SHORT PAPER

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Selective and efficient oxidation of diaryl carbazide to diaryl carbazone with $NaNO_2/NaHSO_4 \bullet H_2O/SiO_2$

Xiao-Chuan Li[a], Yu-Lu Wang[a]* and Jin-Ye Wang[b]

[a]*College of Chemical and Environmental Science, Henan Normal University, Xinxiang, Henan, 453002, PR. China*
[a]*The Key Laboratory of Environmental Science and Technology of High Education of Henan Province, PR. China*
[b]*Shanghai Institute of Organic Chemistry, Chinese Academy of Science, Shanghai, 200032, P.R. China*

Ten diaryl carbazide are shown to undergo selective and rapid oxidation to the diaryl carbazones using $NaNO_2/NaHSO_4 \bullet H_2O/SiO_2$ as a novel mild oxidising agent.

Keywords: selective oxidation, diaryl carbazone, $NaNO_2/NaHSO_4 \bullet H_2O/SiO_2$

Azo compounds are widely used as dyes and analytical reagents.[1] They can also be used as materials for non-linear optics and for the storage of optical information on laser disks.[2] Recent studies have shown that some azo compounds possess excellent optical memory and photoelectric properties.[3,4]

We have examined the oxidation of diaryl carbazide into a diaryl carbazone; in previous work, NBS/pyridine[5] and $FeCl_3/H_2SO_4$[6] have been used as effective oxidants in liquid phase $K_3Fe(CN)_6/KOH$[7] has been used as an oxidant in solid state for the first time in our laboratory. All these methods have limitations, such as: tedious operation;[5] the use of a large amount of solvent;[5] accurate control of molar ratio of oxidants;[6] strong acid or basic media.[6,7]

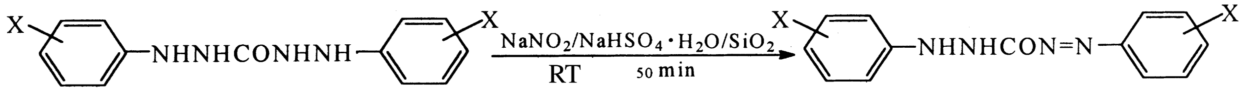
In continuation of our studies on the synthesis of azo compounds, we decided to develop a new reagent system to overcome these limitations. The combination of sodium nitrite and sodium hydrogen sulfate in the presence of wet SiO_2 has been used as an elfective oxidising agent for the dehydrogenation of 4-substituted-1,2,4-triazole-3,5-diones.[8] The $[NO^+ \bullet \text{crown} \bullet H(NO_3)_2^-]$ complex has also been reported as an effective oxidising agent for the dehydrogenation of 4-substituted-l,2,4-triazole-3,5-diones, affording a fast and easy work-up.[9] The 18-crown-6 could be recycled and reused. We considered that this method might be suitable for the oxidation of diaryl carbazide to corresponding azo compounds. Indeed, diaryl carbazides were oxidised to their azo compounds efficiently by this method with a slight modification. All the reactions can be carried out at room temperature smoothly (Scheme 1) and are complete within 50min. Furthermore, this method only requires simple equipment cheap oxidants and an easy work-up procedure. Ten diaryl carbazones were synthesised in excellent yields. The results are summarised in Table 1. In addition, it is worth noting that the diaryl carbazide were not oxidised to diaryl carbodiazone under these conditions even if excess oxidant was used.

In the oxidation study, we selected 1,5-diphenylcarbazide as a model. The optimum molar ratio was established by a reaction using 1,5-diphenylcarbazide (1 mmol) and SiO_2 (0.3g, 60–100mesh) with various molar ratio of $NaNO_2 : NaHSO_4 \bullet H_2O$. The results are summarised in Table 2. If $NaNO_2$ was used for the oxidation alone, the reaction did not occur even after stirring 24h. The oxidation of 1,5-diphenylcarbazide was efficiently achieved with this oxidation system. The presence of SiO_2 is crucial. Although the reaction occurs without SiO_2, the reaction period is much longer and good yield is not obtained. Therefore, we thought that the presence of SiO_2 will act as a media and will provide a heterogeneous effective surface area for the generation of HNO_2. It will also make easy work-up. No additional products were identified from this reaction.

In summary, a simple and efficient method for the oxidation of diaryl carbazide with $NaNO_2/NaHSO_4 \bullet H_2O/SiO_2$ has

Table 1 The synthesis of diaryl carbazone using the oxidation system of $NaNO_2/NaHSO_4 \bullet H_2O/SiO_2$

Product	X	Yield/%	M.p./°C	Lit. m.p./°C[5–7]
2a	H	95	155–157	155–156.5
2b	2-Me	92	125–127	127–128
2c	3-Me	90	165–167	166–168
2d	4-Me	94	131–133	133–134
2e	2,3-Me_2	90	115–117	116–118
2f	2,5-Me_2	91	158–160	–
2g	2,6-Me_2	92	194–196	195–196
2h	3,4-Me_2	89	93–96	–
2i	4-EtO	95	158–161	160–161
2j	4-NO_2	89	242–245	243–245



1a–1j **2a–2j**

a. X = H **b.** X = 2-Me **c.** X = 3-Me **d.** X = 4-Me **e.** X = 2,3-Me_2 **f.** X = 2,5-Me_2 **g.** X = 2,6-Me_2 **h.** X = 3,4-Me_2 **i.** X = 4-EtO **j.** X = 4-NO_2

Scheme 1

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* To receive any correspondence. E-mail: xiaochuanli@263.net

† This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M)*.

Table 2 Oxidation of 1,5-diphenylcarbazide (1 mmol) in the presence of SiO$_2$(0.3g, 60-100mesh) with different molar ratio of NaNO$_2$[a]: NaHSO$_4$•H$_2$O[a]

Entry	NaNO$_2$: NaHSO$_4$• H$_2$0	Reaction time	Yield/%
1	5 : 0	24h	A little
2	1 : 1	50min	53
3	2 : 1	50min	70
4	3 : 1	50min	81
5	4 : 1	50min	90
6	5 : 1	50min	95
7	6 : 1	50min	95
8	5 : 1	3h	94
9	5 : 1	3h	66[b]

[a]Crushed to a fine powder. [b]Without SiO$_2$

been described. The significant advantages of it are: (a) operational simplicity; (b) no over oxidation; and (c) mild conditions and excellent yields. In all cases, clean transformation could be detected by TLC. We believe that this method will be a useful addition to the existing methods for the synthesis of azo compounds.

Experimental

Melting points were determined on Kolfler micro melting points 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}H NMR spectra were measured in CDCl$_3$ using TMS as internal standard with a JEOL-90Q NMR spectrometer.

A 50ml, one-necked, round-bottomed flask equipped with magnetic stirrer was charged with 1mmol of diaryl carbazide, 0.345g of NaNO$_2$ (5mmol), 0.108g of NaHSO$_4$• H$_2$O (1mmol), 0.3g of SiO$_2$ (60–100mesh) and 20ml dichloromethane. The mixture was vigorously stirred at room temperature. After completion of the reaction (TLC), the reaction mixture was filtered. Dichloromethane was removed on a water bath (50°C) by simple distillation. The resulting solid was recrystallised from EtOH-H$_2$O (3 : 1) mixture. All the products were identified by IR, ^{1}H NMR and element analysis.

Compound **2a**: orange needle; IR (KBr) ν_{max}: 3443, 3305, 3030, 1710, 1660, 1605, 1530, 1485 (cm^{-1}); ^{1}H NMR (CDCl$_3$) δ(ppm): 7.90–8.12 (d, 2H,NHNH), 7.11–7.55 (m, 10H, 2C$_6$H$_5$),. Anal. Calcd. for C$_{13}$H$_{12}$N$_4$O: C, 64.99; H, 5.03; N, 22.98. Found: C,64.71; H, 4.97; N, 23.04.

Compound **2b**: yellow needle; IR (KBr) ν_{max}: 3430, 3340, 3055, 2920, 2855, 1675, 1605, 1550, 1490, 1452 (cm^{-1}); ^{1}H NMR (CDCl$_3$) δ(ppm): 7.65–7.97 (d, 2H,NHNH), 6.97–7.35 (m, 8H, 2C$_6$H$_4$), 2.72 (s, 3H, CH$_3$), 2.30 (s, 3H, CH$_3$); Anal. Calcd. for C$_{15}$H$_{16}$N$_4$O: C, 67.14; H, 5.96; N, 20.88. Found: C, 66.74; H, 5.79; N, 20.55

Compound **2c**: brown leaflet; IR (KBr) ν_{max}: 3385, 3330, 3042, 2922, 1648, 1610, 1584, 1465, 1410 (cm^{-1}); ^{1}H NMR (CDCl$_3$) δ(ppm): 7.21–7.62 (d, 2H,NHNH), 6.73–7.15 (m, 8H, 2C$_6$H$_4$), 2.51 (s, 3H, CH$_3$), 2.32 (s, 3H, CH$_3$); Anal. Calcd. for C$_{15}$H$_{16}$N$_4$O: C, 67.14; H, 5.96; N, 20.88. Found: C, 66.77; H, 5.43; N, 20.50.

Compound **2d**: orange leaflet; IR (KBr) ν_{max}: 3396, 3285, 3045, 2920, 2869, 1712, 1651, 1600, 1513, 1465 (cm^{-1}); ^{1}H NMR (CDCl$_3$) δ(ppm): 7.21–7.62 (d, 2H,NHNH), 6.73–7.15 (m, 8H, 2C$_6$H$_4$), 2.51 (s, 3H, CH$_3$), 2.32 (s, 3H, CH$_3$); Anal. Calcd. for C$_{15}$H$_{16}$N$_4$O: C, 67.14; H, 5.96; N, 20.88. Found: C, 66.77; H, 5.43; N, 20.50.

Compound **2e**: orange leaflet; IR (KBr) ν_{max}: 3410, 3319, 3045, 2916, 2862, 1689, 1591, 1490, 1475, 1450 (cm^{-1}); ^{1}H NMR (CDCl$_3$) δ(ppm): 7.38–7.87 (d, 2H,NHNH), 6.64–7.17 (m, 6H, 2C$_6$H$_3$), 2.40 (s, 6H, 2CH$_3$),2.13 (s, 6H, 2C11$_3$); Anal. Calcd. for C$_{17}$H$_{20}$N$_4$O: C, 68.90; H, 6.80; N, 18.90. Found: C, 68.73; H, 6.53; N, 18.47.

Compound **2f**: yellow leaflet; IR (KBr) ν_{max}: 3475, 3321, 3043, 2913, 2874, 1690, 1605, 1574, 1478, 1411 (cm^{-1}); ^{1}H NMR (CDCl$_3$) δ(ppm): 7.35–7.86 (d, 2H, NHNH), 6.58–7.12 (m, 6H, 2C$_6$H$_3$), 2.30 (s, 6H, 2CH$_3$), 2.36 (s, 6H, 2CH$_3$); Anal. Calcd. for C$_{17}$H$_{20}$N$_4$O: C, 68.90; H, 6.80; N, 18.90. Found: C, 68.67; H, 6.48; N, 18.76.

Compound **2g**: yellow leaflet; IR (KBr) ν_{max}: 3466, 3310, 3050, 2911, 2891, 1670, 1610, 1563, 1477, 1418 (cm^{-1}); ^{1}H NMR (CDCl$_3$) δ(ppm): 7.27–7.86 (d, 2H, NHNH), .6.51–7.23 (m, 6H, 2C$_6$H$_3$), 2.17 (s, 6H, 2CH$_3$), 2.35 (s, 6H, 2CH$_3$); Anal. Calcd. for C$_{17}$H$_{20}$N$_4$O: C, 68.90; H, 6.80; N, 18.90. Found; C, 68.32; H, 6.67; N, 18.44.

Compound **2h**: yellow leaflet; IR (KBr) ν_{max}: 3423, 3307, 3031, 2907, 2860, 1681, 1610, 1574, 1464, 1450 (cm^{-1}); ^{1}H NMR (CDCl$_3$) δ(ppm): 7.33–7.81 (d, 2H, NHNH), 6.49–7.14 (m, 6H, 2C$_6$H$_3$), 2.40 (s, 6H, 2CH$_3$),2.13 (s, 6H, 2CH$_3$); Anal. Calcd. for C$_{17}$H$_{20}$N$_4$O: C, 68.90; H, 6.80; N, 18.90. Found: C, 68.70; H, 6.53; N, 18.55.

Compound **2i**: brown leaflet; IR (KBr) ν_{max}: 3390, 3205, 3027, 2973, 1705, 1675, 1600, 1566, 1503, 1450 (cm^{-1}); ^{1}H NMR (CDCl$_3$) δ(ppm): 7.89–8.04 (d, 2H,NHNH), 6.91–7.33 (m, 6H, 2C$_6$H$_3$), 3.94–4.25 (q, 4H, 2CH$_2$),1.37–1.65 (t, 6H, 2CH$_3$); Anal. Calcd. for C$_{17}$H$_{20}$N$_4$O$_3$: C, 62.18; H, 6.14; N, 17.06. Found: C, 61.78; H, 6.13; N, 16.97.

Compound **2j**: brown leaflet; IR (KBr) ν_{max}: 3451, 3335, 3057, 2915, 2850, 1655, 1630, 1587, 1517, 1492 (cm^{-1}); ^{1}H NMR (CDCl$_3$) δ(ppm): 8.13–9.14 (d, 2H, NHNH), 6.59–7.45 (m, 8H, 2C$_6$H$_4$); Anal. Calcd. for C$_{13}$H$_{10}$N$_6$O$_5$: C, 47.28; H, 3.05; N, 25.45. Found: C, 46.75; H, 3.52; N, 24.69.

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