2, and 5), while the strongly electron-withdrawing groups such as the fluorine atom decreased the yield (Entry 3). Some acid-



Scheme 5. Representative reactions of 1,3-diaryltriazene **3** (X = Me).

Table 2. Iodination with Sodium Iodide in the Presence of Boron Trifluoride$^{a)}$



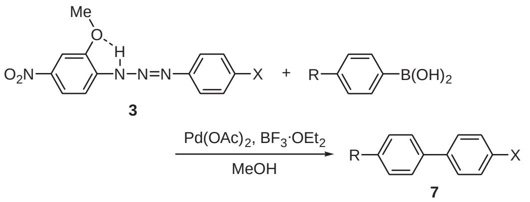
Entry	X	Yield/%$^{b)}$
1	Me	73
2	OMe	70
3	F	53
4	Cl	73
5	Br	87
6	OSi(i-Pr)$_3$	69
7		48
8		36$^{c)}$

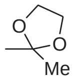
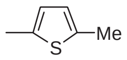
a) Reaction conditions: 1,3-diaryltriazene (0.30 mmol), NaI (0.60 mmol), $BF_3 \cdot OEt_2$ (0.30 mmol), MeCN (3.0 mL), 40 °C, 3 h. b) Yields determined by GC analysis with tetradecane as an internal standard. c) 1-Iodo-2-methoxy-4-nitrobenzene was also detected in 12% yield.

sensitive triisopropylsilyl ether and acetal moieties remained intact under the present Lewis acidic conditions, but the yields were lowered to a certain extent (Entries 6 and 7). Only in the case of the thienyl-substituted derivative, was the undesired 4-iodo-3-methoxynitrobenzene exceptionally formed in 12% yield due to unknown factors (Entry 8).

Palladium-Catalyzed Arylation with Arylboronic Acids and Aryltrifluorosilane. As shown in Scheme 5, as a typical example, the 1,3-diaryltriazene **3** (X = Me) was treated with 4-methoxyphenylboronic acid in the presence of a catalytic amount of $Pd(OAc)_2$ and equimolar amount of boron trifluoride.[5] The cross-coupling reaction readily proceeded at room temperature to exclusively give the corresponding biaryl **7** in 76% yield (81% GC yield); the undesired biaryl **8** was not detected at all. In this reaction, the starting arylamine **1** also had an 80% recovery.

Table 3. Palladium-Catalyzed Arylation with Arylboronic Acids$^{a)}$



Entry	X	R	Yield/%$^{b)}$
1	Me	OMe	81
2	OMe	Me	78
3	F	OMe	36
4	Cl	OMe	49
5	Br	OMe	55
6	OSi(t-Bu)Ph$_2$	OMe	72$^{c),d)}$
7	OSi(t-Bu)Ph$_2$$^{e)}$	OMe	62$^{d)}$
8		OMe	62$^{c),d)}$
9		OMe	77

a) Reaction conditions: 1,3-diaryltriazene (0.30 mmol), arylboronic acid (0.60 mmol), $BF_3 \cdot OEt_2$ (0.30 mmol), $Pd(OAc)_2$ (0.015 mmol), MeOH (3.0 mL), room temperature, 3 h. b) Yields determined by GC analysis with docosane as an internal standard. c) Protective groups cleaved during purification. d) Isolated yields. e) *meta*-Substitution.

The reaction system was applied to some functionalized substrates (Table 3). In a trend similar to that observed for the iodination, electron-withdrawing groups decreased the yields of the coupled products (Entries 3 and 4). The halogenated substrates afforded the corresponding biaryls in moderate yields with good chemo-selectivity (Entries 4 and 5), and silyl ether at the *meta*-position and thienyl group were retained through the coupling process (Entries 7 and 9), while the silyl ether at the *para*-position and acetal protection reverted back to phenol and carbonyl moiety, respectively, during the purification (Entries 6 and 8).

A similar cross-coupling reaction of the 1,3-diaryltriazene **3** (X = Me) with 4-methoxyphenyltrifluorosilane *in the absence of* the extra Lewis acid was also carried out to afford the biaryl **7** in 43% GC yield.[6]

Azo-Coupling with Silyl Enol Ether. Another example is the reaction of the 1,3-diaryltriazene **3** (X = Me) with the dimethylketene methyl trimethylsilyl acetal in the presence of boron trifluoride (Scheme 5).[16] The corresponding α-arylazo ester **9** was obtained in 82% yield together with an almost quantitative recovery of the arylamine **1**. The α-azo carbonyl compounds can be easily converted to the corresponding α-amino derivatives by simple hydrogenation using a Pd/C catalyst.[16,17] It is noted again that the arylamine **4** (X = Me) was practically diazotized by the treatment with the diazonium-transfer agent **2** and the controlled tautomerism of the resulting diaryltriazene **3** (X = Me) to afford the arylazo adduct **9**.

In summary, we realized the tautomerism control of the unsymmetrical 1,3-diaryltriazenes by the introduction of the 2-methoxy-4-nitrophenyl group as one of the two aryl substituents. The iodination and palladium-catalyzed arylation of the diaryltriazenes readily proceeded in the presence of boron trifluoride to afford the corresponding aryl iodides and biaryls, respectively, thus providing a deaminative transformation process of primary arylamines without direct diazotization.

Experimental

A Typical Procedure for the Preparation of 1,3-Diaryltriazenes. To a solution of *p*-toluidine (1.07 g, 10.0 mmol) and potassium carbonate (2.07 g, 15.0 mmol) in water/THF (1:1) (20 mL) was added a suspension of 2-methoxy-4-nitrobenzenediazonium chloride (**2**) [prepared from 2-methoxy-4-nitrophenylamine (**1**) (1.68 g, 10.0 mmol) and sodium nitrite (759 mg, 11.0 mmol) in hydrochloric acid (3 mol/L, 10 mL) at 0 °C] dropwise at 0 °C and the mixture was stirred for 30 min. The resulting mixture was extracted with AcOEt three times and the combined organic layer was washed with brine and dried over anhydrous magnesium sulfate. After filtration and evaporation under reduced pressure, the remaining crude product was purified by column chromatography on silica gel [$R_f = 0.41$, hexane/AcOEt/benzene (4:1:1) as an eluent] to afford 1-(4-methylphenyl)-3-(2-methoxy-4-nitrophenyl)triazene **3** (X = Me) (1.99 g, 6.95 mmol; 70%) as yellow solids, which was recrystallized from hexane/AcOEt (4:1). mp: 165–166 °C (dec). ^{1}H NMR δ 2.14 (s, 3H), 2.88 (s, 3H), 7.09 (d, $J = 8.3$ Hz, 2H), 7.39 (d, $J = 8.7$ Hz, 1H), 7.41 (d, $J = 2.3$ Hz, 1H), 7.68 (d, $J = 8.3$ Hz, 2H), 7.85 (dd, $J = 8.7$, 2.3 Hz, 1H). Anal. Calcd for $C_{14}H_{14}N_4O_3$: C, 58.73; H, 4.93; N, 19.57%. Found: C, 58.63; H, 4.85; N, 19.59%.

A Typical Procedure for the Iodination of 1,3-Diaryltriazenes. To a solution of **3** (X = Me) (86 mg, 0.30 mmol) and NaI (90 mg, 0.60 mmol) in MeCN (3.0 mL) was added $BF_3 \cdot OEt_2$ (38 µL, 0.30 mmol) dropwise at room temperature and the mixture was stirred at 40 °C for 2 h. After quenching with water, the mixture was extracted with diethyl ether three times and the combined organic layer was washed with brine and dried over anhydrous magnesium sulfate. After filtration and evaporation under reduced pressure, the remaining crude product was purified by column chromatography on silica gel ($R_f = 0.65$, hexane as an eluent) to afford 4-iodomethylbenzene **6** (X = Me) (46 mg, 0.21 mmol; 70%) as colorless oil. ^{1}H NMR δ 1.89 (s, 3H), 6.50 (d, $J = 8.0$ Hz, 2H), 7.44 (d, $J = 8.0$ Hz, 1H). 2-Methoxy-4-nitrophenylamine (**1**) (45 mg, 0.27 mmol; 90%) was recovered by flushing the silica gel with polar solvent [$R_f = 0.25$, hexane/AcOEt (2:1) as an eluent].

A Typical Procedure for the Arylation of 1,3-Diaryltriazenes. To a solution of **3** (X = Me) (86 mg, 0.30 mmol), 4-methoxyphenylboronic acid (71 mg, 0.60 mmol), and $Pd(OAc)_2$ (3.5 mg, 0.015 mmol) in MeOH (3.0 mL) was added $BF_3 \cdot OEt_2$ (38 µL, 0.30 mmol) dropwise at room temperature and the mixture was stirred for 3 h. After quenching with water, the mixture was extracted with diethyl ether three times and the combined organic layer was washed with brine and dried over anhydrous magnesium sulfate. After filtration and evaporation under reduced pressure, the remaining crude product was purified by column chromatography on silica gel [$R_f = 0.48$, hexane/AcOEt (10:1) as an eluent] to afford 4-methoxy-4′-methylbiphenyl (**7**) (44 mg, 0.22 mmol; 76%) as white solids. ^{1}H NMR δ 2.22 (s, 3H), 3.38 (s, 3H), 6.90 (d, $J = 9.0$ Hz, 2H), 7.12 (d, $J = 8.0$ Hz, 2H), 7.48 (d, $J = 8.0$ Hz, 2H), 7.49 (d, $J = 9.0$ Hz, 2H).

A Typical Procedure for the Azo-Coupling of 1,3-Diaryltriazenes with Silyl Enol Ethers. To a solution of **3** (X = Me) (86 mg, 0.30 mmol) in MeCN (3 mL) was added dimethylketene methyl trimethylsilyl acetal (52 mg, 0.30 mmol) and $BF_3 \cdot OEt_2$ (38 µL, 0.30 mmol) at room temperature and the mixture was stirred for 3 h. After quenching with water, the mixture was extracted with diethyl ether three times and the combined organic layer was washed with brine and dried over anhydrous magnesium sulfate. After filtration and evaporation under reduced pressure, the remaining crude product was purified by column chromatography on silica gel [$R_f = 0.49$, hexane/AcOEt (4:1) as an eluent] to afford methyl 2-methyl-2-(4-methylphenylazo)-propanoate (**9**) (44 mg, 0.24 mmol; 82%) as yellow oil. ^{1}H NMR δ 1.69 (s, 6H), 2.01 (s, 3H), 3.41 (s, 3H), 6.94 (d, $J = 8.0$ Hz, 2H), 7.83 (d, $J = 8.0$ Hz, 2H). Anal. Calcd for $C_{12}H_{16}N_2O_2$: C, 65.43; H, 7.32; N, 12.72%. Found: C, 65.39; H, 7.38; N, 12.63%.

X-ray Crystallographic Analysis of 3 (X = OMe). Single crystals of **3** (X = OMe) suitable for X-ray crystallography were obtained by recrystallization from DME. Intensity data were collected on a Rigaku Saturn 70 CCD diffractometer with graphite monochromated Mo Kα radiation ($\lambda = 0.71070$ Å). The data were corrected for Lorentz and polarization effects and secondary extinction. The crystal structure was solved by the direct method (SIR92) and a full-matrix least-squares refinement was carried out. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. All calculations were performed using the Crystal Structure crystallographic software package. The analytical conditions are summarized in Table S1 (Supporting Information). Crystallographic data have been deposited with Cambridge Crystallographic Data Centre: Deposition number CCDC-264859 for compound **3** (X = OMe). Copies of the data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

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Supporting Information

Experimental details, spectral data for all new compounds, and crystallographic data for compound **3** (X = OMe). This material is available free of charge on the web at: http://www.csj.jp/journals/bcsj/.

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12 Since most of these diaryltriazenes **3** show only one set of resonance signals in the ^{1}H NMR spectra, the equilibrium seems to shift to one side of the two possible tautomers in solution.

13 The other bond lengths of N1–N2 [1.353(2) Å] and N2=N3 [1.263(2) Å] are comparable to the characteristic values reported for the 1,3-diaryltriazenes: a) A. R. Walton, T. C. Jenkins, and S. Neidle, *Acta Crystallogr., Sect. B*, **47**, 771 (1991). b) R. Anulewicz, *Acta Crystallogr., Sect. C*, **53**, 345 (1997). c) D.-C. Zhang, Z.-H. Fei, T.-Z. Zhang, Y.-Q. Zhang, and K.-B. Yu, *Acta Crystallogr., Sect. C*, **55**, 102 (1999). d) M. Hörner, I. C. Casagrande, J. Bordinhao, and C. M. Mössmer, *Acta Crystallogr., Sect. C*, **58**, o193 (2002). e) M. Hörner, L. Bresolin, J. Bordinhao, E. Hartmann, and J. Strahle, *Acta Crystallogr., Sect. C*, **59**, o426 (2003). f) M. Hörner, A. L. Brancher, A. Silva, J. Bordinhao, and C. M. Mössmer, *Acta Crystallogr., Sect. C*, **60**, o303 (2004).

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