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STEREOSELECTIVE SYNTHESES OF trans-1,2,3,4,4a,5,6,10b-OCTAHYDROPHENANTHRIDINES : PHOTOCYCLIZATION OF CYCLOHEXANONE N-BENZOYLENAMINES

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Trans-1,2,3,4,4a,5,6,10b-Octahydrophenanthridine (Va) is a basic structure of a variety of alkaloids[1] and many pharmacologically active compounds[2], and syntheses of this type of compounds have been mostly depending on rather streneous route including Diels-Alder reaction[2,3]. We now wish to describe very facile and stereoselective synthesis of this basic structure applying the photochemical cyclization[4], which would provide a route approaching to these interesting compounds.

Irradiation with the low pressure mercury lamp was applied to a methanolic solution (0.02 M) of N-benzoylenamine of cyclohexanone (Ia), bp 200/1mm, IR $\nu_{max}^{CHCl_3}$ 1625, NMR δ ($CDCl_3$); 5.27 (1H, m, olefinic H). After 40 hrs. exposure, the reaction mixture was condensed to give a crystalline residue which was readily purified by recrystallization from MeOH, yielding colorless crystals, mp 154-155°, with more than 35 % yield, IR $\nu_{max}^{CHCl_3}$ 1640, NMR δ ($CDCl_3$); 8.2 (1H, m, C_7-H), 7.7-7.1 (3H, m, C_8-, C_9-, C_{10}-H), 7.2 (5H, s, $-CH_2Ph$), 5.35 and 4.55 (2H, AB type q, J=16Hz, $-N-CH_2Ph$). The above spectral data on the photoproduct (IIIa), particularly disappearance of an olefinic proton and lower field shift of C_7-proton due to the anisotropy of the amide carbonyl group unequivocally suggest the validity of the structure (IIIa).

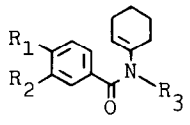
N-Methylenamide (Ib) was similarly photocyclized to IIIb, mp 141-143°, in 15 % yield, which exhibited IR $\nu_{max}^{CHCl_3}$ 1640 and NMR δ ($CDCl_3$); 8.1 (1H, m, C_7-H), 7.6-7.2 (3H, m, aromatic H), 3.1 (3H, s, $-N-CH_3$).

The photoproduct (IIIa) was debenzylated under Birch procedure to give the N-norlactam (IIIc), mp 218-220°, IR ν_{max}^{Nujol} 3120, 1665, which was treated with methyl

iodide to afford the N-methylactam (IIIb) and this was identical with the photoproduct (IIIb), thus assuring the generality of this photocyclization.

Skeletal structure of the photoproduct was established by converting IIIb on dehydration with Pd-C into the phenanthridone (IV), mp 107-109°, which showed identical mp, IR and UV spectra with those reported[5]. The B/C ring juncture in the photoproducts (IIIa, IIIb and IIIc) was assigned as having trans by converting IIIb or IIIc on $LiAlH_4$ reduction into the tertiary amines (Va and Vb), which, upon direct comparisons with the authentic sample prepared by Masamune[6], were identified and therefore these stereoselective photocyclization would be suggested to proceed by either cage or electrocyclic mechanism as suggested previously[4,7].

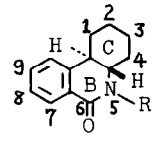
Then, the photocyclization was applied to the compound (II) having a methylenedioxy group in order to see the orientation of cyclization. After 17 hrs. exposure, chromatography of the reaction mixture afforded two photoproducts (VIa and VIb) in about the same amount. The skeletal structure as in IIIb was established by converting VIa into the phenanthridone (VII)[8] and the position of a methylenedioxy group were assigned from their NMR spectra, particularly from patterns of two aromatic protons and the B/C ring juncture was readily assumed from results hitherto obtained.



Ia $R_1=R_2=H$, $R_3=CH_2Ph$

Ib $R_1=R_2=H$, $R_3=CH_3$

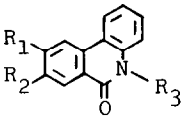
II R_1=-OCH_2O-=R_2, $R_3=CH_2Ph$



IIIa $R=CH_2Ph$

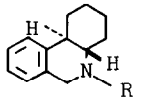
IIIb $R=CH_3$

IIIc R=H



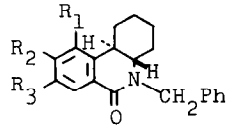
IV $R_1=R_2=H$, $R_3=CH_3$

VII R_1=-OCH_2O-=R_2, $R_3=CH_2Ph$



Va R=H

Vb $R=CH_3$



VIa $R_1=H$, R_2=-OCH_2O-=R_3

VIb R_1=-OCH_2O-=R_2, $R_3=H$

	NMRδ($CDCl_3$)
VIa	7.87(1H,s. C_7-H)
	6.97(1H,s. C_{11}-H)
VIb	8.15(1H,d.J=9Hz, C_7-H)
	7.0(1H,d.J=9Hz, C_8-H)

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