Synthesis of Aryl Nitroso Derivatives by *tert*-Butyl Hypochlorite Oxidation in Homogeneous Media. Intermediates for the Preparation of High-Hyperpolarizability Chromophore Skeletons

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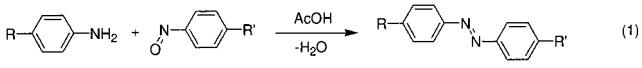
Introduction

Azo-containing chromophores are ubiquitous within the dye industry.[1] They have also been extensively studied in the area of organic nonlinear optics (NLO), often displaying higher hyperpolarizabilities and greater thermal stabilities than their stilbene counterparts.[2] In addition, azo chromophores contained in polymers may be oriented by polarized light irradiation in a process that involves both thermal- and photoisomerization of the azo linkage.[3] When irradiated in an electric field, azo chromophore polar orientation can often be induced at temperatures far below the glass transition temperature of the polymer.[4] Although the classical diazonium coupling reaction[5] is often the synthetic method of choice for the preparation of such chromophores, the Mills[6] coupling reaction between aryl nitroso derivatives and amines (eq 1) offers a valuable complimentary technique, providing that the prerequisite aromatic nitroso derivatives are accessible. In certain cases, the azo derivatives cannot be prepared by diazo coupling procedures due to side reactions.[7]



(1)

The most common procedure for preparing nitroso derivatives involves the heterogeneous oxidation of the corresponding hydroxylamine, using iron (III) chloride.[8] Other heterogeneous procedures involve silver carbonate,[9] tetrabutylammonium cerium(IV) nitrate,[10] Mo(O)$(O_2)_2(H_2O)$(hmpa) with H_2O_2,[11] iridium on carbon,[12] and pyridinium chlorochromate.[13] The heterogeneous oxidation reactions are often slow (frequently requiring several hours for completion), which can lead to the formation of the corresponding azoxy derivatives through coupling of any unconverted hydroxylamine with the nitroso product.[14] Additionally, the slow rate of heterogeneous oxidation can lead to low product yields in cases where either the hydroxylamine starting material and/or the nitroso product has limited stability and, hence, decomposes during the course of the reaction. To avoid azoxy byproduct formation, we have examined the use of *tert*-butyl hypochlorite as an inexpensive, homogeneous oxidizing reagent. *tert*-Butyl hypochlorite has been used in the oxidation of alcohols to ketones,[15] aldehydes to acid chlorides,[16] and sulfides to sulfoxides[17] as well as phosphines and phosphites to phosphine oxides and phosphates,[18] respectively. While sodium hypochlorite has been used to oxidize aromatic *N*-nitrosohydroxylamines to aromatic nitroso compounds,[19] there is to our knowledge no literature precedent for the use of hypochlorites in the oxidation of simple aromatic hydroxylamines to aromatic nitroso products.

Results and Discussion

To examine the general applicability of the hypochlorite oxidation procedure for aromatic nitroso synthesis, we studied comparatively the oxidation of a variety of phenylhydroxylamines, each substituted with electron-withdrawing substituents (Schemes 1−3). For purposes of comparison, we examined both the standard heterogeneous hydroxylamine oxidation with iron(III) chloride and the homogeneous hypochlorite procedure. One gram of each hydroxylamine was oxidized using each procedure, followed by isolation of the nitroso product and derivatization for spectral characterization and yield comparison. The results are compiled in Table 1. Since all of the nitroso products decompose to some degree during attempted purification by column chromatography on silica gel (**4c** is particularly unstable), the product yields from each procedure were estimated by subsequent Mills coupling with *p*-anisidine and isolation of the stable azo product. To confirm that the subsequent Mills coupling reaction was a viable procedure for estimating the yield of the corresponding nitroso product, compound **4d** was first rigorously purified then coupled with *p*-

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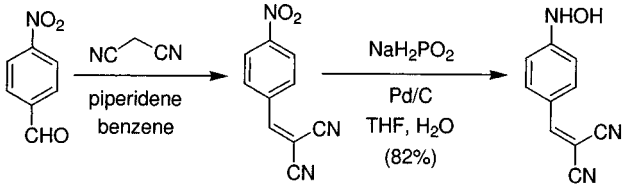
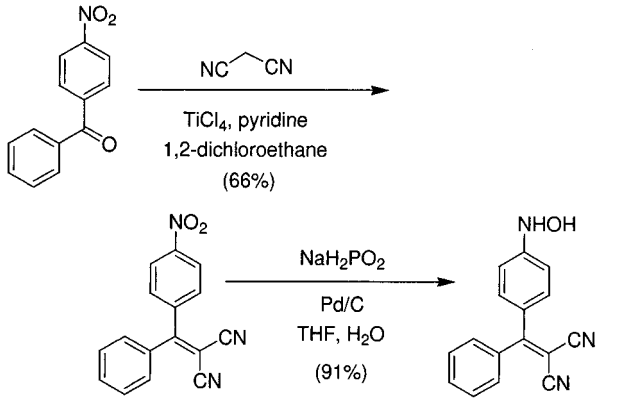
Scheme 1



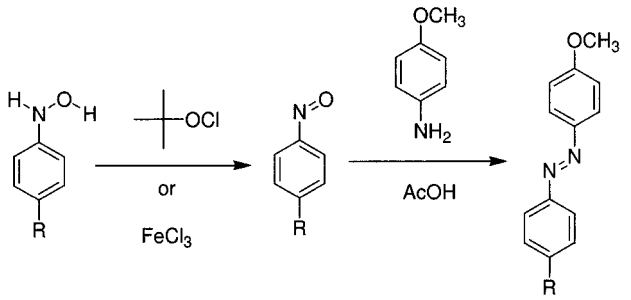
1 3c

Scheme 2



2 3d

Scheme 3



3 4a-e 5a-e

Reactant	R
a	—NO_2
b	—CN
c	NC, CN
d	NC, CN
e	O, O—CH_3

anisidine in acetic acid. The azo product **5d** was isolated in essentially quantitative yield, thus validating the assay.

Examination of the data in Table 1 shows that the *tert*-butyl hypochlorite procedure results in yields exceeding those obtained using the heterogeneous technique in every case. The improvement in yield may be attributed to the lower reaction temperatures and the significantly decreased reaction times. The oxidation with *tert*-butyl hypochlorite is very rapid and is essentially complete after addition of the oxidizing reagent, as evidenced by

Table 1. Comparison of Iron(III) Chloride and *tert*-Butyl Hypochlorite Hydroxylamine Oxidations

Reactant	R	Yield[a] ($FeCl_3$)	Yield[a] (*t*-Butyl Hypochlorite)
5a	—NO_2	56%	89%
5b	—CN	20%	95%
5c	NC, CN, H	0%	70%
5d	NC, CN,	93%	96%
5e	O, O—CH_3	2%	68%

[a] Yields of nitroso derivatives produced upon oxidation were estimated by the isolation and purification of the corresponding azo products derived from reaction with *p*-anisidine.

the formation of a green color characteristic of the nitroso derivative. To control the oxidation, it was necessary to utilize dilute reagents ($\sim 10^{-3}$ M), cool the reaction mixture to −78 °C, and rapidly stir to quickly disperse the oxidant to prevent overoxidation. In each case, the *tert*-butyl hypochlorite is added rapidly in one portion via syringe.

The present rapid oxidation procedure is particularly useful in cases where the starting hydroxylamine is thermally unstable. For example, 2-(4-(hydroxylamino)-phenyl)-1,1-dicyanoethylene (**3c**) is relatively unstable upon standing at room temperature and must be oxidized immediately after synthesis in order to produce the desired nitroso derivative in good yield. In this case, the slower oxidation rate intrinsic to the heterogeneous iron-(III) chloride procedure results primarily in the formation of the corresponding azoxy derivative. In contrast, the *tert*-butyl hypochlorite procedure affords a nearly 70% yield of the desired nitroso product, with no detectible azoxy formation.

In conclusion, we have developed an efficient, inexpensive, high-yielding method of converting arylhydroxylamines to arylnitroso intermediates that are themselves useful precursors for azo chromophore synthesis. This method is particularly applicable to the preparation of nitroso compounds where the standard heterogeneous oxidation procedures lead primarily to the corresponding azoxy derivatives. The nitroso products are formed in high yield, as assayed by isolation of the corresponding azo derivatives via subsequent Mills coupling. This technique provides a useful route to a variety of potentially interesting chromophore skeletons.

Experimental Section

^{1}H NMR and ^{13}C NMR spectra were measured at 250 and 63 MHz, respectively, and the chemical shifts are referenced to tetramethylsilane (TMS). Melting points are reported as the temperature at the peak of the melting point endotherm, measured by differential scanning calorimetry (DSC) at a

heating rate of 20 °C/min. All chromatography was performed as flash column chromatography.[20] All chemicals were obtained from Aldrich Chemical, except where indicated. Commercial grade sodium hypochlorite (Clorox) was used for the preparation of *tert*-butyl hypochlorite.

Reagents. *tert*-Butyl hypochlorite was freshly prepared as described in the literature.[21] The reagent was standardized using potassium iodide followed by titration of iodine using 0.1 N sodium thiosulfate. 2-(4-Nitrophenyl)-1,1-dicyanoethylene (**1**),[22] (4-nitrophenyl)hydroxylamine (**3a**),[8] 4-hydroxylaminobenzonitrile (**3b**),[23] and methyl 4-(hydroxylamino)benzoate (**3e**)[24] were prepared using methods described in the literature.

2-(4-Nitrophenyl)-2-phenyl-1,1-dicyanoethylene (2). In a 1 L three-necked flask equipped with a water-cooled condenser, dropping funnel, thermometer, and magnetic stirring bar, 4-nitrobenzophenone (22.72 g, 0.100 mol) and malononitrile (16.52 g, 0.250 mol) were dissolved in 225 mL of 1,2-dichloroethane. After the mixture was cooled to 5 °C (ice/water bath) under argon, titanium tetrachloride (40 mL, 0.365 mol) was added dropwise over 30 min (bright yellow color). While the solution was maintained at 5 °C, pyridine (80 mL, 0.989 mol) was added dropwise over 30 min. Upon completion of addition, the cooling bath was removed, and the solution was heated to reflux overnight. After the mixture was cooled to room temperature, the reaction mixture was filtered through Celite. The filtered solids were slurried with chloroform, and the solution was filtered and washed 3× with 10% HCl (aq) and 2× with 10% $NaHCO_3$. The organic extracts were combined and dried over $MgSO_4$. After filtration, the filtrate was adsorbed onto silica gel and chromatographed using 20% ethyl acetate/hexane. Colorless needles of **2** were obtained upon recrystallization from 2-propanol: yield, 18.24 g (66%); mp 105 °C; ^{1}H NMR (DMSO-d_6) δ 8.38 (d, 2H, J = 9 Hz), 7.77 (d, 2H, J = 10 Hz), 7.57 (m, 5H); ^{13}C NMR (DMSO-d_6) δ 171.46, 149.27, 141.98, 135.19, 132.90, 131.50, 130.11, 129.04, 123.92, 113.75, 113.63, 84.66; IR (KBr) 2236, 1569, 1522, 1352, 1331 cm^{-1}; UV (THF) λ_{max}, nm (ϵ) 318 (13 790). Anal. Calcd for $C_{16}H_9N_3O_2$: C, 69.81; H, 3.30; N, 15.27. Found: C, 70.15; H, 3.39; N 15.31.

2-(4-(Hydroxylamino)phenyl)-1,1-dicyanoethylene (3c). Into a three-necked flask equipped with an overhead stirrer, were placed 70 mL of THF and 8.00 g (0.04 mol) of **1** under argon. Sodium hypophosphite nonahydrate (10.6 g, 0.10 mol) was dissolved in 70 mL of distilled water and added to the THF solution. After the solution was cooled with an ice/water bath, 10% Pd/C (0.60 g) was added in small portions. Upon completion of the addition, the cooling bath was removed, and the solution was heated to 40−45 °C, while stirring vigorously, and the reaction progress was monitored by TLC (40% THF/hexane). When no further nitro compound was present (2 h), the solution was filtered through Celite. Ethyl acetate (150 mL) was added, the solution washed with distilled water (3×), and the organic phase dried over Na_2SO_4. Next the organic phase was filtered, and the solvent was removed under reduced pressure. The residue was redissolved in 250 mL of THF and filtered through Celite. The filtrate was then chromatographed on silica gel (gradient elution: 40, 60, 80% ethyl acetate/hexane). The solvent was removed under reduced pressure, the residue was dissolved in THF and filtered, and toluene was added. The solution was concentrated until precipitation occurred, and the solid was then collected and dried. The resulting orange solid was used without further purification: yield 6.1 g (82%); mp 132−133 °C; ^{1}H NMR (DMSO-d_6) δ 9.87 (s, 1H, *NH*OH), 9.21 (s, 1H, NH*OH*), 8.06 (s, 1H, vinyl), 7.81 (d, 2H, J = 9 Hz, Ar), 6.82 (d, 2H, J = 9 Hz, Ar); ^{13}C NMR (DMSO-d_6) δ 159.31, 156.29, 133.67, 120.59, 116.06, 115.23, 110.38, 69.92; IR (KBr) 3500−3100, 2225, 1612, 1517 cm^{-1}; EI MS m/z 185 (M$^+$).

2-(4-(Hydroxylamino)phenyl)-2-phenyl-1,1-dicyanoethylene (3d). Into a three-necked flask equipped with an overhead stirrer were placed 40 mL of THF and 6.01 g (0.0218 mol) of **2** under argon. Sodium hypophosphite nonahydrate (5.89 g, 0.0556 mol) was dissolved in 30 mL of distilled water and added to the THF solution. The solution was cooled with an ice/water bath, 10% Pd/C (0.60 g) was added, and the solution was stirred vigorously while the reaction progress was monitored by TLC (5% ethyl acetate/dichloromethane). When the starting material was consumed (45 min), the solution was filtered through Celite, 100 mL of ethyl acetate was added, and the organic phase was washed with distilled water (3×). The organic layer was then separated, dried over $MgSO_4$, filtered, adsorbed onto silica gel, and chromatographed (gradient elution: 0%, 5%, 10% ethyl acetate/methylene chloride). The bright orange product was used without further purification: yield 5.19 g (91%); mp 169 °C dec; ^{1}H NMR (DMSO-d_6) δ 9.49 (s, 1H, *NH*OH), 8.95 (s, 1H, NH*OH*), 7.57 (m, 3H, Ar), 7.43 (d, 2H, J = 7 Hz, Ar), 7.32 (d, 2H, J = 9 Hz, Ar), 6.82 (d, 2H, J = 9 Hz, Ar); ^{13}C NMR (63 MHz, DMSO-d_6) δ 173.40, 155.93, 136.68, 132.87, 131.90, 130.38, 128.67, 124.02, 115.82, 115.46, 110.62, 74.44; IR (KBr) 3500−3350, 2231, 1605, 1513, 1347 cm^{-1}; UV (THF) λ_{max}, nm (ϵ) 380 (26,380); EI MS m/z 261 (M$^+$). Anal. Calcd for $C_{16}H_{11}N_3O$: C, 73.55; H, 4.24; N, 16.08. Found: C, 73.75; H, 4.27; N, 15.78.

General Procedures for the Preparation of Nitroso Derivatives. A. Iron (III) Chloride Standard Procedure. Iron(III) chloride (5.5 equiv) was dissolved in 125 g of ice/water and cooled with an ice/water bath to 20 °C. In a separate flask, 1.0 g of the hydroxylamine was dissolved in 40 mL of ethanol and added dropwise to the stirring iron(III) chloride solution across 20−30 min. The solution was then stirred an additional 30 min and filtered through Celite, 200 mL of ethyl acetate was added, and the solution was extracted 3× with water. The organic layer was dried over Na_2SO_4, filtered, and the solvent was removed under reduced pressure. The crude product was used for derivatization without further purification.

B. *tert*-Butyl Hypochlorite Standard Procedure. The hydroxylamine derivative (1.0 g) was placed into a three-necked 1-L flask fitted with a gas inlet valve, thermometer, and magnetic stirrer and was dissolved in 500 mL of diethyl ether or THF under argon. The solution was cooled to −78 °C and stirred rapidly during the addition of 1.0 equiv of *tert*-butyl hypochlorite. The solution was allowed to stir for an additional 5 min, the cooling bath was removed, and the solution was allowed to warm to −20 °C. The solvent was removed under reduced pressure (25 mmHg) at 0 °C, and the product was dried under high vacuum (0.1 mmHg) at room temperature. The crude product was converted to the corresponding azo derivative without further purification.

4-Nitronitrosobenzene (4a). Using method B and **3a** in diethyl ether, the crude product was obtained in 97% yield and was used without further purification after spectral and chromatographic comparison with an authentic sample.[25]

4-Nitrosobenzonitrile (4b). Using method B and **3b** in diethyl ether, the crude product was obtained in 99% yield and was used without further purification after spectral and chromatographic comparison with an authentic sample.[26]

2-(4-Nitrosophenyl)-1,1-dicyanoethylene (4c). Using method B and **3c** in THF, the crude product was obtained in 82% yield: mp 122−124 °C; ^{1}H NMR (DMSO-d_6) δ 8.70 (s, 1H, vinyl), 8.24 (d, 2H, J = 9 Hz, Ar), 8.13 (d, 2H, J = 9 Hz, Ar); IR (KBr) 2230, 1592, 1566, 1421, 1297 cm^{-1}; EI MS m/z 183 (M$^+$).

2-(4-Nitrosophenyl)-2-phenyl-1,1-dicyanoethylene (4d). Using method B and **3d** in diethyl ether, the crude product was obtained in 95% yield: mp 105 °C; ^{1}H NMR (DMSO-d_6) δ 8.10 (d, 2H, J = 7 Hz, Ar), 7.87 (d, 2H, J = 7 Hz, Ar), 7.57 (m, 5H, Ar); ^{13}C NMR (DMSO-d_6) δ 171.82, 163.92, 142.70, 135.15, 132.87, 131.92, 130.11, 129.05, 120.67, 113.80, 113.70, 84.54; IR (KBr) 2231, 1269, 1159 cm^{-1}; UV (THF) λ_{max}, nm (ϵ) 294 (18 157); EI MS m/z 259 (M$^+$). Anal. Calcd for $C_{16}H_9N_3O$: C, 74.12; H, 3.50; N, 16.21. Found: C, 74.04; H, 3.88; N, 15.95.

Methyl 4-nitrosobenzoate (4e). Using method B and **3e** in THF, the crude product was obtained in 82% yield: mp 130 °C (lit.[25] mp 130 °C); ^{1}H NMR ($CDCl_3$) δ 8.29 (d, 2H, J = 9 Hz, Ar), 7.91 (d, 2H, J = 7 Hz, Ar), 3.96 (s, 3H, OCH_3); ^{13}C NMR ($CDCl_3$)

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δ 165.74, 164.39, 135.21, 131.05, 120.39, 52.77; IR (KBr) 1734, 1443, 1419, 1256, 1029 cm^{-1}; UV ($CHCl_3$) λ_{max}, nm (ϵ) 288 (15 310).

General Procedure for the Preparation of Azo Derivatives from Aryl Nitroso Compounds. Solid crude nitroso compounds (1.0 equiv) were added to a solution of *p*-anisidine (2.0 equiv) dissolved in glacial acetic acid and stirred for 3−24 h at room temperature. The reaction progress was monitored by TLC analysis (ethyl acetate/hexane). After the disappearance of the starting material, ethyl acetate was then added to the reaction mixture, the organic phase was washed with water (3×), and dried over $MgSO_4$. After filtration, the resulting mixture was purified by flash chromatography on silica gel and recrystallized.

(4-Methoxyphenyl)(4-nitrophenyl)diazene (5a). 5a was purified by flash chromatography over silica gel (33% ethyl acetate/hexane) followed by recrystallization from ethanol (89%). The spectral properties were identical to those of an authentic sample.[27, 29]

4-((4-Methoxyphenyl)diazenyl)benzonitrile (5b). 5b was purified by flash chromatography over silica gel (33% ethyl acetate/hexane) followed by recrytallization from ethanol (95%). The spectral properties were identical to those of an authentic sample.[28]

2-(4-((4-Methoxyphenyl)diazenyl)phenyl)-1,1-dicyanoethylene (5c). The product **5c** was purified by flash chromatography over silica gel (20% ethyl acetate/hexane) followed by recrystallization from ethanol (70%): mp 174−175 °C; ^{1}H NMR (DMSO-d_6) δ 8.59 (s, 1H, vinyl), 8.12 (d, 2H, J = 9 Hz, Ar), 7.99 (d, 2H, J = 9 Hz, Ar), 7.93 (d, 2H, J = 9 Hz, Ar), 7.15 (d, 2H, J = 9 Hz, Ar), 3.87 (s, 3H, OCH_3); ^{13}C NMR (DMSO-d_6) δ 162.96, 160.21, 154.64, 146.33, 132.80, 131.97, 125.31, 123.02, 114.84, 114.21, 113.29, 82.12, 55.80; IR (KBr) 2222, 1583, 1500, 1402 cm^{-1}; UV (THF) λ_{max}, nm (ϵ) 392 (46 210). Anal. Calcd for $C_{17}H_{12}N_4O$: C, 70.82; H, 4.19; N, 19.43. Found: C, 70.88; H, 4.23; N, 19.17.

2-(4-((4-Methoxyphenyl)diazenyl)phenyl)-2-phenyl-1,1-dicyanoethylene (5d). Compound **4d** and *p*-anisidine were coupled as described. A small amount of THF was added to the acetic acid solution to improve solubility. Flash chromatography (33% ethyl acetate/hexane) and recrystallization from ethanol gave **5d** in 96% yield: mp 144−145 °C; ^{1}H NMR (DMSO-d_6) δ 7.95 (m, 4H, Ar), 7.62 (m, 7H, Ar), 7.16 (d, 2H, J = 9 Hz, Ar), 3.87 (s, 3H, OCH_3); ^{13}C NMR (DMSO-d_6) δ 172.99, 162.77, 153.96, 146.32, 137.55, 135.78, 132.68, 131.72, 130.28, 128.95, 125.14, 122.40, 114.80, 114.21, 82.52, 55.78; IR (KBr) 2231, 1605, 1507, 1259 cm^{-1}; UV (THF) λ_{max}, nm (ϵ) 380 (50 789). Anal. Calcd for $C_{23}H_{16}N_4O$: C, 75.81; H, 4.43; N, 15.37. Found: C, 76.19; H, 4.72; N, 15.34.

Methyl 4-((4-methoxyphenyl)diazenyl)benzoate (5e). Compound **4e** and *p*-anisidine were coupled as described, adding a small quantity of THF to improve solubility. Flash chromatography (33% ethyl acetate/hexane) followed by recrystallization from ethanol gave **5e** in 68% yield: mp 172 °C (lit.[29] mp 170−171 °C);[29] ^{1}H NMR ($CDCl_3$) δ 8.15 (d, 2H, J = 9 Hz, Ar), 7.93 (d, 2H, J = 9 Hz, Ar), 7.88 (d, 2H, J = 9 Hz, Ar), 7.00 (d, 2H, J = 9 Hz, Ar), 3.93 (s, 3H, CO_2CH_3), 3.87 (s, 3H, OCH_3); ^{13}C NMR (DMSO-d_6) δ 166.63, 162.68, 155.36, 147.02, 131.18, 130.59, 125.20, 122.33, 114.33, 55.62, 52.27; IR (KBr) 1717, 1611, 1501, 1437, 1262, 1029 cm^{-1}; UV (THF) λ_{max}, nm (ϵ) 358 (26 010).

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