THE MECHANISM OF PHOTOLYSIS OF N-METHYLDIHYDROBERBERINE SALTS AND A SEQUENCE FOR TRANSPOSITION OF RING D SUBSTITUENTS

S.V.Kessar, Y.F. Gupta, T.V.Singh, A. Sood, A.K. Nanda and K.R. Agnihotri Department of Chemistry, Panjab University, Chandigarh-160 014, India.

Abstract : Photolysis of N-deuteriomethyl dihydroberberine salt (1b) gave 1-o-toluyl-3,4-dihydroisoquinoline (5b) with a deuterium atom incorporation; a mechanism involving a 1,7-hydrogen shift step is proposed. The keto-imine(5a) on irradiation followed by reduction furnished 11,12-dimethoxy tetrahydroberberine (9a).

Shamma and coworkers have reported ¹ novel photo transformations of N-methyldihydroberberine salts and have proposed the route A (Fig.1) for the formation of 1-o-toluy1-3,4-dihydroisoquinolines (5). An alternate path (B), involving a 1,7-hydrogen shift as the key step,² also seemed feasible to us. Therefore, the deuterium labelled substrate $1b^3$ ($C_{22}H_{19}D_6O_8NS$, m.p.192-95°C) was prepared by reaction of $(CD_3)_2SO_4$ and dihydroberberine. A solution of 1b (0.4 g) in methanol (65 ml) on exposure (2 h) to sunlight (pyrex filter) furnished (0.06 g) $5b(C_{20}H_{18}DO_5N, m/e 354(M^+))$. Its PMR spectrum ($\mathbf{52.5}(s, 2H, CH_2D), 2.74$ (m, 2H, Ar $CH_2CH_2N), 3.88$ (m, 2H, $ArCH_2CH_2N),$ 3.88 (s, 3H, oCH_3), 3.95 (s, 3H, oCH_3), 6.0 (s, 2H, OCH_2O), 6.75-7.5(4H, ArH) was identical with that of 5a except that the intensity of the methyl signal ($\mathbf{52.5}$) was reduced by 1/3rd due to incorporation of a deuterium atom. This result is in accord with B and rules out A as the major reaction pathway.

The above photolysis and the earlier reported⁴ photocyclisation of 1-o-toluy1-3,4-dihydroisoquinolines can constitute a sequence for transposition of ring D substituents in protoberberine alkaloids. Irradiation⁴ of 5a in methanol followed by sodium borohydride reduction indeed gave (10 %) the tetracyclic base 9a as an oil [m/e (rel. intensity)] 339 (M⁺, 81), 338(33), 308(4), 176(12), 174(21), 164(100), 149(89). Switching of substituent positions was clear from a comparison with 9b, particularly the mass spectrum⁵ (m/e (rel. intensity)) 339 (M⁺, 65), 338(33), 308(10), 176(10), 174(17), 164(100), 149(55). The two spectra were similar except for the marked increase in the intensity of the m/e 308 (M-OCH₃) peak. The relative abundance of this fragment is



diagnostic⁶ of the presence of a methoxy substituent at C-9 in tetrahydroberberines.

References

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