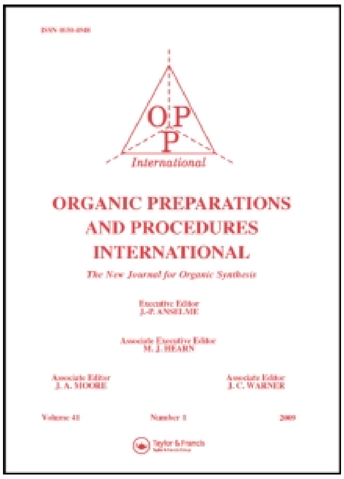

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A NEW AND EFFICIENT SOLVENT-FREE SYNTHESIS OF *bis*-ARYL CARBODIAZONES

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Azo compounds are very important in organic chemistry. Recently many studies have shown that they are also widely utilized in modern technology.[1] There is continued interest in efficient syntheses of new types of azo compounds in our laboratory. As a result, several methods for preparing new azo compounds in which one side of the –N=N- is connected with a carbonyl group have been reported.[2-5] All the useful synthetic routes available for the solution-state synthesis have their own merits, but some have drawbacks such as expensive phase-transfer catalysts,[2] large amounts of solvent,[3] tedious work to prepare the oxidant system[4] and complicated heating and stirring apparatus.[5] In the last few years, particularly intense interest has been directed towards methods for generating small organic molecules by solid-phase reactions. These solvent-free reactions are especially appealing for their own advantages including ease of set-up, work-up, high yields and working with open vessels. A variety of classical reactions have been adapted to solid-phase synthesis to generate C=C[6] and C=O[7-8] bonds. By comparison, the formation of N=N bonds remains relatively unexplored. This has led us to investigate the synthesis of azo compounds. As an improvement to our previous work,[2-5] we now report an effective solid-phase method for the rapid oxidation of aryl substituted carbohydrazides to the corresponding bisaryl carbodiazones [(ArN=N)$_2$CO], using $Fe(NO_3)_3{\bullet}9H_2O$ as oxidant. All the reactions occurred under mild conditions and yields were fair to excellent.

Our work started with the choice of oxidant. Several oxidants were attempted with the following results: **(a)** CrO_3-Al_2O_3 can react easily with aryl substituted carbohydrazides (judging from the color change of the reactants), but none of the expected product was obtained. **(b)** $Fe_2(SO_4)_3{\bullet}10H_2O$ can lead to the formation of bisazo compounds at room temperature, but the yields were seldom above 60%. **(c)** $Cu(NO_3)_2{\bullet}3H_2O$ gave similar results as $Fe_2(SO_4)_3{\bullet}10H_2O$ but with lower yields. Finally, we found $Fe(NO_3)_3{\bullet}9H_2O$, a low cost and highly stable commercially available crystalline solid, can serve as the best oxidant. Eight aryl substituted carbohydrazides were oxidized into the corresponding bisaryl carbodiazones efficiently. The results are presented in the table.

$$\underset{\mathbf{1}}{\text{ArNHNHCONHNHAr}} \xrightarrow{Fe(NO_3)_3{\bullet}9H_2O} \underset{\mathbf{2}}{\text{ArN=NCON=NAr}}$$

Compared with the reported methods, the advantages of the solid-phase oxidation lie in operational simplicity, the use of an inexpensive oxidizing agent, easy separation, purification and environmental acceptability. The analytical and spectral data of products (2a-2h) are in agreement with those reported in literature[5].

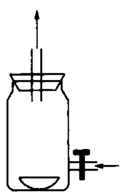
TABLE. Yields and mps. of bisAryl Carbodiazones

Product	Ar	Yield (%)	mp. (°C)	Lit mp. (°C) [5]
2a	2-MeC_6H_4	96	162-164	160-161
2b	3-MeC_6H_4	93	68-69	67-69
2c	4-MeC_6H_4	92	136-138	137-139
2d	4-$EtOC_6H_4$	95	154-155	156-157
2e	2,3-$Me_2C_6H_3$	95	97-99	98-100
2f	2,5-$Me_2C_6H_3$	90	162-163	159-161
2g	2,6-$Me_2C_6H_3$	94	117-119	118-119
2h	3,4-$Me_2C_6H_3$	95	96-97	94-96

EXPERIMENTAL SECTION

The melting points were determined with a Kofler micro melting apparatus and were uncorrected. Elemental analyses were carried out in a Carlo-Erba 1102 elemental analyzer. IR spectra were recorded on a SP3-300 spectrophotometer as KBr film, ^1H NMR spectra were measured on a FT-80A spectrometer using TMS as internal standard and $CDCl_3$ as solvent. Mass spectra were obtained on a VG-2AS-HS at 70ev.

Compound (2a-2h). General Procedure.- A mixture of bisaryl substituted carbohydrazide[9] (1mmol) and $Fe(NO_3)_3{\cdot}9H_2O$ (4mmol) was ground thoroughly in an agate mortar, then treated with HCl gas in a sealed vessel for 5 minutes at room temperature. The color of the solid mixture changed from white to yellow. Afterwards the reaction mixture was dissolved with 8-10 mL acetone. Then, ice-cold water was poured into the solution to precipitate the product. The crude product was collected, washed with water (3x20mL) until the washing became neutral and dried in vacuum to yield the product.



***bis*(2-Methyphenyl) Carbodiazone (2a):** ^1H NMR($CDCl_3$): δ 2.18 (S, 6H, 2xCH_3), 7.15-7.64 (m, 8H, Ar-H); IR (KBr): 3061, 2964, 2865, 1655, 1617, 1485, 1450, 1375 cm^{-1}.

Anal. Calcd. for $C_{15}H_{14}N_4O$: C, 67.64; H, 5.31; N, 21.04. Found: C, 67.29; H, 5.30; N, 21.03

***bis*(3-Methyphenyl) Carbodiazone (2b):** ^1H NMR($CDCl_3$): δ 2.43 (S, 6H, 2xCH_3), 7.32-7.81 (m, 8H, Ar-H); IR (KBr): 3072, 2948, 2856, 1700, 1640, 1598, 1571, 1495, 1444, 1354 cm^{-1}.

Anal. Calcd. for $C_{15}H_{14}N_4O$: C, 67.64; H, 5.31; N, 21.04. Found: C, 67.39; H, 5.22; N, 21.22

***bis*(4-Methyphenyl) Carbodiazone (2c):** ^{1}H NMR(CDCl$_3$): δ 2.39 (S, 6H, 2xCH$_3$), 7.27-7.88 (m, 8H, Ar-H); IR (KBr): 3060, 2965, 2860, 1687, 1599, 1502, 1477, 1353 cm^{-1}.

Anal. Calcd. for $C_{15}H_{14}N_4O$: C, 67.64; H, 5.31; N, 21.04. Found: C, 67.42; H, 5.29; N, 21.22

***bis*(4-Ethyloxyphenyl) Carbodiazone (2d):** ^{1}H NMR(CDCl$_3$): δ 1.49 (t, 6H, 2xCH$_3$), 4.18 (q, 4H, 2xCH$_2$), 7.00-7.36 (m, 8H, Ar-H); IR (KBr): 3084, 2975, 2887, 2928, 2852, 1704, 1600, 1575, 1500, 1253 cm^{-1}.

Anal. Calcd. for $C_{17}H_{18}N_4O_3$: C, 62.55; H, 5.57; N, 17.17. Found: C, 62.57; H, 5.59; N, 17.53

***bis*(2,3-Dimethylphenyl) Carbodiazone (2e):** ^{1}H NMR(CDCl$_3$): δ 2.41 (s, 6H, 2xCH$_3$), 2.64 (s, 6H, 2xCH$_3$), 7.06-7.56 (m, 6H, Ar-H); IR (KBr): 3063, 2967, 2860, 1734, 1615, 1492, 1452, 1342 cm^{-1}.

Anal. Calcd. for $C_{17}H_{18}N_4O$: C, 69.35; H, 6.18; N, 19.04. Found: C, 69.57; H, 6.10; N, 19.20

***bis*(2,5-Dimethylphenyl) Carbodiazone (2f):** ^{1}H NMR(CDCl$_3$): δ 2.17 (s, 6H, 2xCH$_3$), 2.23 (s, 6H, 2xCH$_3$), 6.72-7.44 (m, 6H, Ar-H); IR (KBr): 3037, 2965, 2865, 1652, 1617, 1575, 1500, 1455, 1365 cm^{-1}; MS(m/z): 294(M$^+$), 133, 105.

Anal. Calcd. for $C_{17}H_{18}N_4O$: C, 69.35; H, 6.18; N, 19.04. Found: C, 69.17; H, 5.91; N, 19.33

***bis*(2,6-Dimethylphenyl) Carbodiazone (2g):** ^{1}H NMR(CDCl$_3$): δ 2.46 (s, 12H, 4xCH$_3$), 7.10-7.43 (m, 6H, Ar-H); IR (KBr): 3071, 2967, 2865, 1692, 1635, 1596, 1505, 1438, 1355 cm^{-1}.

Anal. Calcd. for $C_{17}H_{18}N_4O$: C, 69.35; H, 6.18; N, 19.04. Found: C, 69.39; H, 6.19; N, 19.40

***bis*(3,4-Dimethylphenyl) Carbodiazone (2h):** ^{1}H NMR(CDCl$_3$): δ 2.32 (s, 6H, 2xCH$_3$), 2.38 (s, 6H, 2xCH$_3$), 7.04-7.85 (m, 6H, Ar-H); IR (KBr): 3058, 2970, 2884, 1712, 1609, 1575, 1492, 1450, 1337 cm^{-1}.

Anal. Calcd. for $C_{17}H_{18}N_4O$: C, 69.35; H, 6.18; N, 19.04. Found: C, 69.25; H, 6.08; N, 19.28

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