SHORT PAPER

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Effective solvent-free synthesis of a-acylazo compounds with active manganese dioxide catalysed by sulfuric acid supported on silica gel†

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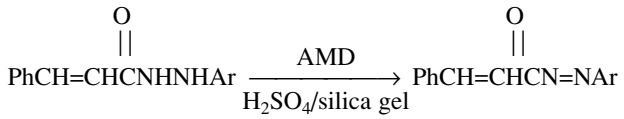
Under solvent-free conditions eight azo compounds were prepared using active manganese dioxide as the oxidant catalysed by H_2SO_4 supported on silica gel.

Keywords: aryl substituted α,β-unsaturated acylazo compounds, active manganese dioxide, hydrazides

Azo compounds have been employed widely for the photoregulation of polypeptide function.[1] They can also be used as materials for non-linear optics and for storage of optical information on compact discs.[2] The preparation of new azo compounds has received our attention recently.[3] In this paper, eight new aryl substituted α,β-unsaturated acylazo compounds (**2**) are reported. They were synthesised by the dehydrogenation of aryl substituted α,β-unsaturated acyl hydrazides (**1**) under solvent-free conditions at room temperature. In this reaction, active manganese dioxide (AMD) is used as the oxidant with sulfuric acid supported on silicagel as the catalyst.



1 **2**

(a) Ar = *p*-ClC_6H_4; (b) Ar = *o*-ClC_6H_4; (c) Ar = *p*-BrC_6H_4; (d) Ar = *p*-IC_6H_4; (e) Ar = 2,4-$Cl_2C_6H_3$; (f) Ar = *p*-$NO_2C_6H_4$; (g) Ar = *o*-MeC_6H_4; (h) Ar = 3,4-$Me_2C_6H_3$

Oxidations with AMD in solution[4-12] typically require long reaction times (72–85h) and excess amounts of oxidants[11] in some cases. Moreover, the work-up of the reaction mixtures is tedious and time-consuming. On the other hand, there have been reports on selective dehydrogenation[13] with AMD. In this paper, the environmentally benign solvent-free oxidative reactions of AMD for the preparation of **2** with a supported acid are described. The dehydrogenation reaction time needed for the solvent-free reactions is much shorter (3–5min.), the preparative operations are more convenient and the work-up is usually easier.[14]

Solid acidic catalysts supported on silica gel and their applications have been described previously.[15] In this paper, the solid acidic catalyst , a mixture of H_2SO_4 and silicagel (1:2 by weight), is used after being dried in an oven at 90°C overnight for the oxidation from PhCH=CHCONHNHAr to the corresponding PhCH=CHCON=NAr. The catalyst proved to be efficient and easy to use.

The eight azo compounds prepared are summarised in Table 1.

Table 1 Colours, melting points and yields of the azo compounds prepared

Product	Ar	Colour	m.p./°C	Yield/%
2a	*p*-ClC_6H_4	Purple	64.5–66.0	84
2b	*o*-ClC_6H_4	Brown	56.0–57.5	85
2c	*p*-BrC_6H_4	Deep-red	83.0–85.0	83
2d	*p*-IC_6H_4	Purple	93.0–94.5	85
2e	2,4-$Cl_2C_6H_3$	Orange	99.0–101.0	82
2f	*p*-$NO_2C_6H_4$	Brown	132.0–134.0	75
2g	*o*-$CH_3C_6H_4$	Orange	48.5–50.0	78
2h	3,4-Me_2 C_6H_3	Red	79.5–81.0	80

Experimental

Melting points were determined with a Kofler micro melting point apparatus and are uncorrected. IR spectra were obtained in KBr using an SP3-300 spectrophotometer. ^{1}H NMR spectra were measured on a JEOL-Fx-90Q spectrometer using TMS as internal standard and $CDCl_3$ as solvent. Elemental analyses were performed on a Carlo-Erba 1102 elemental analyzer.

General procedure for the preparation of PhCH=CHCON=NAr: The catalyst was prepared by mixing H_2SO_4 and silicagel (1:2 by weight) and drying in an oven at 90°C overnight. All solvent-free reactions were performed by grinding together 1 mmol of the aryl substituted α,β-unsaturated acyl hydrazide (PhCH=CHCONHNHAr) and a mixture of AMD (0.175 g, 2 mmol) and the catalyst (0.6125 g) which had been ground previously after being activated at 80°C in an oven. The progress of the reaction (3–5 min.) was monitored by thin layer chromatography (TLC) using acetone/petroleum ether (2:5) as the eluent. After the completion of the reaction, the resulting mixture was transferred directly on a silica gel column and eluted with acetone and petroleum ether (1:5). Evaporation of the solvent under vacuum gave the desired aryl substituted α,β-unsaturated acylazo compounds (**2**).

The products were characterised using elemental analysis, IR and ^{1}H NMR spectroscopy.

Compound **2a:** IR (KBr) 3061, 1689, 1615, 1563, 1516, 1448, 1403 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ: 7.15–7.65 (m, 9H, Ar-H), 6.56 (d, 1H, C*H*=CHCO), 5.95 (d, 1H, CH=C*H*CO).

Anal. calcd. for $C_{15}H_{11}Cl\ N_2O$: C 66.55, H 4.10, N 10.35. Found: C 66.32, H 4.07, N 10.42%.

Compound **2b:** IR (KBr) 3080, 1683, 1630, 1579, 1495, 1448, 1425 cm^{-1}; 1H NMR ($CDCl_3$) δ: 7.20–7.85 (m, 9H, Ar-H), 6.55 (d, 1H, CH=CHCO), 6.35 (d, 1H, CH=CHCO).

Anal. calcd. for $C_{15}H_{11}ClN_2O$: C 66.55, H 4.10, N 10.35. Found: C 66.60, H 4.02, N 10.28%.

Compound **2c:** IR (KBr) 3060, 1680, 1610, 1575, 1500, 1448, 1400 cm^{-1}; 1H NMR ($CDCl_3$): δ 7.20–7.95 (m, 9H, ArH), 6.85 (d, 1H, CH=CHCO), 6.38 (d, 1H, CH=CHCO).

Anal. calcd. for $C_{15}H_{11}BrN_2O$: C 57.32, H 3.53, N 8.92. Found: C 56.99, H 3.60, N 8.79%.

Compound **2d:** IR (KBr) 3025, 1680, 1619, 1564, 1516, 1447, 1393 cm^{-1}; 1H NMR ($CDCl_3$) δ 7.02–8.02 (m, 9H, Ar-H), 6.90 (d, 1H, CH=CHCO), 5.95 (d, 1H, CH=CHCO).

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

Anal. calcd. for $C_{15}H_{11}IN_2O$: C 49.72, H 3.06, N 7.74. Found: C 50.21, H 3.01, N 7.63%.

Compound **2e:** IR (KBr) 3083, 1689, 1614, 1575, 1487, 1449, 1385 cm^{-1}; 1H NMR ($CDCl_3$) δ 7.20–7.98 (m, 8H, Ar-H), 7.02 (d, 1H, CH=CHCO), 6.85 (d, 1H, CH=CHCO).

Anal. calcd. for $C_{15}H_{10}Cl_2N_2O$: C 59.21, H 3.32, N 9.21. Found: C 59.32, H 3.43, N 9.17%.

Compound **2f:** IR (KBr) 3020, 1680, 1595, 1575, 1515, 1450, 1410 cm^{-1}; 1HNMR ($CDCl_3$) δ: 7.22–8.44 (m, 9H, Ar-H), 7.02 (d, 1H, CH=CHCO), 6.82 (d, 1H, CH=CHCO).

Anal. calcd. for $C_{15}H_{11}N_3O_3$: C 64.04, H 3.94, N 14.95. Found: C 64.17, H 3.82, N 14.89%.

Compound **2g:** IR (KBr) 3026, 1688, 1578, 1505, 1450, 1410 cm^{-1}; 1H NMR ($CDCl_3$) δ 2.01 (s, 3H, CH3), 7.10–7.92 (m, 9H, Ar-H), 6.50 (d, 1H, CH=CHCO), 6.30 (d, 1H, CH=CHCO).

Anal. calcd. for $C_{16}H_{14}N_2O$: C 76.77, H 5.64, N 11.07. Found: C 76.58, H 5.60, N 11.27%.

Compound **2h:** IR (KBr) 3033, 1680, 1620, 1483, 1448, 1387 cm^{-1}; 1H NMR ($CDCl_3$) δ: 7.22–8.00 (m, 8H, Ar-H), 7.10 (d, 1H, CH=CHCO), 6.90 (d, 1H, CH=CHCO), 2.4 (s, 6H, 2CH3).

Anal. calcd. for $C_{17}H_{16}N_2O$: C 77.24, H 6.11, N 10.80. Found: C 77.02, H 6.07, N 10.57%.

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