

## NOTE

**Preparation and Characterisation of 1-Halobenzimidazoles**

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Two new N-halo compounds have been introduced. Preparation of 1-halobenzimidazoles and their characterization by spectral and electrochemical methods have been discussed.

The utility of N-halocompounds for the effective and selective oxidation of several organic substrates has been well documented.<sup>1</sup> In our search for new N-halo compounds we found that there is no exhaustive report about the 1-halo (or N-halo) derivatives of benzimidazole (BI)<sup>2,3</sup> and hence attempts were made to prepare 1-halo derivatives of benzimidazole. In this communication, we present a detailed method of preparing 1-chloro and 1-bromo benzimidazoles and their characterisation by elemental analysis, IR, <sup>1</sup>H NMR and mass spectral data. It is found that these reagents have certain advantages over similar oxidising agents in terms of mild reaction conditions, stability and high yield.

1-Chlorobenzimidazole (CBI) was prepared by passing a slow stream of chlorine gas into a solution of 5 g of benzimidazole dissolved in 20 mL of glacial acetic acid (0.04 mol) at 32°C for 30 min. On dilution with water, the product formed as a dirty white precipitate was filtered, washed with water, dried and recrystallized from ethanol. Its melting point was 224–226°C. Yield 3.8 g, 62.5%.

1-Bromobenzimidazole (BBI) was prepared by the bromination of benzimidazole. Benzimidazole (10 g, 0.08 mol) was dissolved in aqueous NaOH (40 mL, 10%). The solution was cooled to 0°C. Bromine was added to the mixture (20 mL) and the reaction mixture was stirred for 15 min. Any residual bromine was removed by washing with sufficient amount of water followed by grinding the solid in a mortar and filtering. The thoroughly drained solid was dried over CaCl<sub>2</sub> in a desiccator. It was recrystallized from ethanol. Yield 11.7 g (75%). Melting point 197–199°C.

The presence of N—X (N—Cl and N—Br) bond present in N-halo benzimidazoles has been confirmed by estimating the amount of iodine liberated by a given amount of N-halo compound iodometrically. Moreover, the stock solutions of 1-chloro and 1-bromo benzimidazoles prepared in glacial acetic acid did not show any noticeable change in concentration over a period of three months.

Both 1-halobenzimidazoles are found to be soluble in acetic acid, ethanol, ether and dioxane and insoluble in water and benzene.

The purity of CBI and BBI was confirmed by their elemental analysis.

IR spectra of CBI and BBI show the absence of N—H absorption and the two peaks very near to  $16200$  and  $1580\text{ cm}^{-1}$  indicating that they are 1-substituted or N-substituted benzimidazoles.  $^1\text{H}$  NMR shows the absence of N—H broad band absorption in the aromatic proton regions of CBI and BBI. The IR and  $^1\text{H}$  NMR of CBI and BBI are found to be similar to 1-chlorobenzotriazole<sup>4</sup> and 1-bromobenzotriazole<sup>5</sup> respectively which also belong to N-halogeno imide. The electron impact mass spectra of both CBI and BBI show a characteristic M—X peak at  $m/e$  117. The structures of BI (Fig. 1), CBI (Fig. 2) and BBI (Fig. 3) are shown.

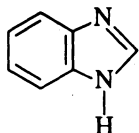


Fig. 1

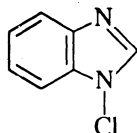


Fig. 2

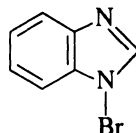


Fig. 3

The formal redox potential of CBI/BI couple was determined by measuring the potentials in the mixtures containing varying concentration ratios of CBI and BI in glacial acetic acid. Since dilute solutions of both CBI and BI were used, the activities were replaced by concentration terms in the Nernst equation (1).

$$E_{\text{obs}} = E^{\circ} + \frac{2.303 RT}{F} \log \frac{[\text{CBI}]}{[\text{BI}]} \quad (1)$$

A plot of  $E_{\text{obs}}$  against  $\log [\text{CBI}]/[\text{BI}]$  from equation (1) was made which yielded a straight line with non-zero intercept<sup>6</sup> (Fig. 4) and that the potential from that was calculated to be  $+1.08\text{ V}$  at  $25^{\circ}\text{C}$ . Similarly the formal redox potential of BBI/BI couple was found to be  $+1.18\text{ V}$ . The values of formal redox potentials

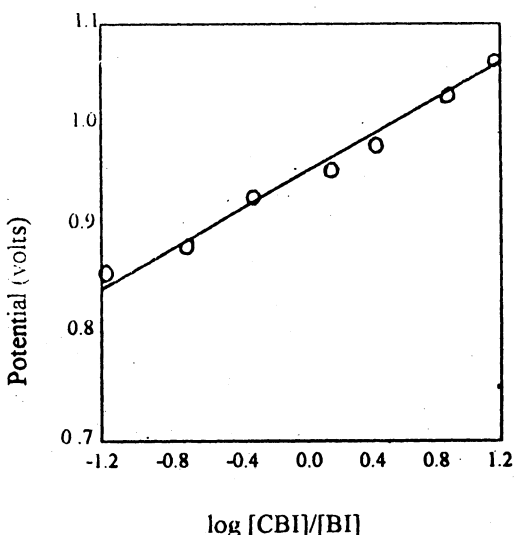


Fig. 4. Redox Potential of CBI/BI System

of CBI/BI couple (+1.08 V at 25°C) and BBI/BI couple (+1.18 V at 25°C) are comparable to the values of +1.02 V for N-chloronicotinamide<sup>7</sup> and +1.14 V for chloramine-T<sup>8</sup> and +1.24 V for N-chlorosuccinimide<sup>9</sup>. The kinetic study on the oxidation of aromatic aldehydes by CBI is under investigation.

### Conclusion

The possibility of the compounds serving as effective source of positive halogens is established. The results hitherto obtained with 1-halobenzimidazoles are very satisfactory and suggest that the new agents can be added to the existing oxidising agents.

### ACKNOWLEDGEMENT

The author thanks the authorities of National College, Trichy-1, for laboratory facilities.

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(Received: 30 October 2000; Accepted: 17 February 2001)

AJC-2262