Dearomatisation by Use of Multifunctional Reagents: Reaction of Bis-(1-chloroformyl)-diphenylamine with Imidazole Derivatives

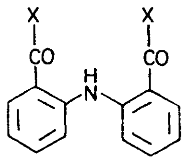
By Julian C. Cass and Alan R. Katritzky*
(*School of Chemical Sciences, University of East Anglia, Norwich* NR4 7TJ)
and Richard L. Harlow and Stanley H. Simonsen
(*Department of Chemistry, University of Texas at Austin, Austin, Texas* 78712)

Summary Benzimidazole is dearomatised by the diphenylamine derivative (**1**) to the novel hexacyclic system (**5**), the structure of which is confirmed by *X*-ray analysis; imidazole under similar conditions yields the bimolecular derivative (**7**).

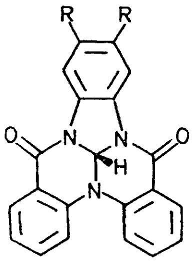
We are studying heterocycle dearomatisation by reaction with multifunctional reagents. Compound (**1**) reacts with imidazole, benzimidazole, and 5,6-dimethyl-benzimidazole to give the bisamides (**2**), (**3**), and (**4**), respectively.† When these compounds are heated in a sublimation apparatus, in each case just one mole of the heterocyclic base originally used sublimes out of the reaction mixture. From the benzimidazoles (**3**) and (**4**), the products were the anticipated novel dearomatised systems (**5**) and (**6**) as shown by the n.m.r. [especially 1 proton singlets at δ 6·39 (**5**) and 6·25 (**6**) for the unique central proton] and mass (especially very intense $M - 1$ peaks) spectra and, for (**5**), conclusively, by *X*-ray structure determination.

Crystal data: orthorhombic, space group $Pca2_1$, $Z = 4$; at -40 °C, $a = 18{\cdot}458(4)$, $b = 10{\cdot}924(2)$, $c = 7{\cdot}673(2)$ Å. Intensity measurement: Syntex $P2_1$ diffractometer, Mo-$K\alpha$ radiation, low-temperature apparatus to maintain crystal at -40 °C, 1322 unique reflections measured, $4° < 2\theta < 48°$, ω-scan technique, 1118 reflections considered observed [$I > 2\sigma(I)$]. Solution and refinement: direct methods (MULTAN), full-matrix least-squares, non-hydrogen atoms refined with isotropic thermal parameters, hydrogen atoms located *via* a difference Fourier and positional parameters refined, conventional R of 0·065 (observed reflections only).

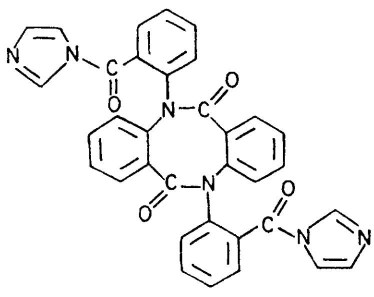
The imidazole derivative (**2**) on pyrolysis gave the bimolecular diazocine derivative (**7**) which was hydrolysed to the corresponding acid (**8**) and esterified to give (**9**). The ester (**9**) was characterised by n.m.r., i.r., and mass spectra. We believe that the higher loss of resonance energy involved in the complete dearomatisation of imidazole as compared to just the heterocyclic ring of benzimidazole is responsible for the different behaviour observed.



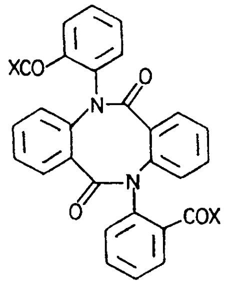
(1) X = Cl
(2) X = imidazol-1-yl
(3) X = benzimidazol-1-yl
(4) X = 5,6-dimethylbenzimidazol-1-yl



(5) R = H
(6) R = Me



(7)



(8) X = OH
(9) X = OMe

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† All new compounds reported were satisfactorily characterised.