# Dehydrogenation and Methylation of 1,2,3,4-Tetrahydro-9-methylcarbazoles during Vilsmeier–Haack Formylation

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*Summary* Formylation of 1,2,3,4-tetrahydro-9-methylcarbazoles under Vilsmeier–Haack conditions affords 3-formyl-1,9-dimethylcarbazoles, in contrast to a previous report.

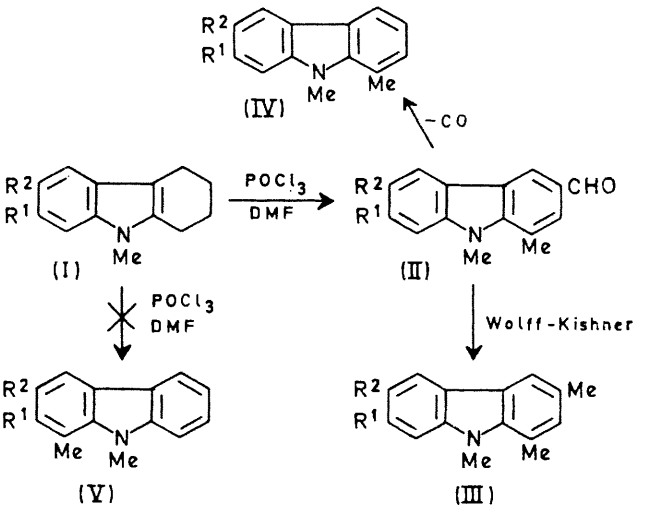
KUCHEROVA, EVDAKOV, and KOCHETKOV[1] have reported that Vilsmeier–Haack formylation of 1,2,3,4-tetrahydro-9-methylcarbazole (I; $R^1 = R^2 = H$) affords 7-formyl-1,2,3,4-tetrahydro-9-methylcarbazole (I; $R^1 = CHO$, $R^2 = H$), mainly on the evidence of the apparent identity of the (Wolff–Kishner) derived dimethyl compound (m.p. 102—104°) with authentic 1,2,3,4-tetrahydro-7,9-dimethylcarbazole (I; $R^1 = Me$, $R^2 = H$), m.p. 102—104°, prepared separately by *N*-methylation of 1,2,3,4-tetrahydro-7-methylcarbazole (from Bischler cyclisation of *m*-toluidine and 2-chlorocyclohexanone). Since this route appeared to offer a simple entry into the otherwise difficultly accessible 7-formyl-1,2,3,4-tetrahydrocarbazole series,[2] we re-examined the reaction, but found it took a totally different course.

Formylation of 1,2,3,4-tetrahydro-9-methylcarbazole with 1·3 molar proportions[1] of $POCl_3$ in dry dimethylformamide afforded a crystalline formyl derivative, m.p. 163—164°, in 55% yield. The n.m.r. spectrum revealed that the product was a totally aromatized carbazole and that, in addition to the 9-methyl substituent, a second methyl group was present; n.m.r. [60 MHz in $(CD_3)_2CO$] δ 10·05 (s, 1H, CHO), 8·50 (d, 1 H), 8·23 (m, 1 H), 7·58—7·16 (m, 4 H) (these 6 H carbazole aromatic protons), 4·13 (s, 3 H, *N*-Me), and 2·88 (s, 3 H, Me). Wolff–Kishner reduction afforded a *x,y*,9-trimethylcarbazole, m.p. 102—103°, whose n.m.r. and i.r. spectra indicated that both nuclear methyl groups were in the same aromatic ring and that the two remaining hydrogen atoms of this ring were isolated from one another; n.m.r. (60 MHz in $CCl_4$) δ 7·63 (*q*, 1 H), 7·50 (broad s, 1 H), 7·33 (m, 3 H), 6·73 (broad s, 1 H), 3·61 (s, 3 H, N-Me), 2·48 (s, 3 H, Me), and 2·35 (s, 3H, Me); i.r. ($CS_2$) 720 and 740 $cm^{-1}$ (1,2-disubstituted benzene ring), 840 $cm^{-1}$ (isolated H only on benzene ring). This product was ultimately characterized as 1,3,9-trimethylcarbazole (III; $R^1 = R^2 = H$) by comparison with an authentic specimen, m.p. 102—103°, obtained by *N*-methylation[3] of 1,3-dimethylcarbazole.[4] Finally, decarbonylation of the initial formyl derivative with tris(triphenylphosphine)-chlororhodium in toluene[5] afforded 1,9-dimethylcarbazole (IV; $R^1 = R^2 = H$), m.p. 114—115° (lit.[6] 114·5—115·0°). The product from the formylation reaction is thus 3-formyl-1,9-dimethylcarbazole (II; $R^1 = R^2 = H$), the above series of transformations being covered by (I—IV) in the Scheme.

The formylation of *Bz*-substituted 1,2,3,4-tetrahydro-9-methylcarbazoles proceeded similarly and revealed an additional interesting feature, *viz.* the 1-methyl and 3-formyl substituents in the final dehydrogenated carbazole are located at the 1- and 3-positions of the original 1,2,3,4-tetrahydrocarbazole ring system and not at the alternative

6- and 8-positions. Thus, the formylation of 1,2,3,4-tetrahydro-7,9-dimethylcarbazole[1] (I; $R^1$ = Me, $R^2$ = H) afforded a product, m.p. 156—157°, which, by Wolff–Kishner reduction yielded 1,3,7,9-tetramethylcarbazole (III; $R^1$ = Me, $R^2$ = H), m.p. 117—118° (identical with authentic material from *N*-methylation[3] of 1,3,7-trimethylcarbazole[7]) and not the alternative 1,2,3,9-tetramethylcarbazole (V; $R^1$ = $R^2$ = Me). The formylation product is consequently (II; $R^1$ = Me, $R^2$ = H) and not (V; $R^1$ = Me, $R^2$ = CHO), methylation, dehydrogenation, and formylation of the alicyclic ring occurring in preference to attack on the benzenoid ring by the Vilsmeier–Haack complex. Similarly, 6-chloro-1,2,3,4-tetrahydro-9-methylcarbazole (I; $R^1$ = H, $R^2$ = Cl), m.p. 53—54°, from *N*-methylation of 6-chloro-1,2,3,4-tetrahydrocarbazole,[8] afforded 6-chloro-3-formyl-1,9-dimethylcarbazole (II; $R^1$ = H, $R^2$ = Cl), m.p. 168—169°, which yielded, by Wolff-Kishner reduction, 6-chloro-1,3,9-trimethylcarbazole (III; $R^1$ = H, $R^2$ = Cl), m.p. 125—126°. The constitution of the latter was confirmed by lithium–t-butyl alcohol–tetrahydrofuran reductive dechlorination[9] to 1,3,9-trimethylcarbazole (above).

Although we defer discussion of the overall mechanism pending further studies, we believe that the process involves initial attack at the 1-methylene group of the tetrahydrocarbazole ring system by the Vilsmeier–Haack complex[10] and that the production of the 1-methyl group from the resultant intermediate may be intimately connected with dehydrogenation.




SCHEME

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