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A New and Regioselective Synthesis of Aromatic Diazene Derivatives

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A new method for the preparation of aromatic diazene derivatives **3a–l, 5, 7a, b, 9** under very mild conditions is described. The reaction of trialkylarylstannanes with nitro-substituted benzenediazonium tetrafluoroborates leads, by strict *ipso* substitution, to the corresponding diaryldiazenes in satisfactory to high yields. Due to the excellent leaving group quality of the stannyl group azo compounds may be prepared which are not accessible by normal electrophilic azo coupling. The products can be valuable precursors, obtained by reduction to the amines or other derivatizations, for consecutive aromatic compounds.

The continuous interest in aromatic azo chemistry[2,3] is partly due to the dye industry, but also to the use of azo compounds as starting material for a variety of other aromatics. Thus, these compounds can be derivatized by e.g. NO_2[4a], SO_3H[4b], Cl, Br[4a], oxidized to form the azoxy group[4c], or reduced to yield aromatic amines[2].

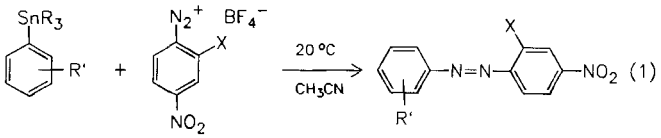
Direct couplings of diazonium salts[5] are normally strongly restricted to activated aromatic compounds like anilines and phenols. The intention to prepare diaryl diazenes by a regioselective azo coupling has led to attempts to use organometallics like zinc halide reagents[6] as coupling components, but the yields were mostly poor.

Better results were obtained with zinc diaryls[7] prepared from organomercurials. These reactions, however, are handicapped because i) they are extremely sensitive to water or oxygen, ii) a coupling reaction with a diazonium salt substituted by a nitro or keto group is impossible, iii) the zinc diaryls are difficult to obtain.

To avoid these problems we present a new route to diaryl diazenes using the outstanding leaving ability of the trialkylstannyl group in aromatic substitutions. So far, the *ipso* substitution of a trialkyltin group has led to aromatic aldehydes, ketones, carboxamides, thio compounds, and isocyanato sulfones with high or strict regioselectivity[1]. In most cases, the yields are high or quantitative, the conditions applied mild, the reaction times short, and many of the isomer patterns have not been obtained in normal electrophilic substitutions so far. Now we are able to control one of the most prestigious electrophilic substitution reactions, the azo coupling, by the use of trialkylarylstannanes as coupling partners.

Results and Discussion

Trialkylarylstannanes **1** and **4** react slightly exothermally with nitro-substituted benzenediazonium tetrafluoroborates **2** to give the azo derivatives **3** and **5**, respectively, in satisfactory to excellent yields at room temperature. The stannanes **1a–k** completely disappear (NMR), eq. (1). As coupling product the *ipso* isomer is obtained exclusively. In some cases up to ten colored byproducts in very small amounts must be separated from **3** by column chromatography. The differences between the high raw yields and the yields of isolated, pure products **3**, see eq. (1) and Experimental Section, are due to these particularities of isolation with regard to the small-scale experiments.



(1)

1 2a: X = NO_2 2b: X = H 3

	1 R, R'	2 X	3 R', X	Yield (%)
a	Bu, H	NO_2	H, NO_2	31
b	Me, 2-Me	NO_2	2-Me, NO_2	53
c	Me/, 3-Me	NO_2	3-Me, NO_2	53/
c	Bu			67
d	Me, 4-Me	NO_2	4-Me, NO_2	62
e	Me, 4-Et	NO_2	4-Et, NO_2	54
f	Bu, Mes	NO_2	Mes, NO_2	65
g	Me, 2-OMe	H	2-OMe, H	16
h	Bu, 2-OMe	NO_2	2-OMe, NO_2	66
i	Me, 4-OMe	H	4-OMe, H	57
j	Me, 4-OMe	NO_2	4-OMe, NO_2	83
k	Me, 4-$SiMe_3$	NO_2	4-$SiMe_3$, NO_2	36
l	Me, 4-Cl	NO_2	4-Cl, NO_2	14

  0009–2940/91/1010–2297 $ 3.50+.25/0

When starting from 3-trimethylstannyl- and 3-tributylstannyltoluene (**1c**) a comparison of the yields of coupling products reveals that the use of tributyltin reagents gives the same or even better results than with trimethyltin-substituted aromatic compounds. The low toxicity of the tributyltin analogs is in favor of their preparative use. Nevertheless, trimethylarylstannanes are also applied in this investigation because of their clear-cut, unequivocal NMR spectra in pilot experiments.

Besides the azo compound **3**, trialkyl tetrafluoroborates are formed which can easily be separated, especially when bearing the trimethyltin group, by column chromatography. For example no tin can be detected in the products **3c,d** by atomic absorption spectroscopy[8]. The mild reaction conditions and the effective workup without heating predestinates the reaction described in eq. (1) to be used in the synthesis of e.g. valuable biomolecules, which have to be pure and free of tin.

For the coupling reaction a polar solvent is necessary which does not react with the diazonium salt. Dry acetonitrile is suitable for this purpose; the dissolved salt is then stable for several days. The solvent is essential to dissociate the ion pair of the salt and to increase the mobility of the electrophile. No reaction occurs without a polar solvent.

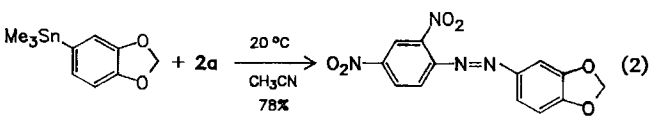
The reactivity is strongly increased by the trialkyltin group. Whereas **1a–e** and even more deactivated aromatic compounds like **1l** readily undergo coupling, their nonstannylated parent compounds do not at all. Oppositely directing effects of the substituents like the *ortho/para* regioselektive effect of the methyl group in **1c** are easily overcome. The couplings of **1b**, **1c** and **1h** exclusively yield the *ipso* products, though, as mentioned above, especially the *para* position is attacked in usual azo couplings.

Another proof for the high reactivity of trialkylarylstannanes are the reactions of **1h** and **1j** with **2a** from which within 30 min, or even 120 s, the *ipso* isomers **3h** or **3j** are obtained in up to 83% yield [see eq. (1)].

Anisole itself yields only 19% of the *p*-substituted azo compound under the same conditions after 22 h. **2b** does not react with anisole at all, but from the stannylated methoxy benzenes **1g,i** the azo derivatives **3g** and **3i** are obtained. Again, the *ipso* products have been isolated, and no traces of other isomers can be found.

Acetals normally cannot be coupled in aqueous acidic solution. By using **4**, however, no reaction to the aldehyde and the diol occurs under these conditions, and 78% of **5** can be obtained after 120 s.

The question whether the trimethyltin or the trimethylsilicon group is first attacked in an azo coupling reaction can be answered by using **1k** as coupling component. Only **3k** is obtained. Therefore, the Sn–C bond is cleaved much easier than the Si–C bond.



(2)

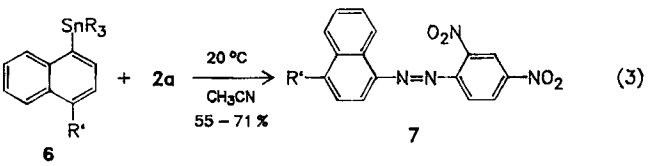
4 5

The very strong deactivating effects of the trifluoromethyl or the cyano group in the benzene ring cannot be overcompensated by trialkyltin groups. Thus no reaction occurs with **2a,b**.

Also the directing effect of a *N,N*-dimethylamino group lastly determines the outcome and overcompensates the stannyl group, i.e. the *p*-substituted product is formed.

The high reactivity of trialkylarylstannanes in the coupling reactions presented is probably based on the extension of the coordination sphere of the tin atom in the transition state, thus localizing the electrophile, as has been discussed previously[1a].

The coupling of stannanes with diazonium salts can be easily applied to polycyclic analogs, e.g. the naphthylazo compounds **7a,b** and **9** are obtained from the stannylated starting compounds **6a–c** [eq. (3)] and **8** [eq. (3)]. Even in the case of the 2-substituted naphthalene **8** only the *ipso* isomer **9** has been isolated in high yield. No traces of other isomers can be detected. Further applications of the tin-mediated synthesis of diarylazo compounds are in progress.

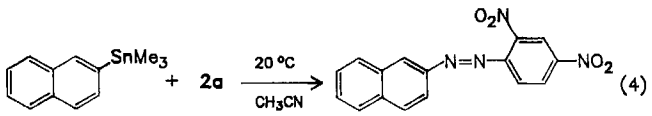


(3)

6 7

	R	R'
a	Me	H
b	Bu	H
c	Me	Me

	R'
a	H
b	Me



(4)

8 9

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Experimental

All melting points have been determined with a Büchi SMP 20. – IR spectra: Shimadzu 3289. – NMR spectra: Varian EM 360 (60 MHz, ^{1}H) and Bruker AM 300 (300 MHz, ^{1}H, 75.47 MHz, ^{13}C). – Mass spectra: Finnigan Mat 8230, 70 eV. – Elemental analyses: Carlo Erba 1106. – UV/Vis spectra: Hitachi U-2000.

Diaryldiazenes **3a–l, 5, 7a,b, 9**. – *General Procedure:* To a suspension of a benzenediazonium tetrafluoroborate **2**[9] (5 mmol) in 20 ml of dry acetonitrile under argon a trialkylarylstannane **1, 4, 6, 8**[10] (5 mmol) is added (dry nitromethane increases the reaction rate up to three times but acetonitrile is preferred because of safety aspects.) and the suspension is stirred at room temperature until **2** is completely dissolved (higher temperatures lead to decomposition of **2**). From the dark red solution the solvent is removed in vacuo (15 Torr/25°C) and the residue is worked up by column chromatography (2 × 60 cm Al_2O_3, acidic, activity II, toluene, the first orange red zone must be taken). After removal of the toluene the

crude product is recrystallized from ethanol and washed with pentane.

2,4-Dinitroazobenzene (**3a**): From 1.3 g (3.5 mmol) of **1a** and 1.0 g (3.5 mmol) of **2a**, 0.3 g (31%) of **3a** is obtained after 18 h, m.p. 115°C (ref.[11a] 116–119°C). – ^{1}H NMR ([D$_6$]acetone): δ = 6.81–7.53 (m, 5H, aromatic H), 7.31 (ABX, 1H, $^3J_{AB}$ = 9 Hz), 8.00 (ABX, 1H, $^3J_{AB}$ = 9 Hz, $^4J_{BX}$ = 4 Hz), 8.26 (ABX, 1H, $^4J_{AB}$ = 4 Hz). – UV/Vis (acetonitrile): λ_{max} (lg ε) = 453 nm (2.812), 323 (4.178), 201 (4.256).

2'-Methyl-2,4-dinitroazobenzene (**3b**): From 1.4 g (5.3 mmol) of **1b** and 1.5 g (5.3 mmol) of **2a**, 0.8 g (53%) of **3b** are obtained after 16 h, m.p. 140°C (ref.[11b] 150°C). – ^{1}H NMR ([D$_6$]acetone): δ = 2.20 (s, 3H, Me), 6.60–7.20 (m, 4H, aromatic H), 7.30 (ABX, 1H, $^3J_{AB}$ = 9 Hz), 8.06 (ABX, 1H, $^3J_{AB}$ = 9 Hz, $^4J_{BX}$ = 3 Hz), 8.3 (ABX, 1H, $^4J_{XB}$ = 3 Hz). – ^{13}C NMR ([D$_6$]acetone): δ = 17.73 (CH$_3$), 116.88, 121.16, 122.24, 127.91, 129.23, 132.90, 134.81 (CH), 141.40, 149.07, 149.68, 151.63 (C). – MS (70 eV): *m/z* (%) = 286 (8) [M$^+$], 119 (11) [CH$_3$-C$_6$H$_4$-N$_2^+$], 91 (100) [CH$_3$-C$_6$H$_4^+$]. – UV/Vis (acetonitrile): λ_{max} (lg ε): 343 nm (4.322), 263 (3.904), 200 (4.438).

3'-Methyl-2,4-dinitroazobenzene (**3c**): From 1.4 g (5.5 mmol) of 3-(trimethylstannyl)toluene and 1.6 g (5.7 mmol) of **2a** or from 1.2 g (3.2 mmol) of 3-(tributylstannyl)toluene and 0.9 g (3.2 mmol) of **2a**, 0.8 g (53%) or 0.6 g (67%) of **3c** are obtained after 12 h or 16 h, m.p. 135°C. – ^{1}H NMR ([D$_6$]acetone): δ = 1.93 (s, 3H, Me), 6.87–7.23 (m, 4H, aromatic H), 7.37 (ABX, 1H, $^3J_{AB}$ = 9 Hz), 8.10 (ABX, 1H, $^3J_{AB}$ = 9 Hz, $^4J_{BX}$ = 4 Hz), 8.30 (ABX, 1H, $^4J_{XB}$ = 4 Hz). – ^{13}C NMR ([D$_6$]acetone): δ = 21.42 (CH$_3$), 121.17, 121.41, 122.22, 125.07, 129.31, 130.52, 135.39 (CH), 140.79, 147.74, 149.13, 149.48, 153.68 (C). – MS (70 eV): *m/z* (%) = 286 (20) [M$^+$], 181 (2) [N$_2$C$_6$H$_3$(NO$_2$)$_2^+$], 119 (29) [CH$_3$-C$_6$H$_4$-N$_2^+$], 91 (100) [CH$_3$-C$_6$H$_4^+$]. – UV/Vis (acetonitrile): λ_{max} (lg ε) = 336 nm (4.346), 202 (4.448). – In an AAS analysis of **3c** no tin can be detected (sensitivity limit <115 ppm).

C$_{13}$H$_{10}$N$_4$O$_4$ (286.25) Calcd. C 54.54 H 3.52 N 19.57
Found C 54.60 H 3.70 N 18.80

4'-Methyl-2,4-dinitroazobenzene (**3d**): From 1.3 g (5.1 mmol) of **1d** and 1.5 g (5.3 mmol) of **2a**, 0.9 g (62%) of **3d** is obtained after 16 h, m.p. 138°C (ref.[2b] 137–138°C). – ^{1}H NMR ([D$_6$]acetone): δ = 1.93 (s, 3H, Me), 6.73–7.36 (AA'BB', 4H, aromatic H), 7.30 (ABX, 1H, $^3J_{AB}$ = 9 Hz), 8.03 (ABX, 1H, $^3J_{AB}$ = 9 Hz, $^4J_{BX}$ = 3 Hz), 8.30 (ABX, 1H, $^4J_{XB}$ = 3 Hz). – ^{13}C NMR ([D$_6$]acetone): δ = 21.89 (CH$_3$), 121.11, 121.29, 124.93, 129.20, 131.30 (CH), 146.04, 147.96, 149.01, 149.40, 151.81 (C). – MS (70 eV): *m/z* (%) = 286 (15) [M$^+$], 119 (34) [CH$_3$-C$_6$H$_4$-N$_2^+$], 91 (100) [CH$_3$-C$_6$H$_4^+$]. – UV/Vis (acetonitrile): λ_{max} (lg ε) = 348 nm (4.428), 264 (4.009), 197 (4.451). – In the AAS analyses of **3d** no tin can be detected (sensitivity limit <120 ppm).

4-Ethyl-1-(trimethylstannyl)benzene (**1e**): To the Grignard reagent prepared from 50.0 g (0.27 mol) of *p*-bromoethylbenzene and 6.6 g (0.27 mol) of magnesium turnings in 250 ml of anhydrous THF is added a solution of 54.0 g (0.27 mol) of Me$_3$SnCl in 50 ml of anhydrous THF at 20°C during 30 min. After heating the reaction mixture at reflux for 2.5 h the solution is hydrolyzed with 200 ml of water. Twofold extraction of the aqueous phase with 100 ml of diethyl ether, drying of the combined organic phases with Na$_2$SO$_4$ and fractionating distillation yield 46.5 g (64%) of colorless **8**, b.p. 101°C/15 Torr. – ^{1}H NMR (CDCl$_3$): δ = 0.32 [s, $^2J_{SnH}$ = 54 Hz, 9H, (CMe$_3$)$_3$Sn], 1.27 (t, 3H, CH$_3$), 2.63 (q, 2H, CH$_2$), 7.30 (AA'BB', 4H, aromatic H). – ^{13}C NMR (CDCl$_3$): δ = –9.57 ($^1J_{SnC}$ = 341.6 Hz, Me$_3$Sn), 15.63 (CH$_3$), 28.85 (CH$_2$), 127.71 ($^2J_{SnC}$ = 47.7 Hz, CH), 135.81 (CH), 138.46 ($^1J_{SnC}$ = 438.1 Hz, Cq), 144.17 (Cq). – ^{119}Sn NMR (CDCl$_3$): δ = –29.13.

C$_{11}$H$_{18}$Sn (268.95) Calcd. C 49.12 H 6.75
Found C 49.30 H 6.10

4'-Ethyl-2,4-dinitroazobenzene (**3e**): From 1.3 g (3.7 mmol) of **1e** and 1.1 g (3.9 mmol) of **2a**, 0.6 g (54%) of **3e** is obtained after 18 h, m.p. 139°C. – ^{1}H NMR ([D$_6$]acetone): δ = 0.68 (t, 3H, Me), 2.17 (q, 2H, CH$_2$), 6.72–7.47 (AA'BB', 4H, aromatic H), 7.27 (ABX, 1H, $^3J_{AB}$ = 9 Hz), 8.00 (ABX, 1H, $^3J_{AB}$ = 9 Hz, $^4J_{BX}$ = 4 Hz), 8.27 (ABX, 1H, $^4J_{XB}$ = 4 Hz). – ^{13}C NMR ([D$_6$]acetone): δ = 15.61 (CH$_3$), 29.89 (CH$_2$), 120.95, 121.13, 124.89, 129.03, 129.97 (CH), 147.63, 148.8, 149.27, 151.80, 151.99 (C). – MS (70 eV): *m/z* (%) = 300 (27) [M$^+$], 105 (100) [Et-C$_6$H$_4^+$], 77 (23) [C$_6$H$_5^+$]. – UV/Vis (acctonitrile): λ_{max} (lg ε) = 467 nm (2.973), 344 (4.286), 263 (3.898), 194 (4.349).

C$_{14}$H$_{12}$N$_4$O$_4$ (300.27) Calcd. C 56.00 H 4.03 N 18.66
Found C 55.30 H 4.10 N 17.90

2',4',6'-Trimethyl-2,4-dinitroazobenzene (**3f**): From 2.4 g (5.9 mmol) of **1f** and 1.7 g (6.0 mmol) of **2a**, 1.2 g (65%) of **3f** is obtained after 6 h, m.p. 168°C (ref.[11b] 163–164°C). – ^{1}H NMR (CDCl$_3$): δ = 2.33 (s, 3H, Me), 2.50 (s, 6H, Me), 6.90 (s, 2H, aromatic H), 7.70 (ABX, 1H, $^3J_{AB}$ = 9 Hz), 8.40 (ABX, 1H, $^3J_{AB}$ = 9 Hz, $^4J_{BX}$ = 4 Hz), 8.60 (ABX, 1H, $^4J_{XB}$ = 4 Hz). – MS (70 eV): *m/z* (%) = 314 (13) [M$^+$], 119 (100) [(CH$_3$)$_3$C$_6$H$_6^+$]. – UV/Vis (acetonitrile): λ_{max} (lg ε) = 495 nm (3.079), 366 (4.298), 266 (3.914), 193 (4.561).

2'-Methoxy-4-nitroazobenzene (**3g**): From 1.3 g (4.8 mmol) of **1g** and 1.0 g (4.8 mmol) of **2b**, 0.2 g (16%) **3g** is obtained after 27 h. For the column chromatography CHCl$_3$ is used, m.p. 143°C. – ^{1}H NMR ([D$_6$]acetone/CDCl$_3$; 3:1): δ = 3.70 (s, 3H, OMe), 6.30–7.50 (m, 4H, aromatic H), 7.90 (AA'BB', 4H, aromatic H). – ^{13}C NMR ([D$_6$]acetone/CDCl$_3$; 3:1): δ = 55.03 (CH$_3$), 112.43, 115.44, 119.58, 122.46, 123.68, 133.31 (CH), 140.94, 147.60, 155.19, 157.16 (C). – MS (70 eV): *m/z* (%) = 257 (68) [M$^+$], 135 (76) [CH$_3$O-C$_6$H$_4$-N$_2^+$], 122 (36) [NO$_2$-C$_6$H$_4^+$], 92 (80) [C$_6$H$_4$O$^+$], 77 (100) [C$_6$H$_5^+$]. – UV/Vis (acetonitrile): λ_{max} (lg ε) = 376 nm (4.054), 325 (4.124), 211 (4.189), 192 (4.470).

C$_{13}$H$_{11}$N$_3$O$_3$ (257.23) Calcd. C 60.70 H 4.31 N 16.34
Found C 60.40 H 4.40 N 15.70

2'-Methoxy-2,4-dinitroazobenzene (**3h**): From 1.2 g (3.0 mmol) of **1h** and 0.9 g (3.2 mmol) of **2a**, 0.6 g (66%) of **3h** is obtained after 90 min, m.p. 169°C (from ethanol), no column chromatography is used. – ^{1}H NMR ([D$_6$]acetone, [D$_6$]DMSO, 1:1): δ = 3.55 (s, 3H, OMe), 6.26–7.23 (m, 4H, aromatic H), 7.38 (ABX, 1H, $^3J_{AB}$ = 9 Hz), 8.16 (ABX, 1H, $^3J_{AB}$ = 9 Hz, $^4J_{BX}$ = 4 Hz), 8.43 (ABX, 1H, $^4J_{XB}$ = 4 Hz). – ^{13}C NMR ([D$_6$]acetone, [D$_6$]DMSO; 1:1): δ = 56.04 (CH$_3$), 113.91, 116.70, 120.11, 120.39, 120.68, 128.36, 135.84 (CH), 141.80, 146.62, 147.68, 148.41, 158.61 (C). – MS (70 eV): *m/z* (%) = 302 (13) [M$^+$], 135 (55) [CH$_3$OC$_6$H$_4$N$_2^+$], 77 (100) [C$_6$H$_5^+$]. – UV/Vis (acetonitrile): λ_{max} (lg ε) = 384 nm (4.012), 329 (4.087), 212 (4.325), 191 (4.464).

C$_{13}$H$_{10}$N$_4$O$_5$ (302.25) Calcd. C 51.66 H 3.33 N 18.54
Found C 51.40 H 3.40 N 17.80

4'-Methoxy-4-nitroazobenzene (**3i**): From 1.3 g (4.8 mmol) of **1i** and 1.0 g (4.8 mmol) of **2b**, 0.7 g (57%) of **3i** is obtained after 7 h, m.p. 154°C (from ethanol) (ref.[11c] 157–158°C). No column chromatography is necessary. – ^{1}H NMR ([D$_6$]acetone, CDCl$_3$; 3:1): δ = 3.50 (s, 3H, OMe), 8.10 (AA'BB', 4H, aromatic H), 8.70 (AA'BB', 4H, aromatic H). – ^{13}C NMR ([D$_6$]acetone, CDCl$_3$; 3:1): δ = 54.45 (CH$_3$), 113.62, 122.14, 123.74, 124.50 (CH), 145.87, 147.46, 154.99, 162.59 (C). – UV/Vis (acetonitrile): λ_{max} (lg ε) = 370 nm (4.082), 191 (4.198).

4'-Methoxy-2,4-dinitroazobenzene (**3j**): From 1.3 g (4.8 mmol) of **1j** and 1.4 g (5.0 mmol) of **2a**, 1.2 g (83%) of **3j** is obtained after 120 s. No column chromatography is used, m.p. 178°C (from 250 ml of ethanol) (ref.[11d] 178°C). – ^{1}H NMR ([D$_6$]acetone, [D$_6$]DMSO; 1:1): δ = 3.68 (s, 3H, OMe), 6.77–7.87 (AA'BB', 4H, aromatic H), 7.67 (ABX, 1H, $^3J_{AB}$ = 9 Hz), 8.40 (ABX, 1H, $^3J_{AB}$ = 9 Hz, $^4J_{BX}$ = 4 Hz), 8.68 (ABX, 1H, $^4J_{BX}$ = 4 Hz). – ^{13}C NMR ([D$_6$]acetone, [D$_6$]DMSO; 1:1): δ = 55.47 (CH_3), 114.71, 119.77, 125.89 (CH), 146.26, 146.37, 147.1, 147.51, 164.02 (C). – UV/Vis (acetonitrile): λ_{max} (lg ε) = 392 nm (4.260), 365 (4.189), 278 (3.876), 249 (4.033), 214 (4.221), 195 (4.296).

2,4-Dinitro-4'-(trimethylsilyl)azobenzene (**3k**): From 1.5 g (4.8 mmol) of **1k** and 1.4 g (5.0 mmol) of **2a**, 0.6 g (36%) of **3k** is obtained after 20 h, m.p. 107°C. – ^{1}H NMR ([D$_6$]acetone): δ = −0.18 (s, 9H, $SiMe_3$), 7.33 (s, 4H, aromatic H), 7.45 (ABX, 1H, $^3J_{AB}$ = 9 Hz), 8.15 (ABX, 1H, $^3J_{AB}$ = 9 Hz, $^4J_{BX}$ = 4 Hz), 8.38 (ABX, 1H, $^4J_{XB}$ = 4 Hz). – ^{13}C NMR ([D$_6$]acetone): δ = −1.19 (CH_3), 121.03, 121.23, 123.56, 129.17, 135.43 (CH), 147.62, 148.94, 149.35, 153.62 (C). – IR (KBr): $\tilde{\nu}$ = 1538 cm^{-1}, 1346, 845, 758. – MS (70 eV): *m/z* (%) = 344 (23) [M$^+$], 149 (100) [Me_3Si-$C_6H_4^+$], 73 (77) [Me_3Si^+]. – UV/Vis (acetonitrile): λ_{max} (lg ε) = 341 nm (4.282), 216 (4.288), 198 (4.422).

$C_{15}H_{16}N_4O_4Si$ (344.40) Calcd. C 52.31 H 4.68 N 16.27
Found C 51.60 H 4.60 N 15.90

4'-Chloro-2,4-dinitroazobenzene (**3l**): From 1.3 g (4.7 mmol) of **1l** and 1.3 g (4.6 mmol) of **2a**, 0.2 g (14%) of **3l** is obtained after 18 h, m.p. 157°C (ref.[11e] 151–152°C). – ^{1}H NMR ([D$_6$]acetone): δ = 7.0–7.6 (m, 4H, aromatic H), 7.43 (ABX, 1H, $^3J_{AB}$ = 9 Hz), 8.15 (ABX, 1H, $^3J_{AB}$ = 9 Hz, $^4J_{BX}$ = 4 Hz), 8.40 (ABX, 1H, $^4J_{XB}$ = 4 Hz). – ^{13}C NMR ([D$_6$]acetone): δ = 121.1, 121.20, 126.15, 129.24, 130.83 (CH), 140.05, 149.05, 149.24, 151.88 (C). – MS (70 eV): *m/z* (%) = 306 (16) [M$^+$], 139 (53) [Cl-C_6H_4-N_2^+], 111 (100) [Cl-$C_6H_4^+$]. – UV/Vis (acetonitrile): λ_{max} (lg ε) = 339 nm (4.355).

5-Trimethylstannyl-1,3-benzodioxole (**4**): To the Grignard reagent prepared from 57.6 g (0.29 mol) of 5-bromo-1,3-benzodioxole and 7.0 g (0.29 mol) of magnesium turnings in 300 ml of anhydrous THF is added a solution of 54.0 g (0.27 mol) of Me_3SnCl in 50 ml of anhydrous THF at 20°C during 30 min. After heating of the reaction mixture at reflux for 8 h the solution is hydrolyzed with 300 ml of water. Twofold extraction of the aqueous phase with 100 ml of diethyl ether, drying of the combined organic phases with Na_2SO_4 and fractionating destillation yield 57.2 g (74%) of colorless **4**, b.p. 75°C/0.04 Torr. – ^{1}H NMR ($CDCl_3$): δ = 0.30 [s, $^2J_{SnH}$ = 72.5 Hz, 9H, $(CH_3)_3Sn$], 5.87 (s, 2H, CH_2), 6.93 (m, 3H, aromatic H). – ^{13}C NMR ($CDCl_3$): δ = −9.40 [$^1J_{SnC}$ = 351.0 Hz, $(CMe_3)_3Sn$], 100.13 (CH_2), 108.79 ($^2J_{SnC}$ = 57.2 Hz, CH), 114.88 ($^2J_{SnC}$ = 45.8 Hz, CH), 128.86 (CH), 134.08 ($^1J_{SnC}$ = 467.9 Hz, Cq), 147.45, 147.72 (Cq). – ^{119}Sn NMR ($CDCl_3$): δ = −22.45.

$C_{10}H_{14}O_2Sn$ (284.91) Calcd. C 42.16 H 4.95
Found C 40.00 H 5.00

(1,3-Benzodioxol-5-yl)(2,4-dinitrophenyl)diazene (**5**): From 1.5 g (5.3 mmol) of **4** and 1.5 g (5.3 mmol) of **2a**, 1.3 g (78%) of **5** are obtained after 120 s. No column chromatography is used, m.p. 177°C (from 250 ml ethanol). – ^{1}H NMR ([D$_6$]acetone): δ = 5.66 (s, 2H, CH_2), 6.57 (ABX, 1H, $^3J_{AB}$ = 8 Hz), 6.73 (ABX, 1H, $^4J_{XB}$ = 3 Hz), 7.20 (ABX, 1H, $^3J_{AB}$ = 8 Hz, $^4J_{BX}$ = 3 Hz), 7.40 (ABX, 1H, $^3J_{AB}$ = 9 Hz), 8.10 (ABX, 1H, $^3J_{AB}$ = 9 Hz, $^4J_{BX}$ = 4 Hz), 8.33 (ABX, 1H, $^4J_{XB}$ = 4 Hz). – UV/Vis (acetonitrile): λ_{max} (lg ε) = 408 nm (4.267), 339 (3.917), 274 (4.031), 197 (4.465). – MS (70 eV): *m/z* (%) = 316 (56) [M$^+$], 149 (58) [$CH_2O_2C_6H_3N_2^+$], 121 (100) [$C_6H_3O_2CH_2^+$].

$C_{13}H_8N_4O_6$ (316.23) Calcd. C 49.38 H 2.55 N 17.72
Found C 49.4 H 2.60 N 17.10

(2,4-Dinitrophenyl)(1-naphthyl)diazene (**7a**): According to the general procedure from 1.4 g (4.8 mmol) of **6a** and 1.4 g (5.0 mmol) of **2a** or from 1.4 g (3.4 mmol) of **6b** and 0.95 g (3.4 mmol) of **2a**, 1.0 g (65%) or 0.6 g (55%) of **7a** is obtained after 6 h, m.p. 192°C (ref.[11] 190°C) (from ethanol). No column chromatography is used. – ^{1}H NMR ([D$_6$]acetone, [D$_6$]DMSO; 1:1): δ = 7.18–8.4 (m, 7H, aromatic H), 8.15 (ABX, 1H, $^3J_{AB}$ = 9 Hz), 8.67 (ABX, 1H, $^3J_{AB}$ = 9 Hz, $^4J_{BX}$ = 4 Hz), 8.97 (ABX, 1H, $^4J_{XB}$ = 4 Hz). – MS (70 eV): *m/z* (%) = 322 (28) [M$^+$], 127 (100) [$C_{10}H_7^+$]. – UV/Vis (acetonitrile): λ_{max} (lg ε) = 414 nm (4.065), 285 (4.181), 220 (4.379).

$C_{16}H_{10}N_4O_4$ (322.28) Calcd. C 59.63 H 3.13 N 17.38
Found C 59.50 H 3.00 N 17.40

(2,4-Dinitrophenyl)(4-methyl-1-naphthyl)diazene (**7b**): According to the general procedure from 1.4 g (4.6 mmol) of **6c** and 1.3 g (4.6 mmol) of **2a**, 1.1 g (71%) of **7b** is obtained after 1 h. No column chromatography is used, m.p. 201°C (from ethanol). – ^{1}H NMR ([D$_6$]acetone, [D$_6$]DMSO; 1:1): δ = 2.47 (s, 3H, Me), 7.00–7.93 (m, 6H, aromatic H), 7.83 (ABX, 1H, $^3J_{AB}$ = 9 Hz), 8.37 (ABX, 1H, $^3J_{AB}$ = 9 Hz, $^4J_{BX}$ = 4 Hz), 8.63 (ABX, 1H, $^4J_{XB}$ = 4 Hz). – MS (70 eV): *m/z* (%) = 336 (18) [M$^+$], 141 (100) [$CH_3C_{10}H_6^+$]. – UV/Vis (acetonitrile): λ_{max} (lg ε) = 426 nm (4.160), 288 (4.200), 223 (4.559), 204 (4.537).

$C_{17}H_{12}N_4O_4$ (336.14) Calcd. C 60.71 H 3.60 N 16.66
Found C 60.40 H 3.55 N 16.70

(2-Naphthyl)(2,4-dinitrophenyl)diazene (**9**): According to the general procedure from 1.2 g (4.1 mmol) of **8** and 1.2 g (4.2 mmol) of **2a**, 1.0 g (76%) of **9** is obtained. No column chromatography is used, m.p. 185°C (from ethanol) (ref.[11f] 178°C). – ^{1}H NMR ([D$_6$]acetone, [D$_6$]DMSO; 1:1): δ = 7.23–8.53 (m, 7H, aromatic H), 7.73 (ABX, 1H, $^3J_{AB}$ = 9 Hz), 8.38 (ABX, 1H, $^3J_{AB}$ = 9 Hz, $^4J_{BX}$ = 4 Hz), 8.67 (ABX, 1H, $^4J_{XB}$ = 4 Hz). – MS (70 eV): *m/z* (%) = 322 (12) [M$^+$], 155 (14) [$C_{10}H_7N_2^+$], 127 (100) [$C_{10}H_7^+$]. – UV/Vis (acetonitrile): λ_{max} (lg ε) = 349 nm (4.306), 278 (4.179), 210.5 (4.563).

$C_{16}H_{10}N_4O_4$ (322.28) Calcd. C 59.63 H 3.13 N 17.38
Found C 59.60 H 3.15 N 17.40

CAS Registry Numbers

1a: 960-16-7 / **1b**: 17113-82-5 / **1c** (R = Me): 937-01-9 / **1c** (R = Bu): 68971-88-0 / **1d**: 937-12-2 / **1e**: 133965-74-9 / **1f**: 1077-62-9 / **1g**: 17113-77-8 / **1h**: 86487-17-4 / **1i**: 940-00-1 / **1k**: 944-32-1 / **1l**: 14064-15-4 / **2a**: 345-12-0 / **2b**: 456-27-9 / **3a**: 51640-16-5 / **3b**: 794-78-5 / **3c**: 133965-75-0 / **3d**: 6562-26-1 / **3e**: 133965-76-1 / **3f**: 973-78-4 / **3g**: 133965-77-2 / **3h**: 133965-78-3 / **3i**: 29418-59-5 / **3j**: 51640-06-3 / **3k**: 133965-79-4 / **3l**: 133965-80-7 / **4**: 69849-38-3 / **5**: 133965-81-8 / **6a**: 944-85-4 / **6b**: 972-09-8 / **6c**: 127686-17-3 / **7a**: 51758-79-3 / **7b**: 133965-82-9 / **8**: 945-77-7 / **9**: 123316-34-7

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