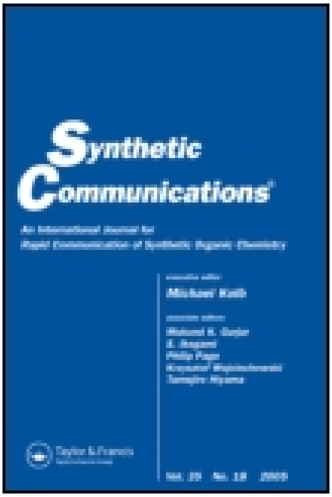

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The Application of Ceric Ammonium Nitrate in the Synthesis of Carbodiazones

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THE APPLICATION OF CERIC AMMONIUM NITRATE IN THE SYNTHESIS OF CARBODIAZONES

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Abstract: The preparation of bisaryl carbodiazone compounds from the aryl substituted carbazides with Ceric Ammonium Nitrate (CAN) has been reported for the first time in excellent yields (80-91%). This method only needs simple instruments and short reaction time. A possible mechanism has been suggested.

It has been reported that Cerium Ammonium Nitrate (CAN) can oxidize phenols to the corresponding quinones[1], and oxidize benzoic alcohols to the corresponding aldehydes or ketones[2-4], Jurg R. P.[5] reported that -CHNH- structure in nitrogenous compounds can be rapidly dehydrogenated to form -C=N- with CAN at room temperature. However dehydrogenation of -NHNH- structure with CAN has not been reported so far.

This paper reports the dehydrogenation of -NHNH- structure with CAN for the first time. Nine bisaryl substituted carbodiazone compounds have been prepared

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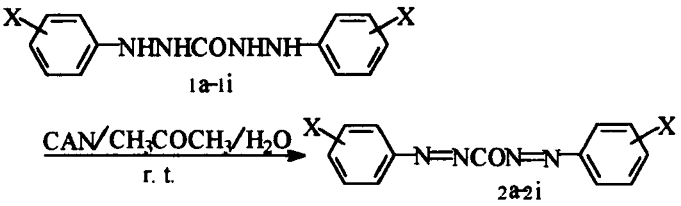
from the aryl substituted carbazides under mild conditions in very short reaction time.The Yields are excellent.



a: X=H   b: X=2-Me   c: X=3-Me   d: X=4-Me   e: X=2,3-Me$_2$

f: X=3,4-Me$_2$ g: X=2,5-Me$_2$ h: X=2,6-Me$_2$ i: X=4-EtO

scheme I

EXPERIMENTAL

Melting points were determined on kofler micro melting point apparatus without correction. Elemental analyses were performed on a Perkin-Elmer 240C analytical instrument. Infrared spectra were recorded on a SP3-300 spectra photometer using KBr pellets. ^{1}HNMR spectra were measured in CDCl$_3$ or DMSO-D$_6$ using TMS as internal standard with a JEOL-Fx-90Q NMR spectrometer. Mass spectra were recorded on a KRTOS-AEI-MS 50 (U.K.) spectrometer.

The preparation of carbodiazones from substituted carbazides. General procedure: 1.0 mmol of carbazide compounds were dissolved in 4-7 mL of acetone and 4.01mmol of CAN were added at room temperature. The color of the mixture changed to purple or brown-red, then 5-7 mL water was added, and the color turned into orange-red, red or dark red immediately. After 10 minutes, the mixture was extracted with dichloromethane three times. The dichloromethane layers were combined and washed with water three times then dried with anhydrous sodium sulfate for four hours. The solvent was evaporated after sodium sulfate was filtered off. The products were washed with ether and dried in vacuum at room temperature. The structures of the products were identified by IR, ^{1}HNMR, MS spectra data and elemental analysis.

Bisphenyl carbodiazone 2a

Pale brown needle; Yield 79%; m.p. 173-175℃; IR ν_{max}(KBr): 3055(w, ArH), 1658(s, C=O), 1630, 1590(m, ArH), 1430(m, N=N)cm^{-1}; ^{1}HNMR(CDCL$_3$): δ 7.31-7.82(m, 10H, Ar-H); Anal. calcd for $C_{13}H_{10}N_4O$: C, 65.54; H, 4.23; N, 23.52; Found: C, 65.50; H, 4.18; N, 23.60.

Bis(2-methylphenyl)carbodiazone 2b

Pale-yellow plate; Yield 90%; m.p. 159.5-161.5℃; IR ν_{max}(KBr): 3060(w, ArH), 2965, 2865(m, CH$_3$), 1655(s, C=O), 1615, 1485(m, ArH), 1455(m, N=N)cm^{-1}; ^{1}HNMR(CDCL$_3$): δ 2.16(s, 6H, 2CH$_3$), 7.16-7.60(m, 8H, ArH); Anal. calcd for $C_{15}H_{14}N_4O$: C, 67.65; H, 5.30; N, 21.04; Found: C, 67.57; H, 5.32; N, 21.01.

Bis(3-methylphenyl)carbodiazone 2c

Red needle; Yield 81%; m.p. 65-68℃; IR ν_{max}(KBr): 3073(w, ArH), 2950, 2850(m, CH$_3$), 1700(s, C=O), 1595, 1575(m, ArH), 1444(m, N=N)cm^{-1}; ^{1}HNMR(CDCL$_3$): δ 2.42(s, 6H, 2CH$_3$), 7.32-7.83(m, 8H, ArH); Anal. calcd for $C_{15}H_{14}N_4O$: C, 67.65; H, 5.30; N, 21.04; Found: C, 67.55; H, 5.24; N, 21.10.

Bis(4-methylphenyl)carbodiazone 2d

Orange red needle; Yield 82%; m.p. 137-139℃; IR ν_{max}(KBr): 3065(w, ArH), 2965, 2860(m, CH_3), 1680(s, C=O), 1595, 1500(m, ArH), 1470(m, N=N)cm^{-1}; ^{1}HNMR($CDCL_3$): δ 2.40(s, 6H, $2CH_3$)7.25-7.88(m, 8H, ArH); Anal. calcd for $C_{15}H_{14}N_4O$: C, 67.65; H, 5.30; N, 21.04; Found : C, 67.70; H, 5.28; N, 21.12.

Bis(2,3-dimethylphenyl)carbodiazone 2e

red plate; Yield 84%; m.p. 98-101℃; IR ν_{max}(KBr): 3058(w, ArH), 2965, 2850(m, CH_3), 1720(s, C=O), 1602, 1490(m, ArH), 1455(m, N=N)cm^{-1}; ^{1}HNMR($CDCL_3$): δ 2.39(s, 6H, $2CH_3$), 2.63(s, 6H, $2CH_3$), 7.08-7.60(m, 6H, ArH); Anal. calcd for $C_{17}H_{18}N_4O$: C, 69.37; H, 6.16; N, 19.03; Found: C, 69.40; H, 6.15; N, 19.20.

Bis(3,4-dimethylphenyl)carbodiazone 2f

Yellow Red plate; Yield 80%; m.p. 93-96℃; IR ν_{max}(KBr):3050(w, ArH), 2970, 2850(m, CH_3), 1715(s, C=O), 1610, 1570(m, ArH), 1450(m, N=N)cm^{-1}; ^{1}HNMR($CDCL_3$): δ 2.30(s, 6H, $2CH_3$), 2.36(s, 6H, $2CH_3$), 7.05-8.00(m, 6H, ArH); Anal. calcd for $C_{17}H_{18}N_4O$: C, 69.37; H, 6.16; N, 19.03; Found: C, 69.35; H, 6.19; N, 19.23.

Bis(2,5-dimethylphenyl)carbodiazone 2g

Yellow plate; Yield 85%; m.p. 158-161℃; IR ν_{max}(KBr): 3030(w, ArH), 2965, 2860(m, CH_3), 1710(s, C=O), 1610, 1570(m, ArH), 1450(m, N=N)cm^{-1}; ^{1}HNMR($CDCL_3$): δ 2.30(s, 6H, $2CH_3$), 2.36(s, 6H, $2CH_3$), 7.05-8.00(m, 6H, ArH); Anal. calcd for $C_{17}H_{18}N_4O$: C, 69.37; H, 6.16;N, 19.03; Found: C, 69.35; H, 6.19; N, 19.23.

Bis(2,6-dimethylphenyl)carbodiazone 2h

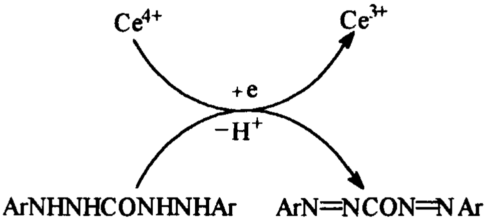
Red needle; Yield 86%; m.p. 117-120℃; IR ν_{max}(KBr): 3060(w, ArH), 2964, 2850(m, CH_3), 1700(s, C=O), 1620, 1570(m, ArH), 1445(m, N=N)cm^{-1}; ^{1}HNMR($CDCL_3$): δ 2.50(s, 12H, $4CH_3$), 2.36(s, 6H, $2CH_3$), 7.10-7.40(m, 6H, ArH); Anal. calcd for $C_{17}H_{18}N_4O$: C, 69.37; H,6.16; N, 19.03; Found: C, 69.38; H, 6.20; N, 19.09.

Bis(4-ethyloxyphenyl)carbodiazone 2i.

Orange red plate ;Yield 91%; m.p. 159-162℃; IR ν_{max}(KBr): 3080(w, ArH), 2975, 2885, 2925, 2850(m, CH_3 or CH_2), 1700(s, C=O), 1602, 1580(m,ArH), 1450(m,N=N)cm.^{1}; ^{1}HNMR($CDCL_3$): δ 1.50(t, 6H, $2CH_3$), 4.20(q, 4H, $2CH_2$), 7.01-7.35(m, 8H, ArH); Anal. calcd for $C_{17}H_{18}N_4O_3$: C, 62.55; H, 5.57; N, 17.17; Found: C, 62.59, H, 5.54; N, 17.42.

Result and Discussion

CAN is a single-election oxidant in this reation, and a possible mechanism was showed as following:



Scheme II

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