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297. Stereospecific Synthesis of a 9, 11, 12, 13, 13a, 14-hexahydro-dibenzo(*f*, *h*)pyrrolo(1,2-*b*)isoquinoline-alkaloid

Preliminary communication

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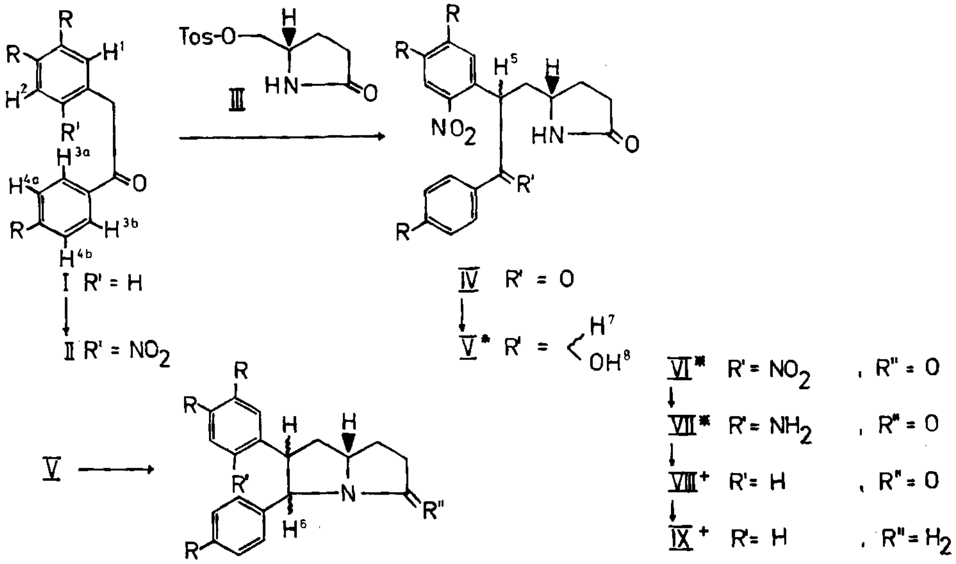
(12. XI. 73)

Several syntheses of the title-type alkaloids starting from chiral proline-derivatives, are described in the literature [1–4]. All these routes produce racemates because they include intermediates with a carbonyl-group α to the asymmetrically substituted carbon-atom C(13a). We avoided racemisation by using the proline derivative III [5] and cyclising the phenanthrene-moiety at a late stage of our synthetic route, shown in the following schemes:

Scheme 1

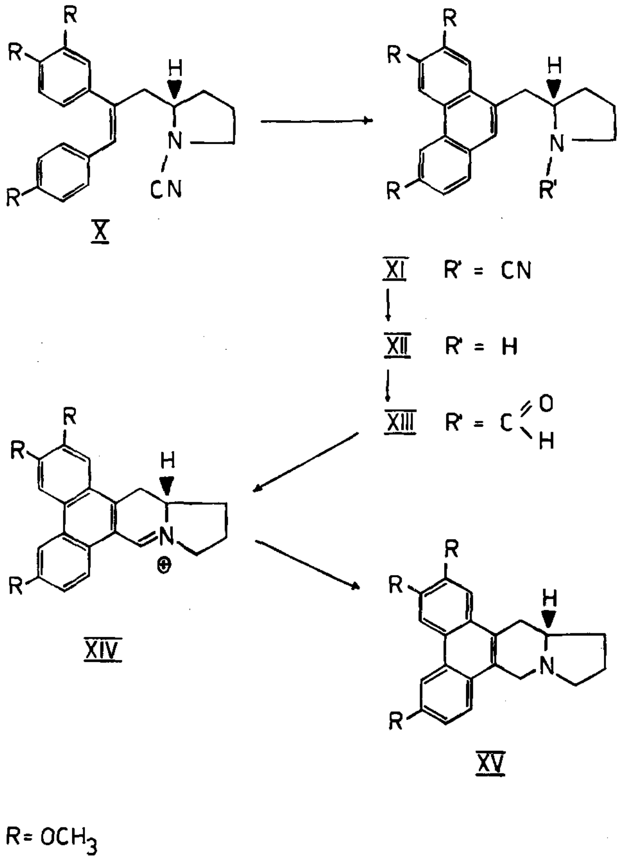


*) diastereomers were isolated +) mixture of diastereomers $R = OCH_3$

We obtained III by $LiBH_4$-reduction of 5-oxo-proline methyl ester to 5-oxo-proinol which was subsequently tosylated. The optical purity of 5-oxo-prolinol was only 51% of that of *Hardegger's* [5] product, who used $LiAlH_4$. This disadvantage is compensated by a better yield of 5-oxo-prolinol, as compared with the $LiAlH_4$-reduction.

Anisole + homoveratroylchloride → I [6]. – I + 65% HNO_3 in glacial AcOH → II, m.p. 197°; NMR. (chem. shift in δ): H_1: 6.80, 1*s*; H_2: 7.83, 1*s*; $H_{3a,b}$: 8.09, 2*d* × *d*, $J_o = 7$ Hz, $J_m = 1{,}7$ Hz; $H_{4a,b}$: 7.03, 2*d* × *d*, $J_o = 7$ Hz, $J_m = 1.7$ Hz. – *II* + *III* in acetone/K_2CO_3, 110°, 4–5 atm → IV; yellow oil; M^+: 428. NMR.: H_5: 5.67, 1*t*, $J = 7.5$ Hz; $[\alpha]_D^{20} = +22°$ (MeOH). – IV + $NaBH_4$ (70% EtOH) → V. Va, low Rf., NMR.: H_7: 4.74, 1*d*, $J = 7$ Hz; H_8: 3.00, 1*s*. – Vb, high Rf, NMR.: H_7: 4.77, 1*d*, $J = 7$ Hz; H_8: 3.00, 1*s*. – V (a or b) + 1.25% HCl in glacial AcOH (20°) → VI (a or b respectively). VIa (high Rf); m.p. 152°; phenylgroups *cis*; NMR.: H_6: 5.08, 1*d*, $J = 8.5$ Hz; $[\alpha]_D^{19} = +89°$ ($CHCl_3$). – VIb (low Rf); m.p. 194°; phenylgroups *trans*; NMR.: H_6: 4.83, 1*d*, $J = 1.7$ Hz; $[\alpha]_D^{20} = +43{,}5°$ ($CHCl_3$). – VI (a or b) + H_2 (*Raney*-Ni/EtOH) → VII (a or b respectively). MS.: M^+: 382, dominating peaks at 203 and 175. – VII (mixture of diastereomers) + $NaNO_2$/2.5% aqueous HCl, followed by 30% H_3PO_2 → VIII. MS. of both diastereomers: M^+: 367, dominating peaks 203 and 175. – VIII (mixture of diastereomers) + $LiAlH_4$/THF → IX; diastereomers (colourless oils) were separated. IXa (low Rf), $[\alpha]_D^{25} = -214°$ (MeOH); IXb (high

Scheme 2



Rf), $[\alpha]_D^{25} = -173°$ (MeOH). MS. (both diastereomers): M^+ 353, base peak: 189. – IX (mixture of a and b) + BrCN in abs. $C_6H_6 \rightarrow$ X. IR. ($CHCl_3$): 2200/cm. *M*S.: M^+: 378, dominating peaks 283 and 95. – X (4.6 × 10^{-5} M in C_6H_{12}, saturated with air) was irradiated (254 nm) → XI; m.p. 151–2°; UV.: λ_{max} (log ε): 257 (4.73), 285 (4.44), 311 (3.90), 342 (2.89), 359 nm (2.31); $M^{\oplus}$: 376; $[\alpha]_D^{25}$ = + 74.7 ($CHCl_3$). – XI + $LiAlH_4$ in THF → XII (viscous oil). M^+: 351, small intensity [7], dominating peaks 349, 282 and 70; $[\alpha]_D^{22} = +8.1°$. – XII + 98% HCOOH/180° → XIII; cyclisation (without further purification) with $POCl_3$/toluene → XIV; UV.: λ_{max}: 259; 268; 282; 320; 420 nm. XIV + $NaBH_4$/MeOH → XV, m.p. 206–11°. $[\alpha]_D^{22} = +66°$ ($CHCl_3$); antofine: $[\alpha]_D^{22} = -131°$ ($CHCl_3$). XV was identical with natural antofine [8] (TLC., UV., MS., IR.) but shows opposite optical rotation, 50% in magnitude for the reason stated. Because XV has *S*-configuration, antofine is of the *R*-configuration. This is in accord with our degradation of antofine to D-proline [9].

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298. Zur Photochemie von $\Delta^{1,9}$-10-Methyl-2-octalon

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(13. XI. 73)

Summary. Some aspects of the photochemistry of $\Delta^{1,9}$-10-methyl-2-octalone (**1**) were reinvestigated. In view of the hitherto neglected substantial thermal reversibility of the photolytic double bond shift under previous conditions of analysis (1) the solvent-dependent selectivity in product formation in C_6H_6 and *t*-BuOH was confirmed, (2) the essentially exclusive double bond shift and its intermolecular nature in C_6F_6 were established, (3) the quantum yields of the major products in these three solvents were measured, and (4) the dependence of triplet quenching data on temperature, enone concentration and conversion was shown in C_6F_6 for the double bond shift. In conclusion, the previously published experimental basis for the postulate of two differentially reactive triplet states of **1** is insufficient, although the postulate itself is not necessarily disproved.

Das photochemische Verhalten der Titelverbindung **1** ist bereits von mehreren Arbeitsgruppen untersucht worden. *Zimmerman & al.* [1] bestimmten für die Umlagerung von **1** in das «Lumiketon» **2** Quantenausbeuten von $3{,}8 \cdot 10^{-3}$ in *t*-Butylalkohol und $6{,}1 \cdot 10^{-3}$ in Benzol. *Schaffner & al.* [2] hingegen fanden ausgeprägte Lösungsmitteleffekte auf die photochemische Umsetzung von **1**: in *t*-Butylalkohol wurden überwiegend **2** und **3**[2]), in Benzol hingegen bevorzugt das β,γ-ungesättigte Keton

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[1]) Beurlaubt vom *Max-Planck*-Institut für Kohlenforschung, Abt. Strahlenchemie, Mülheim a.d. Ruhr.

[2]) Der prozentuale Anteil des Photoisomeren **3** ist vernachlässigbar klein.