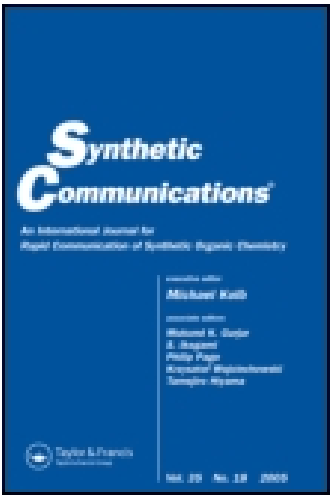

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SOLID STATE SELECTIVE SYNTHESIS OF DIARYL CARBAZONE

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SOLID STATE SELECTIVE SYNTHESIS OF DIARYL CARBAZONE

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ABSTRACT

The selective synthesis of diaryl carbazone using $K_3Fe(CN)_6$ as oxidant under alkaline condition in solid state is reported for the first time. Eight diaryl carbazone have been synthesized in excellent yields, and this method only needs cheap reagents, and simple procedure under mild condition.

Solid state organic reactions have caused great interest in recent years, having many advantages such as high efficiency and selectivity,[1] easy separation and purification, mild reaction condition,[2] and environmental acceptability, etc.[3,4] This method has been widely used in a variety of organic syntheses, but its application in synthesis of diaryl carbazone under alkaline condition in solid state has not been reported before. Diaryl carbazone is an important organic analytical reagent normally synthesized by the oxidation of aryl substituted carbazide, and $KClO_3/H_2SO_4/FeSO_4$ or $FeCl_3/H_2SO_4$ [5] have been used as oxidant.

In the previous work, our laboratory has used 2,4,6-t-(t-C_4H_9)$_3$ $C_6H_2OH/K_3Fe(CN)_6/KOH$ phase transfer system as oxidant system, diaryl carbodiazone was the only product although the amount

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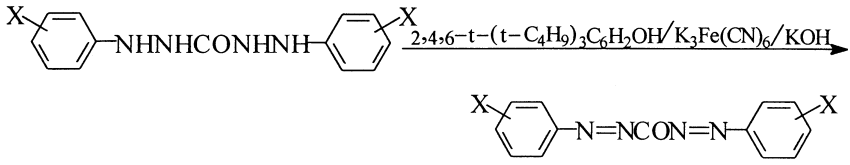
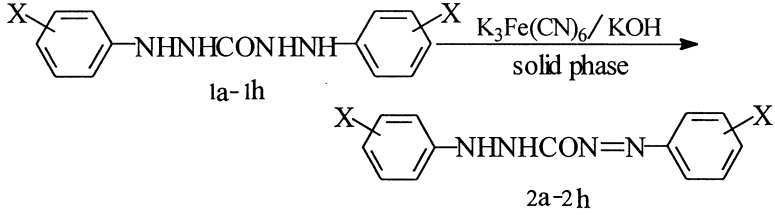
of $K_3Fe(CN)_6$ was controlled (Scheme 1). $FeCl_3$ has also been used as oxidant under acid condition in solid state, if the amount of oxidant was controlled, diaryl carbazone and diaryl carbodiazone were prepared respectively. In this paper, We used $K_3Fe(CN)_6$/KOH oxidation system to synthesize diaryl carbazone from aryl substituted carbazide in solid state for the first time (Scheme 2), at room temperature diaryl carbazone is the only product even the excess oxidant is used, furthermore this method only requires simple instrument, short reaction time and easy work-up procedure. Eight diaryl carbazone compounds have been synthesized in excellent yields.



Scheme 1.



a: X=H b:X=2-Me c: X=3-Me d: X=4-Me

e: X=2,3-Me_2 f: X=2,6-Me_2 g: X=4-EtO h: X=4-NO_2

Scheme 2.

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 $CDCl_3$ using TMS as internal standard with a JEOL-Fx-90Q NMR spectrometer.

General Procedure of the Preparation of Diaryl Carbazone

A mixture of 0.01 mol of **1** and 0.041 mol of $K_3Fe(CN)_6$ and 0.3–0.4 mmol of KOH was ground in an agate mortar. After 20–30 minutes, The color of the mixture turned orange yellow, orange or dark green. Then 20 ml of water was added, then yellow, orange and orange red and dark green products were precipitated. The product was isolated by filtration, and washed with water four times. The products were recrystallized from a mixture of ethanol and water, and dried under vacuum. Structures of these products were characterized by elemental analysis, IR and ^{1}HNMR spectroscopy.

Diphenyl Carbazone 2a

Orange needle; yield 89%; m.p. 154–155°C; IR(KBr)ν: 3448, 3306, 3035, 1710, 1665, 1604, 1527, 1485 cm^{-1}; ^{1}HNMR($CDCl_3$) δ: 7.91~8.11 (d,2H, NHNH), 7.13~7.58(m, 10H, $2C_6H_5$). Anal. Calcd. for $C_{13}H_{12}N_4O$: C, 64.99, H, 5.03; N, 22.98. Found: C, 64.72; H, 4.98; N, 23.02.

Di(2-Methylphenyl) Carbazone 2b

Yellow needle; yield 87%; m.p. 126–127°C; IR(KBr)ν: 3430, 3340, 3050, 2920, 2855, 1677, 1605, 1547, 1487 cm^{-1}; ^{1}HNMR($CDCl_3$) δ: 7.66~7.97(d, 2H, NHNH), 6.97~7.34(m, 8H, $2C_6H_4$), 2.73(s, 3H, CH_3); 2.31(s, 3H, CH_3). Anal. Calcd. for $C_{15}H_{16}N_4O$: C, 67.14; H, 5.96; N, 20.88. Found: C, 66.94; H, 5.73; N, 20.54.

Di(3-Methylphenyl) Carbazone 2c

Brown Yellow leaflet; yield 84%; m.p. 167–168°C; IR(KBr)ν: 3380, 3330, 3040, 2920, 1645, 1610, 1585, 1465, 1410 cm^{-1}; ^{1}HNMR($CDCl_3$) δ: 7.20~7.62(d, 2H, NHNH), 6.72~7.15(m, 8H, $2C_6H_4$), 2.50(s, 3H, CH_3); 2.32(s, 3H, CH_3). Anal. Calcd. for $C_{15}H_{16}N_4O$: C, 67.14; H, 5.96; N, 20.88. Found: C, 66.75; H, 5.42; N, 20.51.

Di(4-Methylphenyl) Carbazone 2d

Orange red leaflet; yield 81%; m.p. 132–133°C; IR(KBr)ν: 3390, 3280, 3045, 2920, 2870, 1712, 1650, 1600, 1515, 1465 cm^{-1}; ^{1}HNMR($CDCl_3$)

δ: 7.25~7.70(d, 2H, NHNH), 6.60~7.12(m, 8H, $2C_6H_4$), 2.45 (s, 3H, CH_3); 2.25 (s, 3H, CH_3). Anal. Calcd. for $C_{15}H_{16}N_4O$: C, 67.14; H, 5.96; N, 20.88. Found: C, 66.93; H, 5.68; N, 20.18.

Di(2,3-Methylphenyl) Carbazone 2e

Orange leaflet; yield 86%; m.p. 116–117°C; IR(KBr)ν: 3410, 3320, 3035, 2916, 2860, 1690, 1590, 1490, 1475, 1455 cm^{-1}; ^{1}HNMR($CDCl_3$) δ: 7.37~7.85(d, 2H, NHNH), 6.64~7.20(m, 6H, $2C_6H_3$), 2.13(s, 6H, $2CH_3$); 2.41(s, 6H, $2CH_3$). Anal. Calcd. for $C_{17}H_{20}N_4O$: C, 68.90; H, 6.80; N, 18.90. Found: C, 68.53; H, 6.62; N, 18.51.

Di(2,6-Methylphenyl) Carbazone 2f

Yellow leaflet; yield 90%; m.p. 193–194°C; IR(KBr)ν: 3480, 3320, 3040, 2910, 2875, 1690, 1605, 1575, 1480, 1410 cm^{-1}; ^{1}HNMR($CDCl_3$) δ: 7.25~7.83(d, 2H, NHNH), 6.50~7.25(m, 6H, $2C_6H_3$), 2.15(s, 6H, $2CH_3$); 2.37(s, 6H, $2CH_3$). Anal. Calcd. for $C_{17}H_{20}N_4O$: C, 68.90; H, 6.80; N, 18.90. Found: C, 68.22; H, 6.56; N, 18.40.

Di(4-Ethyloxyphenyl) Carbazone 2g

Orange leaflet; yield 89%; m.p. 159–161°C; IR(KBr)ν: 3390, 3205, 3027, 2970, 1705, 1675, 1601, 1573, 1503, 1465 cm^{-1}; ^{1}HNMR($CDCl_3$) δ: 7.89~8.10(d, 2H, NHNH), 6.94~7.26(m, 8H, $2C_6H_4$), 3.94~4.25(q, 4H, $2CH_2$); 1.37~1.65(t, 6H, $2CH_3$). Anal. Calcd. for $C_{17}H_{20}N_4O_3$: C, 62.18; H, 6.14; N, 17.06. Found: C, 61.78; H, 6.13; N, 16.97.

Di(4-Nitrophenyl) Carbazone 2h

Brown leaflet; yield 70%; m.p. 240–242°C; IR(KBr)ν: 3450, 3335, 3060, 2915, 2850, 1655, 1630, 1585, 1519, 1490 cm^{-1}; ^{1}HNMR($CDCl_3$) δ: 8.12~9.15(d, 2H, NHNH), 6.60~7.45(m, 8H, $2C_6H_4$), Anal. Calcd. for $C_{13}H_{10}N_6O_5$: C, 47.28; H, 3.05; N, 25.45. Found: C, 46.91; H, 3.42; N, 24.89.

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