

Reductive cleavage of azo compounds catalysed by commercial zinc dust and hydrazinium monoformate as a new hydrogen donor for heterogeneous catalytic transfer hydrogenation[†]

Shankare Gowda, K. Abiraj and D. Channe Gowda*

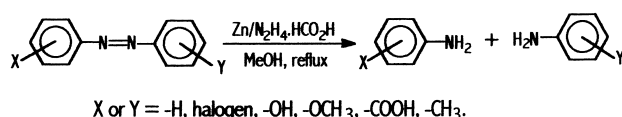
Department of Studies in Chemistry, University of Mysore, Mysore-570 006, India

Azo compounds are reductively cleaved to amine/s at reflux temperature within 15 min by employing less expensive commercial zinc dust and hydrazinium monoformate, a new hydrogen donor for catalytic transfer hydrogenation.

Keywords: 0

Heterogeneous catalytic transfer hydrogenation^{1–4} is gaining more potential over traditional hydrogenation and other methods of reduction⁵ due to the simple work-up and selectivity. The earlier methods reported in the literature^{5–9} for the reductive cleavage of azo compounds employ stronger acidic or basic conditions, some systems like cyclohexene/5% Pd on asbestos,⁷ cyclohexene/10% Pd–C,⁸ hydrazine/10% Pd–C⁹ or hydrazine/raney Ni⁹ require as long as 23–48 hours at reflux temperature and expensive catalysts.

During our investigation on catalytic transfer hydrogenation, we found that Zn/hydrazinium monoformate effectively cleaved symmetrical and unsymmetrical azo compounds to their constituent amine/s (Scheme 1). Hydrazine derivatives like methyl hydrazine⁴ and unsymmetrical dimethyl hydrazine⁴ and phenyl hydrazine¹⁰ are used as hydrogen donors for catalytic transfer hydrogenation, but not hydrazinium monoformate. Our investigations have proved that this is a more effective donor than cyclohexene.



Scheme 1

The cleavage of azo compounds in the presence of zinc dust and hydrazinium monoformate was completed within 3 to 15 min. The course of reaction was monitored by thin layer chromatography (TLC) and IR spectra. The work-up and isolation of the products were easy. Thus, the azo compounds reduced (a few examples are listed in Table 1) by this system were obtained in good yields (90–95%). The products were characterised by comparison of their melting points, TLC, and IR spectra with authentic samples. The disappearance of strong absorption band between 1630 and 1575 cm^{–1} due to –N=N– stretching and appearance of a strong absorption band between 3500 and 3300 cm^{–1} of –NH₂ group clearly shows that the azo compounds are cleaved to their constituent amine/s. Further, there is no absorption between 2290 and 2440 cm^{–1}, which clearly indicates that the absence of the –NH–NH– group. A control experiment, carried out using azo

compounds with hydrazinium monoformate but without zinc dust, does not yield the desired product. The appearance of one spot in the case of symmetrical azo compounds, and two spots in the case of unsymmetrical azo compounds, in the TLC also indicates that no hydrazo compounds were formed as intermediates during the reductive cleavage of azo compounds. In order to test the selectivity, the reduction was attempted with *p*-dichloro benzene, *p*-chloro-*m*-cresol, β-naphthol, acetanilide, benzoic acid, anisole and phenyl acetate at reflux temperature. However, the reaction failed to give any reduced product.

Further, hydrazinium monoformate/zinc system is more effective than either cyclohexene/5% Pd on asbestos⁷ or cyclohexene/10% Pd–C⁸ or hydrazine/10% Pd–C⁹ or hydrazine/raney Ni.⁹ Most of the reactions are complete in less than 10 min as monitored by the disappearance of the starting materials and concomitant formation of the product(s) via TLC methods.

Experimental

Equal moles of 85% formic acid and 99–100% hydrazine hydrate were neutralised slowly, cooling in an ice bath with stirring, to obtain hydrazinium monoformate solution.

Reductive cleavage of azo compounds. General procedure: The azo compounds exhibited in Table 1 (**2g**) were suspended in methanol or any other suitable solvent (10ml). About 5ml of hydrazinium monoformate and about 1g of commercial zinc dust were added and stirred at reflux temperature. The reaction was monitored through TLC and in most of the cases, the colour of the starting material disappears. After the completion of reaction, the mixture was filtered through a celite pad, washed with solvent and then the solvent was evaporated. The residue was dissolved in chloroform or diethyl ether, washed twice with saturated sodium chloride solution and then with water. The organic layer was dried over anhydrous sodium sulfate and evaporated in a vacuum. The residue comprises the amine(s) which is/are further purified/separated either by preparative TLC or by column chromatography. The reaction duration, yields and melting points are shown in Table 1.

Received 2 November 2001; accepted 5 March 2002

Paper 02/1106

References

- 1 R.A.W. Johnstone, A.H. Wilby and I.D. Entwistle, *Chem. Rev.*, 1985, **85**, 129.
- 2 G. Brieger and T.J. Nestrick, *Chem. Rev.*, 1974, **74**, 567.
- 3 S. Ram and R.E. Ehrenkauffer, *Synthesis*, 1988, 91.
- 4 A. Furst, R.C. Berlo and S. Hooton, *Chem. Rev* 1965, **65**, 51.
- 5 J. March, *Advanced Organic Chemistry*, 3rd ed, Wiley Eastern Ltd., New Delhi, 1986; pp.1106, 1109, 1117.

* To receive any correspondence. E-mail: dcgowda@yahoo.com

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

Table 1 Reductive cleavage of azo compounds catalysed by commercial zinc dust, using hydrazinium monoformate

| Substrate | Product | Duration/min | Yield/% ^a | Melting point (°C) | |
|-----------|---------|--------------|------------------------------------|--------------------|------------|
| | | | | Found | Literature |
| | 2 | 4 | 95 ^c | 112 | 114 |
| | 2 | 5 | 94 ^b | 142 | 144 |
| | 2 | 6 | 95 ^b | 126 | 125 |
| | 2 | 6 | 93 ^b | 115 | 116 |
| | 2 | 8 | 94 ^c | 82 | 80 |
| | 2 | 6 | 93 | 100 | 99 |
| | + | 9 | 75 ^{c,d} 90 | 113 188 | 114 186 |
| | | 8 | 95 ^c 95 ^c | 130 113 | 132 114 |
| | | 15 | 91 ^c 80 ^d | 131 146 | 132 145 |
| | | 12 | 92 93 ^b | 65 144 | 64 144 |

^aIsolated yields are based on single experiment and the yields were not optimised.^bIsolated as benzoyl derivative.^cIsolated as acetyl derivative.^dThe low yield is due to its water soluble nature, TLC analysis indicates 95–98% cleavage.6 T.L. Gilchrist, *Comprehensive Organic Synthesis*; Vol. 8; Ch.2.2; eds. I. Fleming, Pergamon press; Oxford, 1991, pp. 381–402.7 T.L. Ho and G.A. Olah, *Synthesis*, 1977, 167.8 E.A. Braude, R.P. Linstead, P.W.D. Mitchell and K.R.H. Wooldridge, *J. Chem. Soc.*, 1954, 3595.9 W.H. Stafford, M. Los and N. Thomson, *Chem. Ind. (London)*, 1956, 1277.10 E. Ochiai and H. Mitarashi, *Chem. Pharm. Bull. (Tokyo)*, 1963, **11**, 1084.