Tetrahedron Letters, Vol.31, No.8, pp 1207-1208, 1990
Printed in Great Britain

0040-4039/90 $3.00 + .00
Pergamon Press plc

MERCURY (II) MEDIATED HETEROCYCLISATION OF 2-CYCLOHEX-2'-ENYL-N-METHYLANILINE

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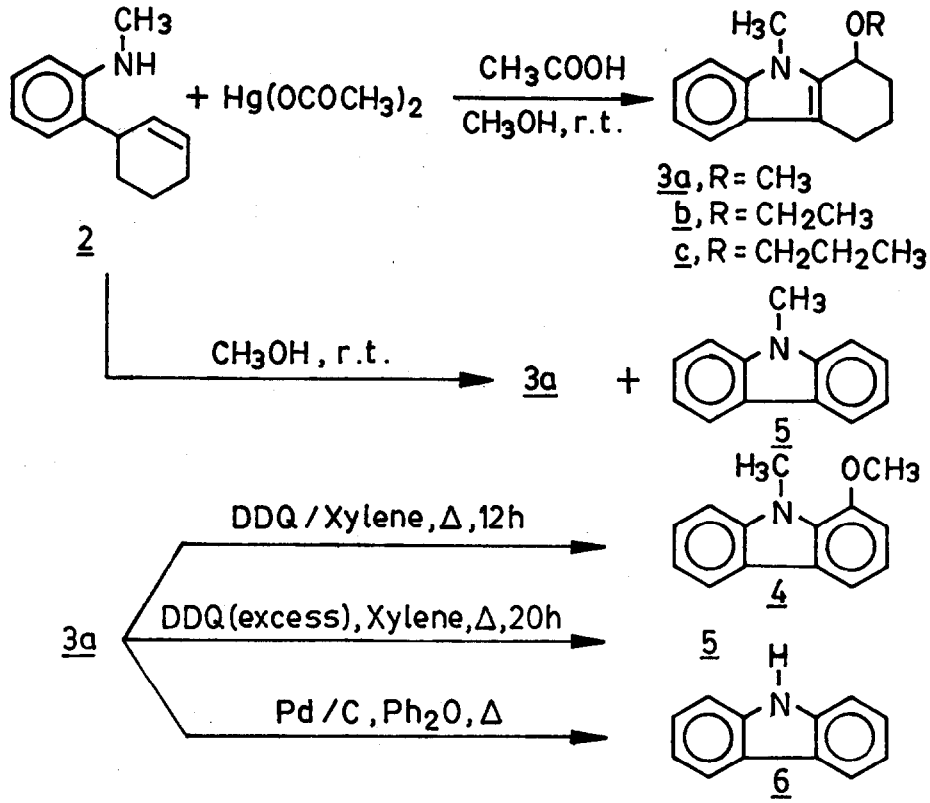
Abstract : 2-[2'-Cyclohexenyl]-N-methylaniline in alcohol is cyclised with mercury (II) acetate in presence of acetic acid to give 1-alkoxy-1, 2, 3, 4-tetrahydrocarbazoles in excellent yield.

The solvomercuration-demercuration reaction remain the most widely used of the organomercurials[1]. Aminomercuration-demercuration have been utilised for the synthesis of nitrogen heterocycles by employing unsaturated amine compounds[2]. In case of solvomercuration and aminomercuration, reduction[3] is essential to get rid of mercury from the initial product. During our work on the sigmatropic rearrangements[4] we became interested in cyclisation[5] of 2-[2'-cyclohexenyl]-N-methylaniline, but our attempt failed[6]. We then considered mediation of mercury (II) for this heterocyclisation. We have made an interesting observation in which heterocyclisation to a tetrahydrocarbazole alkaloid skeleton takes place in a single step. Herein we report the results of our investigation.

Amino Claisen rearrangement of 3-N-methylanilino cyclohexene[7] (**1**), gave 2-[2'-cyclohexenyl]-N-methylaniline (**2**) which was then stirred at room temperature with mercury (II) acetate in methanol in presence of a small amount of glacial acetic acid for 24 h during which black precipitate of metallic mercury separated out and after work-up a viscous oil was obtained. This on column chromatography over basic alumina (pet. either 60-80°) furnished a viscous oil which solidified on standing, **3a**, yield 80%, m.p. 51° C. This product showed λ_{max} 242, 295 nm in the u.v. spectrum and lacked the -NH absorption band in the i.r. spectrum, ^{1}H-n.m.r. ($CDCl_3$, 400 MHz) : δ 1.73-2.84 (m, 6H), 3.45 (s, 3H), 3.72 (s, 3H), 4.5 (t, 1H), 7.03-7.55 (m, 4H), M^+ 215 (23.93%), 216 (M+1), 184 ($M-OCH_3$), 169, 157. On the basis of the above spectral data and elemental analysis the product was assigned the structure **3a**, 1-methoxy-9 methyl-1, 2, 3, 4-tetrahydrocarbazole. This reaction also gave partially oxidised N-mercurated complex m.p. 180° C in 10% yield. The reaction was repeated in ethanol and n-propanol to give products[8] **3b** and **3c** as viscous oils in 85% and 75% yields respectively. Additional supporting evidence for the structure of product **3** was obtained by transformation of **3a** to 1-methoxy-9-methyl carbazole[8] (**4**), yield 83%, viscous oil, N-methyl carbazole[8] (**5**), yield 30%, m.p. 85° C and carbazole[8] (**6**), yield 60%, m.p. 242° C with DDQ in xylene and palladised charcoal in diphenyl ether respectively (Scheme-1).

Several methoxycarbazoles including 1-methoxycarbazole are natural alkaloids[9]. It is interesting to note here that this mild one step heterocyclisation provides a simple entry into 1-alkoxytetrahydro-carbazoles and hence 1-alkoxycarbazole skeleton. Only change of alcohol as solvent in the reaction gives different 1-alkoxytetrahydrocarbazoles in high yield.



SCHEME - 1

Acknowledgement : The authors are thankful to C.S.I.R. (New Delhi) and the University of Kalyani for financial assistance and to Dr. N. C. Ganguly of this department for helpful comments.

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(Received in UK 26 September 1989)