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Synthesis of Azobenzenes from Quinone Acetals and Arylhydrazines

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Direct reaction between quinone bisacetals and arylhydrazines gives azobenzenes. The presence of catalytic amounts of cerium ammonium nitrate strongly accelerates the reaction. When the bisacetal has a substituent at the 2,5-cyclohexadiene framework, only one regioisomer is formed. The method represents a simple, mild, and novel synthetic access to differently substituted azocompounds in high to excellent yield.

Introduction

Azobenzenes have found important applications as dyes.[1] In recent years, an enormous interest has emerged in their light-driven reversible cis−trans isomerization. The photoisomerization of the azo linkage has found important applications in either biologic[2] or physical−chemical[3] systems, such as liquid crystals[4,5] or their dopant agents,[6a] molecular switches,[6,7] photoresponsive gels,[8] ion shuttles,[9] crown ethers,[10] or calixarenes and different molecular devices.[11] Coupling of diazonium salts with activated aromatic compounds is the most common procedure for synthesizing azobenzenes.[12,13] However, the scope of reactions employing diazonium salts presents characteristic problems. Phenols and anilines are the usual activated aromatic compounds used for the coupling of diazonium salts. The method is highly pH dependent, and the substitution partner of the resulting azoarene is limited. Moreover, handling diazonium salts, especially when dried, is highly risky. In some cases, this leads to the generation of diazonium salts in situ, thus water-sensitive compounds cannot be employed. Notwithstanding this risk, coupling of isolated diazonium salts with organometallics[14] or coupling in the presence of Cu salts[15] have also been reported to synthesize azoarenes. The Mills coupling of anilines with nitroso derivatives[16] also allows the synthesis of asymmetrically substituted azo derivatives, and the Wallach rearrangement of azoxy compounds[16b,17] has been shown to be general enough to synthesize azo phenols. Albeit less general, other procedures such as the reduction of nitro compounds,[18] the dehydrogenation of arylhydrazines,[19] and the rearrangement of aryl triazenes[20] also allow the synthesis of azo compounds. Recently, a two-step synthesis based on the Pd-catalyzed reaction of N-Boc aryl hydrazines with aryl halides followed by the oxidation

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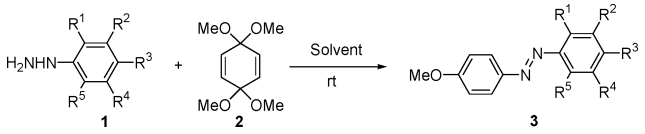
of the resulting hydrazines has been reported.[21] Although noteworthy progress have been made in the development of complementary strategies for the synthesis of such compounds, there remains a need for additional approaches. In connection with a program directed at the synthetic explotation of quinone derivatives, we recently found an efficient synthesis of *N*-arylquinone imine acetals based on the reaction of quinone bisacetals with anilines in the absence of any added catalyst.[22] The available evidence suggested that the reaction was catalyzed by an acidic radical cation formed in situ by the one-electron oxidation of the arylamines.[23] To check the behavior of arylhydrazines in a similar process, we examined their reaction with quinone bisacetals taking into account the possible formation of radical cations from hydrazines.[24] Although quinones have been extensively employed in synthesis,[25] the only reports related to similar reactions on benzoquinone derivatives we have found are related to the synthesis of mono- and dinitrobenzeneazo-4-hydroxy benzenes[26] and other azophenols from *p*-benzoquinone and phenylhydrazines in the absence of catalysts,[27] or in the presence of H_2SO_4.[28] We now report a new, experimentally simple, and high-yielding procedure to synthesize azobenzenes by direct reaction of quinone bisacetals with arylhydrazines and show that it is general enough for the preparation of asymmetrically substituted derivatives. The bis- and monoacetals of quinones are frequently used as synthetic equivalents to overcome reactivity and/or selectivity problems[29,30] that emerge from quinones themselves. Such derivatives allow the regioselective preparation of aromatic systems.[29b] Monoacetals are of special value as regiospecific quinone equivalents for 1,4-conjugate additions[31] and Diels−Alder[30] and Heck reactions.[32] The bisacetals have been utilized to produce carbene complexes[33] or as umpolung reagents for quinones,[34] but to our knowledge, this is their first application as starting materials for azobenzenes.

TABLE 1. Reactions of Bisacetal 2 with Arylhydrazines 1



entry	1	R^1	R^2	R^3	R^4	R^5	solvent	time	3	yield (%)
1	**1a**	NO_2	H	NO_2	H	H	MeCN	5 min	**3a**	99
2	**1b**	NO_2	H	H	H	H	MeCN	19 h	**3b**	71
3	**1c**	H	H	NO_2	H	H	MeCN	19 h	**3c**	66[a]
4	**1d**	Br	H	H	H	H	MeCN	3 h	**3d**	83
5	**1e**	CF_3	H	H	H	H	$CHCl_3$	18 h	**3e**	69
6	**1f**	F	H	H	F	H	$CHCl_3$	48 h	**3f**	78
7	**1g**	F	F	F	F	F	$CHCl_3$	18 h	**3g**	77
8	**1h**	F	F	CF_3	F	F	$CHCl_3$	24 h	**3h**	72
9	**1i**	H	H	H	H	H	MeCN	27 h	**3i**	25 (80)[b]
10	**1j**	H	H	OMe	H	H	MeCN	7 d	**3j**	43 (79)[b]

[a] A 90:10 mixture of **3c** and 4,4-dimethoxy-2,5-cyclohexadienone **4**[37] was formed (ratio determined by ^{1}H NMR). [b] Reaction carried out in the presence of CAN, time 18 h.

Results and Discussion

The starting bis-dimethyl acetal of *p*-benzoquinone **2** is commercially available whereas 2-*p*-tolylsulfinyl-1,1,4,4-tetramethoxy-2,5-cyclohexadiene **5** and the 2-methoxy substituted analogue **7** were readily accessible by anodic oxidation of 2-*p*-tolylsulfinyl-1,4-dimethoxybenzene[35] and 1,2,4-trimethoxybenzene,[36] respectively, using KOH as electrolyte in a methanolic solution.

In the endeavor to search for a simple synthetic procedure, we checked the direct reaction of arylhydrazines **1** with quinone bisacetal **2** in different solvents (CH_3CN, CH_2Cl_2, $CHCl_3$) at room temperature. The best results are shown in Table 1. Thus, 2,4-dinitrophenylhydrazine **1a** reacted with **2** in CH_3CN in a few minutes to give azocompound **3a**, which was isolated pure from the solution by filtration (entry 1, 99% yield). *o*- and *p*-nitrophenylhydrazines **1b** and **1c** reacted more slowly than **1a**, but led to azobenzenes **3b** and **3c** in good yields (entries 2 and 3). Bromo derivative **1d** afforded azobenzene **3d** after 3 h in 83% yield (entry 4). With fluoro-substituted arylhydrazines **1e**−**h** (entries 5−8), best yields were reached in chlorinated solvents which allowed the isolation of azobenzenes **3e**−**h** in 69−78% yield. In contrast, unsubstituted phenylhydrazine **1i** and arylhydrazine **1j**, bearing an electron-donating *p*-OMe group at the aromatic ring, reacted with **2** much more slowly and in lower yields (entries 9 and 10).

We showed that the presence of Et_3N in the CH_3CN solution of **1a** and **2** inhibited the reaction. This evidence reinforced our initial assumption on the existence of an acidic species triggering the reaction. The active species

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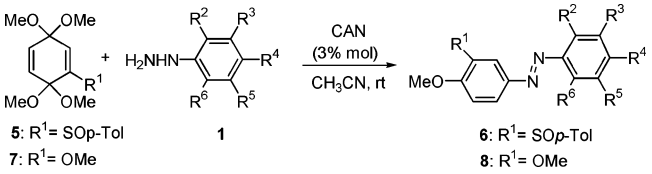
TABLE 2. Reactions of Bisacetal 5 and 7 with Arylhydrazines 1 in the Presence of CAN



5: R^1= SOp-Tol **1** **6**: R^1= SO*p*-Tol
7: R^1= OMe **8**: R^1= OMe

entry	acetal	**1**	R_2	R_3	R_4	R_5	R_6	time	**6**/**8**	yield (%)
1	**5**	**1a**	NO_2	H	NO_2	H	H	30 min	**6a**	85 (77)[a]
	5	**1f**	F	H	H	F	H	1 h	**6f**	98 (45)[a]
3	**5**	**1g**	F	F	F	F	F	2 h	**6g**	60 (59)[a]
4	**5**	**1h**	F	F	CF_3	F	F	2 h	**6h**	98 (98)[a]
5	**7**	**1a**	NO_2	H	NO_2	H	H	1 h	**8a**	99
6	**7**	**1e**	CF_3	H	H	H	H	1 h	**8e**	96
7	**7**	**1f**	F	H	H	F	H	1 h	**8f**	99
8	**7**	**1g**	F	F	F	F	F	5 min	**8g**	98
9	**7**	**1h**	F	F	CF_3	F	F	5 min	**8h**	98
10	**7**	**1k**	H	H	CF_3	H	H	1 h	**8k**	88
11	**7**	**1i**	H	H	H	H	H	1 h	**8i**	85

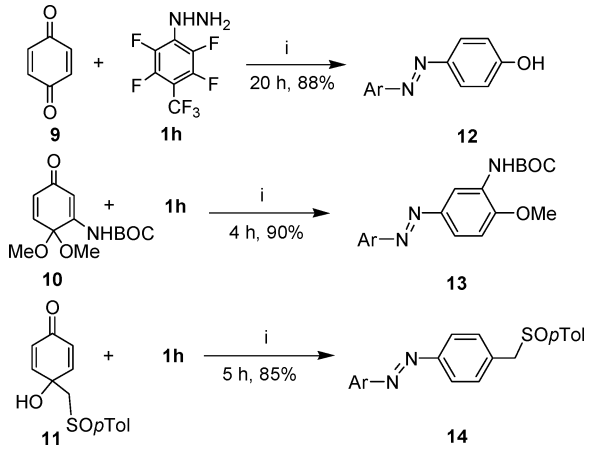
[a] Experiments carried out in the absence of CAN, reaction times ranged from 3 to 4 days.

could be a radical cation resulting from one-electron oxidation of **1a** by air. The higher acidity of the radical cation resulting from hydrazines bearing electron-withdrawing substituents[38] is in accordance with the best results achieved with **1a**−**h**. Such an acidic species must catalyze the condensation of the hydrazine with one of the acetal groups of **2** forming an intermediate hydrazone,[39] which evolve into the azocompound by MeOH elimination. Following this reasoning, we carried out the reaction of **2** with phenylhydrazines **1i** and **1j** in the presence of a one-electron oxidant such as $(NH_4)_2[Ce(NO_3)_6]$ (CAN) and observed a remarkable increase of the reaction rate, being **3i** and **3j** obtained in 18 h in 80% and 79% yield, respectively (Table 1, entries 9 and 10, footnote *b*).

On the other hand, no reaction was observed with alkylhydrazines such as benzyl and *N*,*N*-dimethylhydrazine. These observations also pointed to the existence of an intermediate radical cation catalyzing the reaction,[40] easily formed from aromatic hydrazines.

The excellent yields and shorter reaction times reached in the presence of CAN were shown to be general for other quinone bisacetals. Thus, 2-*p*-tolylsulfinyl-substituted bisacetal **5** also reacted with arylhydrazines **1a**,**f**−**h** to yield azobenzenes **6a**,**f**−**h** (Table 2, entries 1−4, footnote *a*). An essential point to reach good yields in these experiments was the use of dry CH_3CN to avoid partial transformation of **5** into 3-*p*-tolylsulfinyl-4,4-dimethoxy-2,5-cyclohexadien-1-one.[35] Again, catalytic amounts of CAN decreased the reaction times and

SCHEME 1[a]



[a] Reagents and conditions: (i) CAN (3% mol), CH_3CN, rt.

increased the yields for **6a**,**f**−**h** (Table 2, entries 1−4). Reactions of 1,1,2,4,4-pentamethoxy-2,5-cyclohexadienone **7** with arylhydrazines bearing electron-withdrawing substituents **1a**,**e**−**h**,**k** occurred in excellent yields (Table 2, entries 5−10). Even phenylhydrazine **1i** (Table 2, entry 11) afforded **8i** in 85% yield. Asymmetrically substituted bisacetals **5** and **7** reacted exclusively by the less hindered acetal group to give azo derivatives bearing a C-3 substituent at the 4-methoxy-substituted aromatic moiety.

To extend this excellent procedure, we have examined the reaction of some arylhydrazines with other quinone derivatives. We have achieved the synthesis of azophenol **12** in 88% isolated yield by reacting *p*-benzoquinone **9** with 4-trifluoromethyl-2,3,5,6-tetrafluorophenylhydrazine **1h** in acetonitrile solution in the presence of CAN (3 mol %). Amino-substituted azobenzene **13** and the (*p*-tolylsulfinyl)methyl-substituted analogue **14** were also synthesized in excellent yields by reaction of perfluorinated *p*-tolylhydrazine **1h** with quinone monoacetal **10**[41] and *p*-quinol derivative **11**[42,43] (Scheme 1). These results showed that our protocol can be successfully applied to 1,4-benzoquinones and derivatives with doubly conjugated carbonyl groups. In addition, starting from [(S)*R*]-**11**, optically pure [(S)*R*]-**14** {$[\alpha]^{20}_D$ +132 (*c* 1, $CHCl_3$)} was formed, showing that the configurational integrity of the sulfoxide withstood the reaction conditions.

In summary, we have reported a new synthesis of azobenzenes bearing a variety of substituents on the aromatic fragments from quinone bisacetals and aryl hydrazines. The presence of catalytic amounts of CAN significantly increases the reaction rates and improves the yields when the arylhydrazines bear electron-donating substituents. Taking into account that quinone bisacetals are easily obtained by anodic oxidation of 1,4-dimethoxybenzenes, this method opens a direct and simple access to a wide range of substituted azobenzenes under very mild conditions. The reaction was extended to 4,4-disubstituted-2,5-cyclohexadienones and *p*-benzo-

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(40) CAN could also act as a Lewis acid, but the easy reaction occurring from 2,4-dinitrophenylhydrazine in the absence of CAN pointed to a different active acidic species.
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quinone, integrating interesting substituents to the azobenzenes. Nevertheless, the use of bisacetals instead of quinones themselves avoids the frequently observed reduction to the hydroquinone systems. To our knowledge, the present report is the first of such a mild, high-yielding, and feasible synthesis of azocompounds from commercially available or easily accessible materials.

Experimental Section

General Procedure for the Synthesis of Azobenzenes (Method A): Synthesis of 4′-Methoxy-2-trifluoromethylazobenzene (3e). To a solution of 3,3,6,6-tetramethoxy-1,4-cyclohexadiene **2** (1.3 g, 6.5 mmol) in CH_3CN (10 mL), was added 2-trifluoromethyphenylhydrazine **1e** (6.5 mmol). The resulting mixture was stirred at room temperature for 18 h, then the solvent was removed and the crude mixture was purified by column chromatography (AcOEt/hexane 1:40) to give azobenzene **3e** as an orange oil (69% yield). ^{1}H NMR δ 7.99−7.95 (AA′, 2H), 7.04−7.00 (XX′, 2H), 7.81 (dd, 2H, J = 7.9 and 4.0 Hz), 7.63 (ddd, 1H, J = 7.5 and 1.1 Hz), 7.5 (ddd, 1H, J = 7.5 and 1.2 Hz), 3.91 (s, 3H, OMe).^{13}C NMR δ 162.7, 149.7, 147.2, 132.5, 129.7, 128.0 (c, J = 30.5 Hz), 125.5 (2C), 124.1 (c, J = 274.7 Hz), 116.2, 114.3 (2C), 55.6. EM (*m*/*z*) 280(40), 135 (48), 121 (10), 107 (100), 92 (37), 77 (52), 64 (20). HRMS (EI) calcd for $C_{14}H_{11}N_2OF_3$ (M^+) 280.0822, found 280.0823.

General Procedure for the Synthesis of Azobenzenes in the Presence of CAN (Method B): Synthesis of 4′-Methoxy-3′-*p*-tolylsulfinyl-2,5-difluoroazobenzene (6f). To a solution of the bisacetal **2** (1.0 mmol) in CH_3CN (2 mL) were added 2,4-difluorophenylhydrazine **1f** (1.0 mmol) and 16.7 mg (3% mol) of $(NH_4)_2[Ce(NO_3)_6]$. The resulting mixture was stirred at room temperature for 4 days. Water (10 mL) was then added and the mixture was extracted with AcOEt (3 × 20 mL). The combined organic layers were dried over $MgSO_4$, the solvent was removed in vacuo, and the crude product was purified by column chromatography (AcOEt/hexane 1:10) to give azocompound **6f** as a brown oil (98% yield). ^{1}H NMR δ 8.58 (d, 1H, 7.96, J = 2.4 Hz), 7.99 (dd, 1H, J = 8.7 and 2.4 Hz), 7.62−7.60 (AA′, 2H, Tol), 7.21−7.19 (BB′, 2H, Tol), 7.45 (ddd, 1H, J = 9.1, 5.9, and 3.2 Hz), 7.14−7.08 (m, 2H), 6.93 (d, 1H, J = 8.9 Hz), 3.85 (s, 3H, OMe), 2.32 (s, 3H, Me). ^{13}C NMR δ 158.7 (d, J = 247 Hz), 158.0, 156.2 (dd, J = 254 and 2.8 Hz), 147.1, 141.6, 141.5, 141.1 (dd, J = 34.1 and 5.7 Hz), 134.9, 129.7 (2C), 127.5, 125.4 (2C), 120.0, 118.5 (dd, J = 25.6 and 8.5 Hz), 117.8 (dd, J = 22.7 and 8.5 Hz),111.2, 104.0 (d, J = 25.6 Hz), 56.1, 21.3. EM (*m*/*z*) 386 (28.5), 370 (100), 279 (19), 257 (9), 229 (87), 139 (19), 113 (49), 63 (22). HRMS (EI) calcd for $C_{20}H_{16}N_2O_2F_2S$ (M^+) 386.0888, found 386.0901.

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Supporting Information Available: Experimental details and spectral data (^{1}H and ^{13}C NMR) for compounds **3e**,**f**,**h**,**j**, **6f**−**h**, **8a**,**h**,**k**, **12**, **13**, and **14**. This material is available free of charge via the Internet at http://pubs.acs.org.

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