Nitrosation with Sodium Hexanitrocobaltate(III)

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$Na_3Co(NO_2)_6$ has been investigated as a new reagent for the nitrosation of various substrates containing an amino functionality. Reactions took place in an aqueous solution of the reagent. The pH of the reaction mixture remained in the range 4.3−5. Thus, hydrazides were transformed to the corresponding acyl azides, and the reactions with arenesulfonyl hydrazines afforded arenesulfonyl azides. Treatment of aromatic amines with $Na_3Co(NO_2)_6$ gave 1,3-diaryltriazenes in excellent yields; coupling of the initially formed diazo compound to the electron rich aromatic ring was also observed. Nitrosation of aliphatic amines was not possible due to complex formation with the reagent.

Introduction

Cobalt compounds are frequently employed used in organic synthesis as oxidants[1] and as the promoters for the formation of C−C bonds.[2] We herein report on the transformations of nitrogen-containing substrates with $Na_3Co(NO_2)_6$ [trisodium hexakis(nitrito-*N*)cobaltate(III), SHNC].

Our recently reported studies on the reactions of mono- and disubstituted hydrazines demonstrated their use as starting materials leading to one-carbon synthons,[3] as appropriate precursors for N^1-acylformamidoximes,[4] and their application to the preparation of 1,3,4-oxadiazoles or fused 1,2,4-triazoles.[5] We also described an efficient and simple cleavage of the hydrazino moiety using thallium(III) nitrate trihydrate (TTN),[6] which resulted in the formation of the corresponding acids, esters, amides, carbamates, ureas, or heterocyclic methyl ethers, depending on the selection of the starting material and the nucleophile. In order to find a less toxic metal salt for the hydrazino cleavage mentioned above, we turned to cobalt(III) salts. The redox potential (E^o) for $Co^{3+} \rightarrow Co^{2+}$ is 1.82 V in aqueous solution,[1a] and it is known to be influenced by the nature of the ligands and solvents.[1a] We note the report of Olah *et al.*, who successfully applied CoF_3 for the regeneration of the parent carbonyl compounds from *N*,*N*-dimethylhydrazones or oximes in chloroform solution.[7]

We sought a cobalt(III) salt that is relatively stable in water solution and/or in organic solvents and selected SHNC as a possible candidate. A reaction of hydrazide with SHNC similar to that already described with TTN was expected to lead in aqueous solution to the carboxylic acid as the final product. This was not found to be the case.

Results and Discussion

When hydrazides **1a**−**e** were added to a water solution of SHNC, acyl azides **2a**−**e** were isolated in 68−89% yield (Table 1). It should be noted that the reaction of hydrazide **1b** took place selectively at the hydrazino moiety, leaving the amino group intact. Arenesulfonyl hydrazines **1f**−**i** behave similarly to hydrazides **1a**−**e** and were converted under the same conditions to the azides **2f**−**i**. These results led us to the conclusion that SHNC could serve as a new nitrosating agent. Several reagents have previously been used to transform the monosubstituted hydrazines to the corresponding azides:[8] nitrous acid,[9] alkyl nitrites,[10] nitrosyl chloride,[10a,11] nitrosyl tetraflouroborate,[12] clayfen,[13] and dinitrogen tetroxide.[14]

We were aware of numerous examples where SHNC was employed for the synthesis of various Co(III) complexes by the displacement of the nitro groups by amine ligands using ammonia,[15] monodentate, bidentate, or multidentate amines,[16] amino acids,[17] or the mixture of an amine and an amino acid.[18] The nitrosation of the amine function of those substrates with SHNC was not observed. Our preliminary experiments with primary aliphatic amines (isopropylamine, *n*-butylamine, *tert*-

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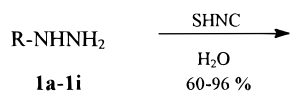
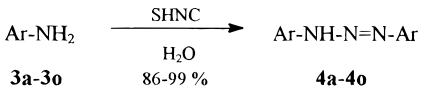
Table 1. Preparation of Acyl Azides and Arenesulfonyl Azides



R	product[a]	reaction time (h)[b]	yield[c] (%)
C_6H_5-CO	**2a**	4.5	83
2-$H_2NC_6H_4$-CO	**2b**	0.5	74
4-ClC_6H_4-CO	**2c**	4	89
2-$O_2NC_6H_4$-CO	**2d**	0.5	68
4-$O_2NC_6H_4$-CO	**2e**	11	79
C_6H_5-SO_2	**2f**	1.5	92
4-MeC_6H_4-SO_2	**2g**	0.75	96
4-ClC_6H_4-SO_2	**2h**	6.5	60
4-$O_2NC_6H_4$-SO_2	**2i**	3.5	85

[a] Products were identical (mp, IR, NMR) to azides obtained from the same starting materials, employing $NaNO_2$/HCl at 0 °C. [b] Reactions were carried out at rt. [c] Isolated yields are given.

Table 2. Transformation of Aromatic Amines to 1,3-Diaryltriazenes



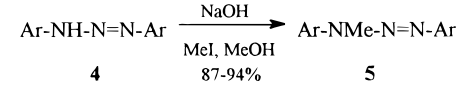
Ar	product	reaction time (h)[a]	yield[b] (%)
4-ClC_6H_4	**4a**	13	91
4-BrC_6H_4	**4b**	11	94
4-IC_6H_4	**4c**	17	94
2-IC_6H_4	**4d**	12	95
3-Cl,4-FC_6H_3	**4e**	4.5	86
3,4-ClC_6H_3	**4f**	16	99
2,4-BrC_6H_3	**4g**	15.5	89
3,4,5-ClC_6H_2	**4h**	27	97
4-AcC_6H_4	**4i**	3	91
3-CF_3,4-ClC_6H_3	**4j**	25	99
4-$EtO_2CC_6H_4$	**4k**	9	96
4-NCC_6H_4	**4l**	18	97
2-NCC_6H_4	**4m**	9	93
3-$O_2NC_6H_4$	**4n**	70	90
4-$H_2NCOC_6H_4$	**4o**	6.5	92

[a] Reactions were carried out at rt. [b] Isolated yields are given.

butylamine, benzylamine) showed similar results. Namely, treatment of those amines with SHNC in H_2O produced dark-brown solutions (or a brown solid in the case of benzylamine) due to the formation of the corresponding complexes. All attempts to recover starting amines by extraction with CH_2Cl_2 failed. Each of the primary amines mentioned above was easily released from the complex upon addition of NaOH, removed from the reaction mixture by extraction with CH_2Cl_2, and isolated as a hydrochloride.

These results, shown in Table 1, encouraged us to extend our work to aromatic amines. In a typical experiment, a selected aromatic amine **3** (1 mmol) was added at room temperature to the solution of SHNC (0.75 mmol) in water (5 mL). The reaction mixture was stirred at room temperature, and the product was filtered off to give the corresponding 1,3-diaryltriazene **4**. Several examples are provided in Table 2. The procedure enables the very convenient preparation of various 1,3-diaryltriazenes, a class of compounds from which representatives are known to possess anorectic activity.[19] Some of them were recently used as starting materials for the preparation of 1,3-diaza-2-azoniaallene salts, novel N_3-building blocks.[20] Our experiments also support the idea

Table 3. *N*-Methylation of Selected 1,3-Diaryltriazenes



Ar	triazene	product	yield[a] (%)
2-IC_6H_4	**4d**	**5d**	89
3-Cl,4-FC_6H_3	**4e**	**5e**	87
3,4-ClC_6H_3	**4f**	**5f**	89
3,4,5-ClC_6H_2	**4h**[b]	**5h**	92
3-CF_3, 4-ClC_6H_3	**4j**	**5j**	94
4-NCC_6H_4	**4l**[b]	**5l**	92

[a] Isolated yields are given. [b] MeONa was used as a base instead of NaOH.

of employing SHNC as a new reagent for the nitrosation.[21] The formation of the triazenes **4** can be explained by the nitrosation of the aromatic amino group, followed by the transformation of the initially formed *N*-nitroso compound to the diazonium salt, and subsequent reaction with another molecule of the aromatic amine. The triazenes **4a**−**o** were identical to those obtained from the corresponding aromatic amines, as described in the synthesis of 1,3-diphenyltriazene from aniline.[22] The crude products by the latter method were always contaminated with various impurities and were isolated in 10−40% lower yields than compared to our procedure. An attempt to prepare **4d** by that alternative route[22] resulted in a complex mixture which was not further investigated.

The structures of hithertho unpublished triazenes (**4d**, **4e**, **4f**, **4h**, **4j**, and **4l**) were supported by elemental analysis and IR, ^{1}H NMR, and mass spectra. However, numerous attempts to obtain their complete ^{13}C NMR spectra were unsuccessful. Several NMR experiments, including DEPT, HMBC and HMQC, were employed, but some signals could not be seen even when the spectra of 0.1−0.3 M solutions of triazenes were recorded. The reason seems to be connected with the tautomerism of the triazene function. The addition of D_2O to an NMR sample, which should result in the exchange of the triazene hydrogen with the deuterium, did not solve the problem. To overcome this, *N*-methyltriazenes **5** were prepared from the corresponding triazenes **4** (Table 3). The fixed position of the introduced methyl group ensured that all of the expected signals appeared in the ^{13}C NMR spectra of **5**.

Our experiments clearly demonstrate the selectivity of SHNC. Namely, the aromatic amino group of **1b** remains unchanged in the presence of the hydrazido moiety. The reaction led to the corresponding acyl azide **2d**. On the other hand, the amine **3o** was transformed to the triazene **4o**, supporting the fact that the amido group did not react. Furthermore, treatment of benzamide with SHNC induced no change within 48 h, but the action of SHNC on 2-aminobenzamide afforded benzotriazinone **6**. Apparently, the aromatic amino group of 2-aminobenzamide reacts first with SHNC to give the diazonium salt. The subsequent participation of the *ortho* amido group results in the cyclization to the final product **6**.

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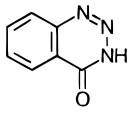

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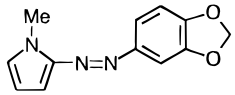
The competition of an aliphatic and an aromatic amine in reaction with SHNC was then studied. Treatment of an aliphatic amine (isopropylamine, *n*-butylamine, *tert*-butylamine, or benzylamine) with SHNC (0.75 mol/mol of amine) in an aqueous solution for 0.5 h, followed by the addition of **3i**, demonstrated that the reagent was "blocked", therefore, **3i** remained unchanged. Introduction of another portion of SHNC to the reaction mixture led to the complete conversion of **3i** to the triazene **4i** in all cases. Moreover, a mixture of isopropylamine and **3i** was added to an aqueous solution of SHNC (a molar ratio 1:1:0.75). The amine **3i** did not react and a second portion of SHNC was required to transform **3i** to **4i**. These observations suggested that the formation of the complex with the more basic aliphatic amine was favored over the nitrosation of the aromatic amine. The first equivalent of SHNC was consumed for the complexation of the aliphatic amine and the second was needed to convert the aromatic amine to the triazene.

In the case of 5-amino-1,3-benzodioxole (3,4-methylenedioxyaniline, **7**), the azo compound **10** was isolated. The formation of the product **10** suggests a reaction pathway that includes the coupling of the diazonium salt **8**, presumably obtained *in situ* from the amine **7** and SHNC, to the benzene ring of the amine **7** itself (Scheme 1, path a). It is worth mentioning that alternatively **10** might derive from the rearrangement of the triazene **9** (path b).[23] This seems unlikely on the basis of an experiment in which a mixture of *N*-methylpyrrole and the amine **7** was treated with SHNC. Comparing the reactivity of *N*-methylpyrrole and the amine **7** toward aromatic diazonium ions, one could expect the coupling of the diazonium salt **8** to either of them.[24] Actually two azo compounds, **11** and **10**, were isolated in a ratio of approximately 4:1. Path b is further unlikely in that the triazenes **4a**−**o** were obtained nearly quantitatively without rearrangement to azo compounds.



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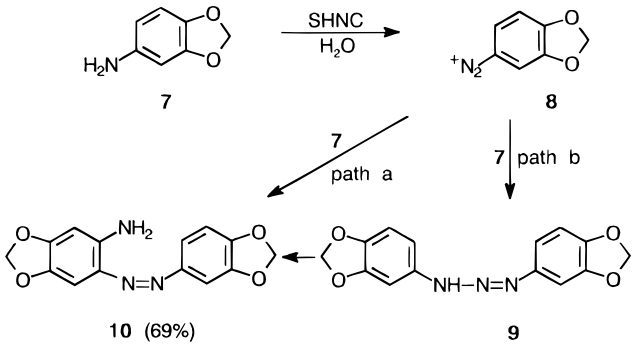
To the best of our knowledge, cobalt(III) salts have not been previously used for the nitrosation of organic substrates. On the other hand, cobalt complexes have served as catalysts. Several applications of bis(dimethylglioxymato)cobalt in the presence of BH_4^- were demonstrated in the nitrosation of aryl substituted olefins by nitric oxide, yielding the corresponding oximes.[25] A similar complex was applied recently to the conversion of allylic alcohols to the corresponding allylamides.[26] An

Scheme 1



aerobic epoxidation of olefins was reported to be catalyzed by square-planar cobalt(III) complexes of bis-*N*,*N*′-disubstituted oxamides.[27] Furthermore, the nitrosation of α,β-unsaturated carboxamides with nitric oxide and triethylsilane, leading to 2-nitrosocarboxamide, required a catalytic amount of *N*,*N*′-bis[2-(ethoxycarbonyl)-3-oxobutylidene]ethylenediaminatocobalt.[28] The success of SHNC in nitrosation can be explained considering the results of Eaton *et al.*,[29] who studied solutions of SHNC by ^{59}Co, ^{14}N, and ^{17}O NMR spectroscopy. They reported the presence of a variety of Co(III) species present in aqueous solution of SHNC. All contain at least four nitro ligands with the remaining two positions being filled by aqua or nitrito groups. Electron transfer leads to the reduction of Co^{3+} to Co^{2+} and the oxidation of NO_2^- to N_2O_4 which is then hydrolyzed to give NO_3^- and NO_2^-. The pH of the aqueous solution of SHNC drops from 5.2 to 4.3 after 8 h, due to the formation of nitric and nitrous acid.

The reduction of Co^{3+} to Co^{2+}, accompanied by the oxidation of NO_2^- to N_2O_4, and the subsequent hydrolysis of N_2O_4 is probably crucial for the successful nitrosation in our experiments. On the other hand, a displacement of NO_2^- ligands with primary aliphatic amines in SHNC seems to give Co^{3+} complexes; nitrite ions, which are liberated, do not act as nitrosating entities. SHNC is a reported starting material for the preparation of stable Co^{3+} complexes with aliphatic amines possessing primary and/or secondary amino groups.[16c,18,30] This also explains our inability to use SHNC for the nitrosation of diaryl or dialkyl amines. Namely, diphenylamine did not react with SHNC, but diisobutylamine, dicyclohexylamine and piperidine were found to form the corresponding Co^{3+} complexes, from which the amines were recovered as described above for primary amines.

Conclusion

We have presented an application of SHNC for the nitrosation of hydrazides, arenesulfonyl hydrazines, and aromatic amines under aqueous conditions. Acyl azides, arenesulfonyl azides, triazenes, and azo compounds were isolated in good to excellent yields. The reactions are clean and the isolation of the products is simple. Nitrosation takes place under mild acidic conditions (pH 4.3−

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5). The reagent enables a selective nitrosation of a hydrazino moiety in the presence of an aromatic amino group. The latter is more reactive than the amide function, which remains intact unless *ortho* participation is possible. SHNC cannot be used for the nitrosation of an aliphatic amine due to complex formation. Experiments concerning the competition of an aliphatic amine and an aromatic amine in reaction with SHNC indicated that complex formation with the aliphatic amine is favored over the nitrosation of the aromatic amine.

Experimental Section

The starting materials were purchased from commercial sources (Fluka, Merck, Aldrich) and used without further purification. TLC was carried out on Fluka silica gel plates (F_{254}). Fluka silica gel 60 (220−440 mesh) was used for column chromatography. Melting points were determined on a hot stage and are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded with TMS as an internal standard.

General Procedure for the Preparation of Acyl Azides and Arenesulfonyl Azides. Monosubstituted hydrazine **1a**−**i** (1 mmol) was added to the solution of SHNC (303 mg, 0.75 mmol) in H_2O (5 mL). The reaction mixture was stirred at room temperature for 0.5−11 h (see Table 1). Azide **2c** was filtered off and washed with H_2O. Other products (**2a**, **2b**, and **2d**−**i**) were isolated by extraction with CH_2Cl_2 or $CHCl_3$ (6 × 20 mL), followed by a treatment with anhydrous Na_2SO_4 and evaporation to dryness under reduced pressure. Azides **2a**−**i** were identical (IR, NMR) with the products prepared from **1a**−**i** (1 mmol) and $NaNO_2$ (1 mmol) in 0.3 M HCl (5 mL) at 0 °C.

Benzoyl azide (2a): 121 mg, yield 83%; mp 28 °C (acetone); lit.[31] mp 29−30 °C.

2-Aminobenzoyl azide (2b): 120 mg, yield 74%; mp 81−82 °C (benzene−petroleum ether); lit.[32] mp 80−81 °C.

4-Chlorobenzoyl azide (2c): 162 mg, yield 89%; mp 41−43 °C (benzene−petroleum ether); lit.[33] mp 43 °C.

2-Nitrobenzoyl azide (2d): 131 mg, yield 68%; mp 36.5−37.5 °C (chloroform); lit.[34] mp 36−38 °C.

4-Nitrobenzoyl azide (2e): 151 mg, yield 79%; mp 70−72 °C (H_2O−MeOH); lit.[35] mp 71−72 °C.

Benzenesulfonyl azide (2f): 168 mg, yield 92%; mp 13.5−14.5 °C (purified by distillation at 40 °C/1 mmHg); lit.[36] mp 13−15 °C.

Tosyl azide (2g): 189 mg, yield 96%; mp 22.5−23.5 °C (purified by distillation at 40 °C/1 mmHg); lit.[36] mp 22−23 °C.

4-Chlorobenzenesulfonyl azide (2h): 130 mg, yield 60%; mp 38.5−39.5 °C (purified by distillation at 40 °C/1 mmHg); lit.[36] mp 37−38 °C.

4-Nitrobenzenesulfonyl azide (2i): 193 mg, yield 85%; mp 99.5−100 °C (acetonitrile−diethyl ether); lit.[36] mp 100−101 °C.

General Procedure for the Synthesis of 1,3-Diaryltriazenes. Aromatic amine **3a**−**o** (1 mmol) was added to the solution of SHNC (303 mg, 0.75 mmol) in H_2O (5 mL). The reaction mixture was stirred at room temperature for 3−70 h (see Table 2). The solid material was filtered off and washed with H_2O (2 × 10 mL) to give **4a**−**o** in 86−99% yield.

1,3-Bis(4-chlorophenyl)triazene (4a): 120 mg, yield 91%; mp 127−129 °C (benzene−petroleum ether); lit.[37] mp 128−130 °C.

1,3-Bis(4-bromophenyl)triazene (4b): 166 mg, yield 94%; mp 145−147 °C (benzene−petroleum ether); lit.[37] mp 146−148 °C.

1,3-Bis(4-iodophenyl)triazene (4c): 211 mg, yield 94%; mp 154−156 °C (diethyl ether−petroleum ether); lit.[37] mp 154−156 °C.

1,3-Bis(2-iodophenyl)triazene (4d): 214 mg, yield 95%; mp 149−151 °C (methanol−diethyl ether); IR (KBr) 3280, 1585, 1500, 1463, 1428, 1410, 1260, 1235, 1186, 1018, 760, 750 cm^{-1}; ^{1}H NMR (300 MHz, DMSO-d_6) δ 7.01 (br d, 2H), 7.44 (m, 2H), 7.55 (m, 2H), 7.91 (br s, 2H), 11.64 (s, 1H); MS *m*/*z* (rel intensity) 449 (M^+, 3), 231 (87), 203 (100), 76 (51); HRMS calcd for $C_{12}H_9I_2N_3$ 448.8886, found 448.8896. Anal. Calcd for $C_{12}H_9I_2N_3$: C, 32.10; H, 2.02; N, 9.36. Found: C, 31.75; H, 1.98; N, 9.48.

1,3-Bis(3-chloro-4-fluorophenyl)triazene (4e): 130 mg, yield 86%; mp 133−134 °C (benzene−petroleum ether); IR (KBr) 3300, 1605, 1585, 1513, 1490, 1480, 1450, 1395, 1265, 1247, 1213, 1190, 820, 809, 777 cm^{-1}; ^{1}H NMR (300 MHz, DMSO-d_6) δ 7.15 (dd, 2H, $J_1 = J_2 = 8.7$ Hz), 7.24 (m, 2H), 7.48 (dd, 2H, $J_1 = 6.5$ Hz, $J_2 = 2.5$ Hz), 9.51 (s, 1H); MS *m*/*z* (rel intensity) 301 (M^+, 6), 157 (78), 129 (100). Anal. Calcd for $C_{12}H_7Cl_2F_2N_3$: C, 47.71; H, 2.34; N, 13.91. Found: C, 47.83; H, 2.29; N, 13.97.

1,3-Bis(3,4-dichlorophenyl)triazene (4f): 165 mg, yield 99%; mp 149−150 °C (methanol); IR (KBr) 3190, 1597, 1510, 1475, 1457, 1435, 1380, 1232, 1197, 1126, 826 cm^{-1}; ^{1}H NMR (300 MHz, DMSO-d_6) δ 7.44 (d, 2H, $J = 8.4$ Hz), 7.65 (m, 4H), 12.87 (s, 1H); MS *m*/*z* (rel intensity) 333 (M^+, 6.5), 173 (65), 145 (100); HRMS calcd for $C_{12}H_7Cl_4N_3$ 332.9394, found 332.9384. Anal. Calcd for $C_{12}H_7Cl_4N_3$: C, 43.02; H, 2.11; N, 12.54. Found: C, 42.91; H, 2.05; N, 12.80.

1,3-Bis(2,4-dibromophenyl)triazene (4g): 229 mg, yield 89%; mp 167−169 °C (methanol−diethyl ether); lit.[38] mp 167.5 °C.

1,3-Bis(3,4,5-trichlorophenyl)triazene (4h): 195 mg, yield 97%; mp 199−200 °C (diethyl ether−benzene); IR (KBr) 3205, 1593, 1570, 1515, 1425, 1377, 1254, 1195, 1185, 1140, 850, 820, 810 cm^{-1}; ^{1}H NMR (300 MHz, DMSO-d_6) δ 7.66 (s, 4H), 13.00 (s, 1H); MS *m*/*z* (rel intensity) 401 (M^+, 17), 207 (45), 181 (100); HRMS calcd for $C_{12}H_5Cl_6N_3$ 400.8615, found 400.8635. Anal. Calcd for $C_{12}H_5Cl_6N_3$: C, 35.68; H, 1.25; N, 10.40. Found: C, 35.72; H, 1.00; N, 10.51.

1,3-Bis(4-acetylphenyl)triazene (4i): 128 mg, yield 91%; mp 191−193 °C (methanol); lit.[39] mp not reported.

1,3-Bis(4-chloro-3-(trifluoromethyl)phenyl)triazene (4j): 198 mg, yield 99%; mp 116.5−117 °C (methanol); IR (KBr) 3335, 1615, 1592, 1503, 1475, 1415, 1327, 1283, 1260, 1233, 1200, 1166, 1145, 1118, 1047, 908, 890, 830 cm^{-1}; ^{1}H NMR (300 MHz, DMSO-d_6) δ 6.61 (m, 6H); 13.06 (s, 1H); MS *m*/*z* (rel intensity) 401 (M^+, 1), 207 (42), 179 (100), 144 (13); HRMS calcd for $C_{14}H_7Cl_2F_6N_3$ 400.9921, found 400.9930. Anal. Calcd for $C_{14}H_7Cl_2F_6N_3$: C, 41.82; H, 1.75; N, 10.45. Found: C, 41.84; H, 1.69; N, 10.62.

1,3-Bis(4-(ethoxycarbonyl)phenyl)triazene (4k): 164 mg, yield 96%; mp 155.5−156.5 °C (methanol); lit.[37] mp 154−156 °C.

1,3-Bis(4-cyanophenyl)triazene (4l): 120 mg, yield 97%; mp 241−241.5 °C (benzene−acetone); IR (KBr) 3235, 2230, 1610, 1520, 1487, 1444, 1408, 1256, 1190, 1180, 1176, 850, 836 cm^{-1}; ^{1}H NMR (300 MHz, DMSO-d_6) δ 7.63 (d, 4H, $J = 8$ Hz), 7.87 (d, 4H, $J = 8$Hz), 13.22 (s, 1H); MS *m*/*z* (rel intensity) 247 (M^+, 3), 130 (52), 102 (100); HRMS calcd for $C_{14}H_9N_5$ 247.0858, found 247.0867. Anal. Calcd for $C_{14}H_9N_5$: C, 68.01; H, 3.67; N, 28.32. Found: C, 67.93; H, 3.64; N, 28.41.

1,3-Bis(2-cyanophenyl)triazene (4m): 115 mg, yield 93%; mp 132−133.5 °C (acetonitrile); lit.[19] mp 143−144 °C.

1,3-Bis(3-nitrophenyl)triazene (4n): 129 mg, yield 90%; mp 198.5−199.5 °C (methanol−acetone); lit.[40] mp 195−196 °C.

1,3-Bis(4-carbamoylphenyl)triazene (4o): 130 mg, yield 92%; mp 227−228 °C (acetone−acetonitrile); lit.[41] mp 219 °C (dec).

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General Procedure for the Synthesis of 3-Methyl-1,3-diaryltriazenes. Powdered NaOH (1 mmol, 40 mg) and MeI (0.2 mL, 456 mg, 3.19 mmol) were added to the solution of 1 mmol of a triazene **4** in MeOH (8 mL) and heated under reflux for 1 h. Then, another portion of MeI (0.2 mL, 456 mg, 3.19 mmol) was added at rt and the reaction mixture was stirred, until the starting triazene disappeared as followed by TLC (0.5−12 h). The reaction mixture was kept at −15 °C for 1−2 h. The product **5** was filtered off and washed with MeOH (2 × 5 mL), precooled to −15 °C.

3-Methyl-1,3-bis(2-iodophenyl)triazene (5d): 410 mg, yield 89%; mp 77−78 °C (methanol); IR (KBr) 1580, 1480, 1455, 1427, 1397, 1263, 1230, 1205, 1128, 1023, 755 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6) δ 3.57 (s, 3H), 7.00 (ddd, 1H, J_1 = 7.8 Hz, J_2 = 7.2 Hz, J_3 = 1.7 Hz), 7.17 (ddd, 1H, J_1 = 7.9 Hz, J_2 = 7.2 Hz, J_3 = 1.8 Hz), 7.37 (ddd, 1H, J_1 = 8.5 Hz, J_2 = 7.2 Hz, J_3 = 1.3 Hz), 7.46 (dd, 2H, J_1 = 7.9 Hz, J_2 = 1.4 Hz), 7.53 (ddd, 1H, J_1 = 7.9 Hz, J_2 = 7.3 Hz, J_3 = 1.4 Hz), 7.93 (d, 1H, J = 7.5 Hz), 8.02 (dd, 1H, J_1 = 7.8 Hz, J_2 = 1.3 Hz); ^{13}C NMR (75 MHz, DMSO-d_6) δ 38.3, 95.8, 97.3, 117.8, 127.5, 128.2, 128.9, 129.3, 129.4, 139.0, 139.8, 147.0, 148.9; MS *m*/*z* (rel intensity) 463 (M^+, 1.4), 231 (97), 203 (100), 76 (55); HRMS calcd for $C_{13}H_{11}I_2N_3$ 462.9043, found 462.9056. Anal. Calcd for $C_{13}H_{11}I_2N_3$: C, 33.72; H, 2.39; N, 9.07. Found: C, 33.53; H, 2.30; N, 9.13.

3-Methyl-1,3-bis(3-chloro-4-fluorophenyl)triazene (5e): 274 mg, yield 87%; mp 128−128.5 °C (methanol); IR (KBr) 1597, 1495, 1455, 1387, 1260, 1235, 1187, 1117, 1055, 830, 760 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6) δ 3.60 (s, 3H), 7.45 (dd, 1H, J_1 = J_2 = 8.9 Hz), 7.46 (dd, 1H, J_1 = J_2 = 8.9 Hz), 7.56 (m, 2H), 7.70 (dd, 1H, J_1 = 7.6 Hz, J_2 = 2.4 Hz), 7.74 (dd, 1H, J_1 = 6.8 Hz, J_2 = 2.7 Hz); ^{13}C NMR (75 MHz, DMSO-d_6) δ 32.8, 117.1 (d, J = 1.6 Hz), 117.4 (d, J = 1.6 Hz), 117.6 (d, J = 7.0 Hz), 118.9, 120.1 (d, J = 18.6 Hz), 120.2 (d, J = 18.8 Hz), 122.0 (d, J = 7.4 Hz), 122.1, 141.5 (d, J = 2.8 Hz), 146.7 (d, J = 3.2 Hz), 154.0 (d, J = 242 Hz), 155.9 (d, J = 244.8 Hz); MS *m*/*z* (rel intensity) 315 (M^+, 10), 157 (76), 129 (100); HRMS calcd for $C_{13}H_9Cl_2F_2N_3$ 315.0142, found 315.0146. Anal. Calcd for $C_{13}H_9Cl_2F_2N_3$: C, 49.39; H, 2.87; N, 13.29. Found: C, 49.24; H, 2.77; N, 13.40.

3-Methyl-1,3-bis(3,4-dichlorophenyl)triazene (5f): 312 mg, yield 89%; mp 88−88.5 °C (methanol); IR (KBr) 1593, 1485, 1450, 1395, 1375, 1350, 1240, 1125, 1110, 1027, 995 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6) δ 3.60 (s, 3H), 7.51 (dd, 1H, J_1 = 8.7 Hz, J_2 = 2.3 Hz), 7.56 (dd, 1H, J_1 = 8.9 Hz, J_2 = 2.5 Hz), 7.63 (dd, 1H, J_1 = 8.9 Hz, J_2 = 0.2 Hz), 7.64 (d, 1H, J = 8.6 Hz), 7.72 (d, 1H, J = 2.3 Hz), 7.76 (d, 1H, J = 2.5 Hz); ^{13}C NMR (75 MHz, DMSO-d_6) δ 32.5, 117.1, 118.4, 121.5, 122.4, 125.9, 129.0, 130.8, 131.0, 131.8, 131.8, 143.9, 149.0; MS *m*/*z* (rel intensity) 347 (M^+, 2.3), 173 (62), 145 (100); HRMS calcd for $C_{13}H_9Cl_4N_3$ 346.9551, found 346.9561. Anal. Calcd for $C_{13}H_9Cl_4N_3$: C, 44.73; H, 2.60; N, 12.04. Found: C, 44.63; H, 2.57; N, 12.12.

3-Methyl-1,3-bis(3,4,5-trichlorophenyl)triazene (5h) was prepared as described in the general procedure, except using MeONa (54 mg, 1 mmol) instead of NaOH. The reaction mixture was stirred after the first addition of MeI at rt for 3 h and after the second addition of the same reagent for 12 h; 386 mg of **5h** was isolated: yield 92%; mp 206−207 °C (dec) (chloroform); IR (KBr) 1585, 1555, 1455, 1427, 1400, 1378, 1340, 1245, 1225, 1190, 1143, 1013, 884, 870, 815 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 3.61 (s, 3H), 7.48 (s, 2H), 7.60 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 32.6, 117.0, 121.7, 126.6, 129.7, 134.6, 134.9, 143.5, 148.3; MS *m*/*z* (rel intensity) 415 (M^+, 0.6), 207 (51), 179 (100); HRMS calcd for $C_{13}H_7Cl_6N_3$ 414.8771, found 414.8788. Anal. Calcd for $C_{13}H_7Cl_6N_3$: C, 37.36; H, 1.69. Found: C, 37.47; H, 1.68.

3-Methyl-1,3-bis(4-chloro-3-(trifluoromethyl)phenyl-)triazene (5j): 391 mg, yield 94%; mp 113−113.5 °C (methanol); IR (KBr) 1605, 1577, 1490, 1475, 1455, 1402, 1355, 1312, 1296, 1228, 1165, 1125, 1105, 1030, 1000 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6) δ 3.69 (s, 3H), 7.76 (m, 2H), 7.87 (m, 4H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 32.7, 116.0 (q, J = 5.4 Hz), 120.5 (q, J = 5.4 Hz), 122.2, 122.6 (q, 2C, J = 273.2 Hz), 125.3 (q, J = 1.8 Hz), 125.7, 127.3 (q, J = 30.9 Hz), 127.4 (q, J = 30.9 Hz), 128.4 (q, J = 2.2 Hz), 132.5, 132.7, 143.2, 148.2; MS *m*/*z* (rel intensity) 415 (M^+, 0.6), 207 (41), 179 (100); HRMS calcd for $C_{15}H_9Cl_2F_6N_3$ 415.0078, found 415.0088. Anal. Calcd for $C_{15}H_9Cl_2F_6N_3$: C, 43.29; H, 2.18; N, 10.10. Found: C, 43.07; H, 2.00; N, 10.20.

3-Methyl-1,3-bis(4-cyanophenyl)triazene (5l) was prepared as described in the general procedure, expect using MeONa (54 mg, 1 mmol) instead of NaOH. The reaction mixture was stirred after the first addition of MeI at rt for 3 h and after the second addition of the same reagent for 23 h: 240 mg of **5l** was isolated, yield 92%; mp 211−212 °C (methanol); IR (KBr) 2230, 1605, 1510, 1450, 1400, 1353, 1317, 1215, 1205, 1160, 1100, 985, 850, 835 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6) δ 3.70 (s, 3H), 7.73 (m, 1H), 7.76 (m, 2H), 7.79 (m, 1H), 7.90 (m, 4H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 32.3, 105.9, 109.3, 117.3 (2C), 118.8 (2C), 122.2 (4C), 133.5 (2C), 147.3, 152.3; MS *m*/*z* (rel intensity) 261 (M^+, 2.1), 130 (50), 102 (100); HRMS calcd for $C_{15}H_{11}N_5$ 261.1014, found 261.1012. Anal. Calcd for $C_{15}H_{11}N_5$: C, 68.95; H, 4.24; N, 26.80. Found: C, 68.81; H, 4.27; N, 27.07.

1,2,3-Benzotriazin-4(3*H*)-one (6) was prepared from 2-aminobenzamide and SHNC as described above for the synthesis of 1,3-diaryltriazenes: reaction time, 41 h; 111 mg, yield 76%; mp 219−220 °C (methanol); lit.[42] mp 220 °C (dec).

5-(6-Amino-1,3-benzodioxol-5-yl)azo-1,3-benzodioxole (10) was prepared from aromatic amine **7** and SHNC, following the above procedure for the synthesis of 1,3-diaryltriazenes: reaction time, 3 h; 98 mg; yield 69% (after column chromatography on silica gel; petroleum ether−ethyl acetate 5:3); mp 216−218 °C (acetonitrile); IR (KBr) 3290, 1614, 1495, 1470, 1255, 1225, 1033, 933 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6) δ 5.95 (s, 2H), 6.10 (s, 2H), 6.41 (s, 1H), 6.43 (s, 2H), 7.02 (d, 1H, J = 8.2 Hz), 7.07 (s, 1H), 7.38 (dd, 1H, J_1 = 8.2 Hz, J_2 = 1.8 Hz), 7.52 (d, 1H, J = 1.8 Hz); ^{13}C NMR (75 MHz, DMSO-d_6) δ 95.8, 96.9, 98.3, 101.0, 101.6, 107.9, 121.3, 129.5, 139.7, 145.6, 148.0, 148.4, 148.5, 151.6; MS *m*/*z* (rel intensity) 285 (M^+, 100), 136 (79), 121 (57), 65 (40); HRMS calcd for $C_{14}H_{11}N_3O_4$ 285.0750, found 285.0751. Anal. Calcd for $C_{14}H_{11}N_3O_4$: C, 58.95; H, 3.89; N, 14.73. Found: C, 59.12; H, 4.07; N, 15.06.

Preparation of 5-(1-Methylpyrrol-2-yl)azo-1,3-benzodioxole (11). A solution of SHNC (3 mmol, 1.212 g) in H_2O (4 mL) was added at room temperature to a solution of aromatic amine **7** (4 mmol, 548 mg) and *N*-methylpyrrole (4 mmol, 324 mg) in MeOH (16 mL). The reaction mixture was stirred for 18 h and then evaporated to dryness. The residue was treated with H_2O (15 mL) and the solid material was filtered off and washed with H_2O (3 × 5 mL). Separation by column chromatography (silica gel, petroleum ether−ethyl acetate 5:3) gave 307 mg (yield 34%) of **11** and 45 mg (yield 8%) of **10**.

11: mp 70−72 °C (from diethyl ether−petroleum ether); IR (KBr) 1603, 1500, 1475, 1453, 1417, 1260, 1250, 1190, 1040, 817, 736 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6) δ 3.91 (s, 3H), 6.12 (s, 2H), 6.25 (dd, 1H, J_1 = 4.1 Hz, J_2 = 2.6 Hz), 6.52 (dd, 1H, J_1 = 4.1 Hz, J_2 = 1.7 Hz), 7.05 (d, 1H, J = 8.2 Hz), 7.21 (m, 1H), 7.32 (d, 1H, J = 1.9 Hz), 7.36 (dd, 1H, J_1 = 8.2 Hz, J_2 = 1.9 Hz); ^{13}C NMR (75 MHz, DMSO-d_6) δ 32.9, 98.0, 99.0, 101.9, 108.1, 109.8, 121.1, 127.3, 145.5, 148.5, 148.6, 148.9; MS *m*/*z* (rel intensity) 229 (M^+, 100), 80 (48); HRMS calcd for $C_{12}H_{11}N_3O_2$ 229.0851, found 229.0802. Anal. Calcd for $C_{12}H_{11}N_3O_2$: C, 62.87; H, 4.84; N, 18.33. Found: C, 62.84; H, 5.05; N, 18.32.

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