

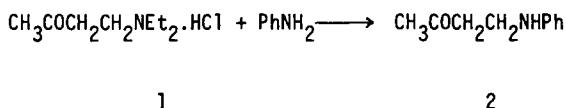
A BASE EXCHANGE REACTION BETWEEN A
1,2-DIKETO-BIS MANNICH BASE AND O-PHENYLENEDIAMINE

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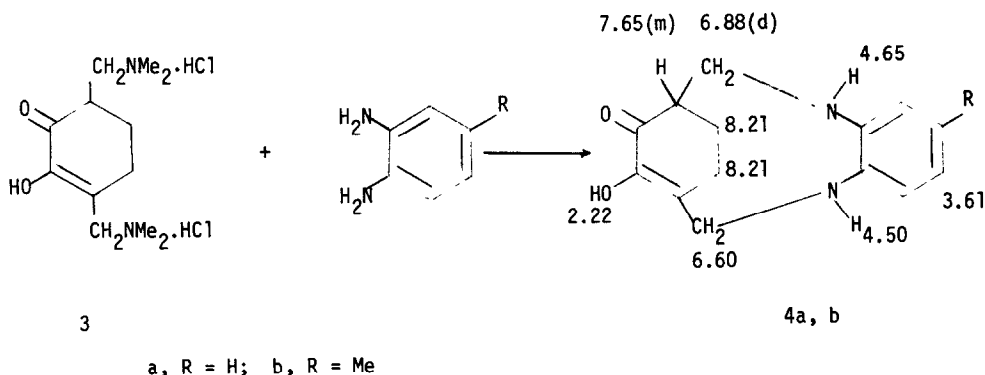
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A few base-exchange reactions involving Mannich bases have been reported, mainly by Craig *et al*¹. For example aniline reacts with 4-diethylaminobutan-2-one hydrochloride (1) to give the arylamine (2) with elimination of diethylamine hydrochloride.



We have discovered a comparable reaction during attempts to prepare the quinoxaline derivative of 3,6-bisdimethylaminomethyl-2-hydroxy-cyclohex-2-enone hydrochloride² (3) under standard conditions (equimolar quantities, 10 mins. reflux in ethanol). No reaction occurred on the 1,2-diketone system, but instead dimethylamine hydrochloride was displaced by the aromatic amine group to give the tricyclic compound 4a (76% m.p. 192-193^o).



This structure agrees with the molecular formula $C_{14}H_{16}N_2O_2$ obtained from high resolution mass spectrometry and elemental analysis. In the i.r. spectrum the starting material (3) free base shows ν 1645cm^{-1} (C=C) and ν 1665cm^{-1} (C=O) and ν 3400cm^{-1} (broad, O-H). The product (4a) shows ν 1630 , 1670 and 3450cm^{-1} indicating that the enolised² 1,2-dione system remains. This was confirmed by its simple conversion to a di-oxime (m.p. $229-230^\circ$) which lacked i.r. peaks in the $1600-1700\text{cm}^{-1}$ region. The compound 4a showed λ max (MeOH) 263nm (ϵ 10 200) in the u.v. This is quite different from quinoxaline λ max (MeOH) 233nm (ϵ 25 700) and 315nm (ϵ 6 166), but similar to compound 3, λ max (EtOH) 274nm (ϵ 200). The assigned structure is confirmed by the n.m.r. spectrum (d_6 DMSO, 100MHz), the tau values for the chemical shifts are shown on the formula for 4a.

A similar reaction occurred when 3,4-diaminotoluene was used in the reaction to give the compound 4b (m.p. $186-187^\circ$).

The mild conditions under which base exchange could occur were emphasised by Craig *et al*¹. Our discovery emphasises this in that one equivalent of o-phenylene diamine gives the bridged ring compound in preference to the alternative reaction to give a quinoxaline derivative. Nucleophilic substitution rather than elimination-addition was shown to be the dominant mechanism.¹

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2. J.V. Greenhill, P.H.B. Ingle and M. Ramli, J. Chem. Soc. (Perkin I) 1972, 1667.