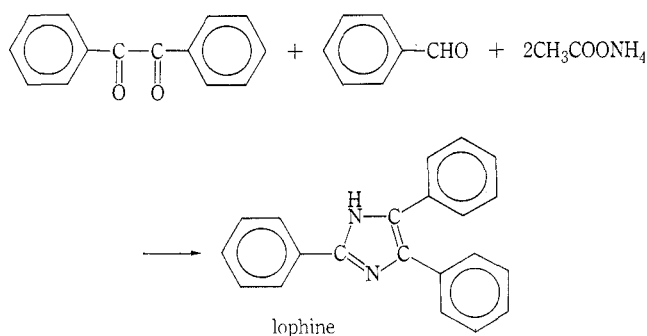


# PREPARATION OF SOME TRIARYL IMIDAZOLES AND THEIR METAL COMPLEXES\*

By T. E. MACDERMOTT†

The simple reaction described by Davidson *et al.*<sup>1</sup> for the preparation of lophine, can be written:



and results in an almost quantitative yield of a very pure product.

Cook and Jones<sup>2</sup> replaced benzaldehyde with a variety of aromatic and aliphatic aldehydes including salicylaldehyde and *o*-nitrobenzaldehyde.

In this work the reaction has been extended further by replacing benzil with 2,2'-dimethoxybenzil and treating this compound with salicylaldehyde to give (I), and *o*-nitrobenzaldehyde to give (II). We also prepared 2- $\alpha$ -hydroxyphenyl-4,5-diphenylimidazole (III) and showed it is a white crystalline material (m.p. 210°) and not a yellow compound melting at 209° as described by the previous workers.<sup>2</sup>

Attempts to replace benzaldehyde with pyridine-2-aldehyde in the reaction used to prepare lophine resulted in the formation of lophine itself. Previous workers<sup>1</sup> have shown that benzil will react with ammonium acetate to give lophine and it is clear that, in the above reaction, pyridine-2-aldehyde played no part. When the reaction was carried out using pyridil and pyridine-2-aldehyde the reaction did not proceed smoothly. A very small yield of a crystalline material was eventually isolated. Its analyses were in fair agreement with the desired tri( $\alpha$ -pyridyl)imidazole but further verification is needed.

Compound (III) was then used to demonstrate the ability of these compounds to form metal complexes. Complexes of copper(II), nickel(II), and cobalt(II) were

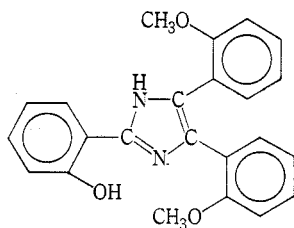
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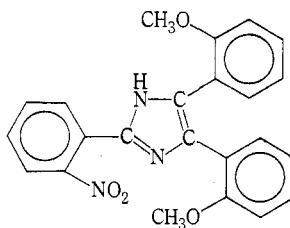
<sup>1</sup> Davidson, D., Weiss, M., and Jelling, M., *J. org. Chem.*, 1937, **2**, 319.

<sup>2</sup> Cook, A. H., and Jones, D. G., *J. chem. Soc.*, 1941, 278.

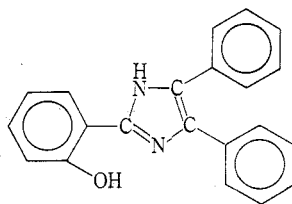
prepared and appear to be simple 2 : 1 complexes in each case. They are all neutral complexes so the ligand must lose one proton in complex formation. The basic structure is therefore postulated as (IV). All three complexes separated as crystalline



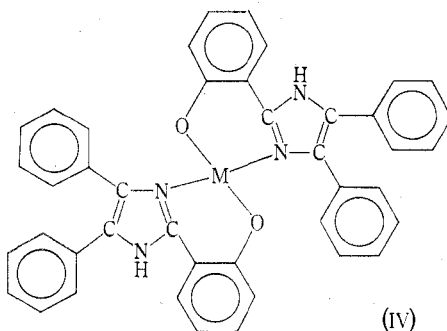
(I)



(II)



(III)



(IV)

material from the reaction mixture and each changed colour on being thoroughly dried. Only in the cobalt(II) case could both colour forms be analysed and here the effect seemed to be due to difference in solvation.

These preliminary studies indicate that such substituted imidazoles are excellent ligands, and work is under way to look at the possible tridentate character of (I) and its demethylated product and the reduced, demethylated product from (II).

### Experimental

#### 2-*a*-Hydroxyphenyl-4,5-diphenylimidazole (III)

This compound was prepared by the method of Cook and Jones.<sup>2</sup> It was recrystallized from acetone and finally ethanol to yield white glistening needles, m.p. 210° (Found: C, 80.6; H, 5.2. Calc. for  $C_{21}H_{16}N_2O$ : C, 80.7; H, 5.1%).

*Bis(2- $\alpha$ -hydroxyphenyl-4,5-diphenylimidazole)copper(II) Monohydrate*

Admixture of hot concentrated methanolic solutions of copper(II) acetate monohydrate (0.5 g) and (III) (1.56 g) gave a deep brown solution. This solution was heated to boiling and dark, almost black, plates separated. The product was collected on a sintered glass funnel and washed with ether, whereupon the dark crystalline material collapsed into a violet *powder* (Found: C, 71.4; H, 4.5; Cu, 9.6.  $(C_{21}H_{15}N_2O)_2Cu \cdot H_2O$  requires C, 71.6; H, 4.5; Cu, 9.3%).

*Bis(2- $\alpha$ -hydroxyphenyl-4,5-diphenylimidazole)nickel(II) Monohydrate*

This complex was prepared as for the copper(II) complex described above, by replacing the copper(II) acetate monohydrate with 0.62 g of nickel(II) acetate tetrahydrate. The yellowish brown crystalline *product* separated on cooling the reaction vessel in a stream of cold water. It was collected as before and dried in a vacuum desiccator over concentrated sulphuric acid. This process caused the colour to change to deep orange (Found: C, 72.0; H, 4.6.  $(C_{21}H_{15}N_2O)_2Ni \cdot H_2O$  requires C, 72.0; H, 4.6%).

*Bis(2- $\alpha$ -Hydroxyphenyl-4,5-diphenylimidazole)cobalt(II)*

Hydrated cobalt(II) acetate (0.45 g) and (III) (1.56 g) were each mixed in the minimum of hot methanol. Mixing of these solutions caused the immediate formation of a curdy pink precipitate. Ethanol was added until the precipitate just dissolved. Water was then added to heavy turbidity and the mixture warmed till it cleared again. Bright orange *crystals* of the product separated as the solution cooled (Found: C, 69.5; H, 4.5.  $(C_{21}H_{15}N_2O)_2Co \cdot 2.5H_2O$  requires C, 69.5; H, 4.8%). When this orange product was washed in the filter with a large volume of acetone it yielded a bright pink *powder* (Found: C, 70.7; H, 5.1.  $(C_{21}H_{15}N_2O)_2Co \cdot 2H_2O$  requires C, 70.4; H, 4.8%).

*2- $\alpha$ -Hydroxyphenyl-4,5-di- $\alpha$ -methoxyphenylimidazole (I)*

2,2'-Dimethoxybenzil (6.0 g) was refluxed in 150 ml of glacial acetic acid, with salicylaldehyde (2.7 g) and ammonium acetate (30 g.) for 1 hr. The reaction mixture was then diluted with a large volume of water, causing the product to precipitate. It was recrystallized from hot ethanol to give white *crystals* melting at 185° (Found: C, 74.6; H, 5.4.  $C_{23}H_{20}N_2O_3$  requires C, 74.3; H, 5.4%).

*2- $\alpha$ -Nitrophenyl-4,5-di- $\alpha$ -methoxyphenylimidazole (II)*

The synthesis was the same as described for the hydroxy analogue above, after replacing the salicylaldehyde with 3.4 g of *o*-nitrobenzaldehyde. Purification of the product by recrystallization from hot ethanol yielded fine yellow *needles*, m.p. 161° (Found: C, 68.2; H, 4.8.  $C_{23}H_{19}N_3O_4$  requires C, 68.8; H, 4.8%).

*Acknowledgments*

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