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## SYNTHESIS AND PYROLYSIS OF 1,3-DIBENZYL-2-ARYL-4-METHYL BENZIMIDAZOLINES

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WHILE extensive work was done on the synthesis and pyrolysis of 1,3-dibenzyl-2-arylbenzimidazolines and their 5-substituted derivatives<sup>1-3</sup>, there is no report in literature regarding the formation and elimination reactions of the 1,3-dibenzyl-2-aryl-4-substituted benzimidazolines. Therefore, as a representative case the synthesis of 1,3-dibenzyl-2-aryl-4-methylbenzimidazolines(V) has been undertaken with a view to studying the effect of the substituent on their formation and elimination reactions.

The condensation of 3-methyl-o-phenylenediamine with formic acid in dilute hydrochloric acid yielded 4 (or 7)-methylbenzimidazole<sup>4</sup>(II). 1,3-dibenzyl-4-methylbenzimidazolium chloride (III) has been prepared by benzylation of this benzimidazole with excess of benzyl chloride. The quarternary salt (III) on

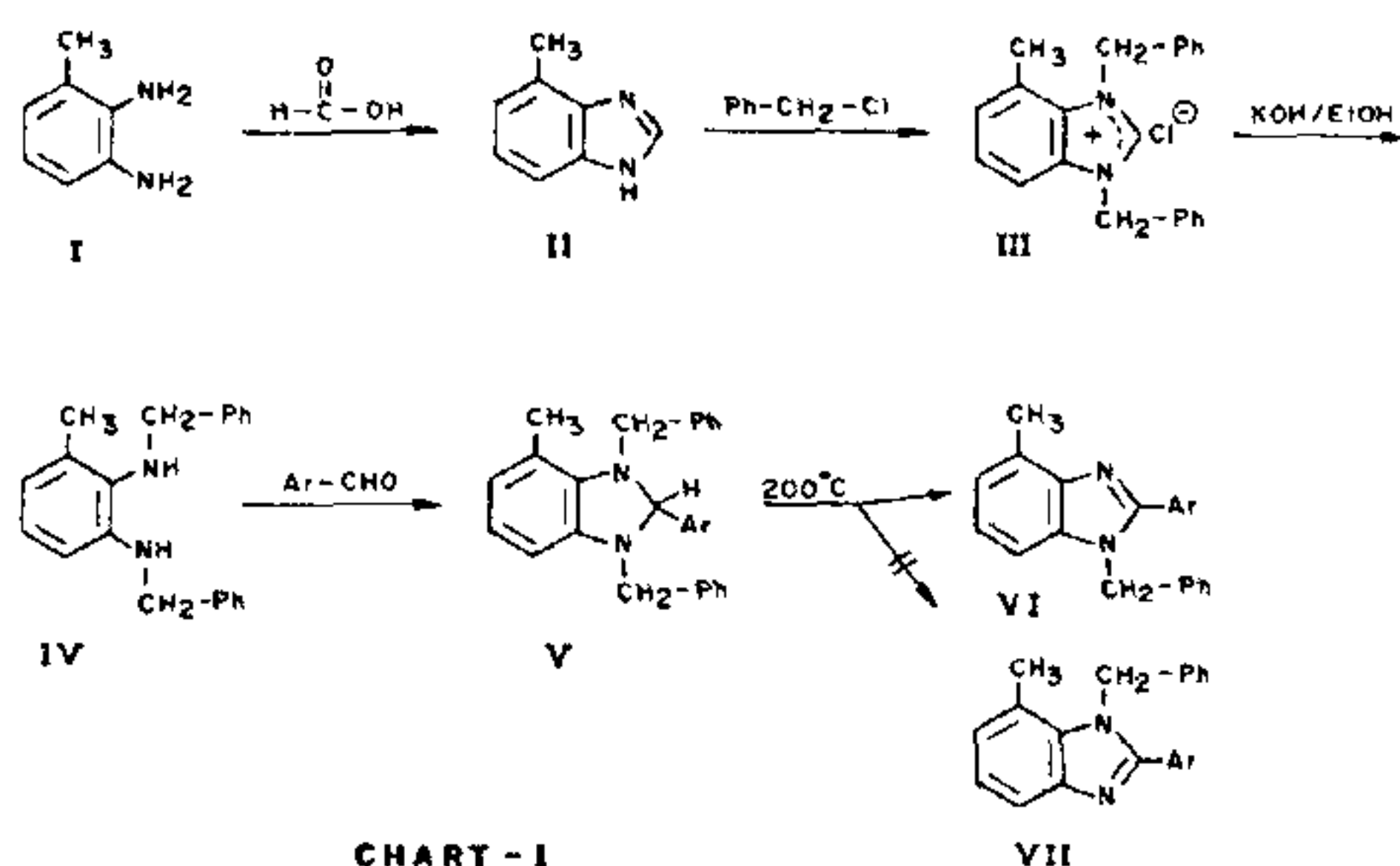
hydrolysis with alcoholic potassium hydroxide afforded N<sup>1</sup>, N<sup>2</sup>-dibenzyl-3-methyl-o-phenylenediamine(IV). The diamine (IV) on condensation with equimolar quantity of benzaldehyde in alcohol-acetic acid medium yielded a colourless crystalline compound, m.p. 136°. This compound has shown no absorption due to N-H in the IR spectrum (KBr). Its PMR\* spectrum has shown signals at 2.26 (s, 3H), at 4.4 (q, J = 10Hz, 4H) at 5.56 (s, 1H) and around 6.7 (m, 18H), assignable for a C-CH<sub>3</sub>, two N-CH<sub>2</sub> groups, a methine and eighteen aromatic protons respectively. The foregoing data is in agreement with the expected, 1,3-dibenzyl-2-phenyl-4-methylbenzimidazoline structure (V Ar=ph) for the compound. The condensation with the diamine (IV) has been carried out with five other aromatic aldehydes and in all the cases, the corresponding benzimidazolines have been obtained in good yields (table 1).

Pyrolysis of 1,3-dibenzyl-2-phenyl-4-methylbenzimidazoline (V Ar=ph) at 200° for one hour yielded a single crystalline colourless compound, m.p. 105°. The mass spectrum of the compound has shown the molecular ion at m/e 298. IR spectrum (CHCl<sub>3</sub>) of the compound revealed the absence of NH and PMR spectrum (CS<sub>2</sub>) [2.6 (3H, C-CH<sub>3</sub>); 5.3 (s, 2H, N-CH<sub>2</sub>-ph); around 7.2 (m, 13H, aromatic protons)] indicated the compound to be a 1,2-disubstituted benzimidazole and the structure was confirmed as 1-benzyl-2-phenyl-4-methylbenzimidazole (VI Ar=ph)<sup>5</sup> by comparison with the authentic sample. Compound (VI) was formed by the elimination of a benzyl radical from N<sup>3</sup> and a hydrogen atom from C<sup>2</sup>. The formation of (VI Ar=ph) and not the isomeric benzimidazole (VII Ar=ph), which could be formed by the elimination of a benzyl radical from N<sup>1</sup> and a hydrogen atom from C<sup>2</sup>, in this elimination reaction indicates that the methyl group at position 4 is exerting a strong steric effect in the benzimidazoline, facilitating exclusive elimination of N<sup>3</sup>-benzyl group (scheme 1). The pyrolysis reaction has been extended to two more benzimidazolines viz 2-p-methylphenyl and 2-p-methoxyphenyl derivative (V Ar=p-methylphenyl, p-methoxyphenyl) and in both the cases the corresponding benzimidazoles (VI) have been obtained.

*1,3-Dibenzyl-4-methylbenzimidazolium chloride (III).*

4 (or 7)-Methylbenzimidazole (15 g) and freshly distilled benzyl chloride (30 ml) were thoroughly mixed in a round bottomed flask and heated in an oil

\* PMR values are given in δ ppm.



bath at 150° for five hours. The gummy material obtained was washed successively with petroleum ether, benzene and ethylacetate to remove the excess of benzylchloride then a small quantity of acetone was added to get a pale-bluish solid (16 g.), recrystallized from alcohol, m.p. 130°. (Found: N, 7.9%; C<sub>22</sub>H<sub>21</sub>N<sub>2</sub>Cl requires N, 8.0%).

#### N<sup>1</sup>, N<sup>2</sup>-Dibenzyl-3-methyl-o-phenylenediamine (IV).

The above benzimidazolium salt (15 g.) was hydrolysed by refluxing with alcoholic potassium hydroxide solution (30%, 120 ml) for 4 hr. After removing the alcohol by distillation under reduced pressure, the mixture was poured into cold water and extracted with chloroform. The chloroform extracts, after a thorough washing with water to remove alkali, were evaporated to yield the crude diamine (7 g.) as viscous pale yellow oil, hydrochloride m.p. 161–162°. (Found: N, 8.1%; C<sub>21</sub>H<sub>22</sub>N<sub>2</sub>.HCl requires N, 8.3%).

#### 1,3-Dibenzyl-2-aryl-4-methylbenzimidazolines (V).

To a solution of the diamine (1 g.) in methyl alcohol (10 ml) an equimolar quantity of the appropriate aromatic aldehyde was added with stirring at room temperature. A drop of acetic acid was added to the reaction mixture when the corresponding benzimidazoline (V) (0.8–0.9 g) separated out almost immediately. The solid in each case was filtered and recrystallized from methanol-acetone mixture (table 1).

#### Pyrolysis of 1,3-dibenzyl-2-aryl-4-methylbenzimidazolines (V).

The appropriate benzimidazoline (0.5 g.) was taken in a boiling tube and heated in an oil-bath at 200° C for a period of one hour. The gummy residue in each case was extracted with hot petroleum ether, yielding

Table 1 1,3-Dibenzyl-2-aryl-4-methylbenzimidazolines (V)

Ar=	m.p. °C	Molecular formula	Analysis of Nitrogen	
			Found	Calculated
Phenyl	136	C <sub>28</sub> H <sub>26</sub> N <sub>2</sub>	7.2	7.2
p-Methylphenyl	113	C <sub>29</sub> H <sub>28</sub> N <sub>2</sub>	6.8	6.9
p-Methoxyphenyl	123	C <sub>29</sub> H <sub>28</sub> N <sub>2</sub> O	6.8	6.7
p-Chlorophenyl	128	C <sub>28</sub> H <sub>25</sub> N <sub>2</sub> Cl	6.7	6.6
p-Nitrophenyl	109	C <sub>28</sub> H <sub>25</sub> N <sub>3</sub> O <sub>2</sub>	9.6	9.7
p-Dimethylamino phenyl	158	C <sub>30</sub> H <sub>31</sub> N <sub>3</sub>	9.9	9.7

#### 1-Benzyl-2-aryl-4-methylbenzimidazoles (VI)\*

Phenyl	105 <sup>s</sup>	—	—	—
p-Methylphenyl	101	C <sub>22</sub> H <sub>20</sub> N <sub>2</sub>	8.9	9.0
p-Methoxyphenyl	107	C <sub>22</sub> H <sub>20</sub> N <sub>2</sub> O	8.5	8.5

The experimental values of C & H analysis of these compounds are in agreement with the calculated ones within the experimental error.

\* % yield of the product VI, Ar=phenyl(75), p-methylphenyl (65), p-methoxyphenyl (55). These compounds have been recrystallized from petroleum ether (60–80°).

the corresponding 1-benzyl-2-aryl-4-methylbenzimidazole (VI) (0.2–0.3 g.) (table 1).

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