

PHOTOCHEMICAL REACTIONS OF N-ACYLENAMINES

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(Received in Japan 16 April 1969; received in UK for publication 2 May 1969)

It has been reported by several groups (1,2,3,4) that photochemical reaction of the N-acylenamines of acyclic and aromatic systems afforded the acyl-migrated products. We have now investigated photochemical reaction of the N-acylenamines of cyclic ketones such as β -tetralone and cyclohexanone and found that similar acyl migrations were also observed in cases of the N-acetylenamines, whereas the hitherto unknown photocyclization occurred predominantly in cases of the N-benzoylenamines, providing an useful preparative means toward heterocyclic systems.

An ethereal solution (0.02M) of Ia was irradiated with 120 watt low pressure mercury lamp at room temperature for 24 hr. Chromatography of the reaction mixture on alumina afforded IIa in 60 % yield. Acid hydrolysis of IIa with dilute hydrochloric acid gave 1-acetyl-2-tetralone (III) in 70 % yield, which was identified with the authentic sample prepared by acetylation of β -tetralone pyrrolidine-enamine (5). Similarly, a variety of N-acetylenamines (Ib-d) were prepared and irradiated to afford 1-acetylenamines (IIb-d), which were then hydrolyzed to give III, as summarized in Table I. And N-acetylcyclohexanone butylenamine was also treated as above to give 2-acetylcyclohexanone in 26 % yield, which was identified with the sample prepared by direct acetylation of the enamine (6).

Structure of the photoproduct, i.e., IIa, was readily assignable from its spectral features; UV λ_{max}^{EtOH} (m μ): 220, 275, 345. IR $\nu_{max}^{CHCl_3}$ (cm $^{-1}$): 1650(w), 1610(sh), 1590(s). NMR δ (CDCl $_2$): 11.9 (1H, broad s, -NH), 6.8-7.25 (4H, m, aromatic H), 2.34 (3H, s, -COCH $_3$), whereas the starting compound (Ia) exhibited UV $\lambda_{max}^{95\%EtOH}$ (m μ): 218, 273. IR $\nu_{max}^{CHCl_3}$ (cm $^{-1}$): 1655(sh), 1635(s), NMR δ (CDCl $_2$): 6.9-7.2 (4H, m, aromatic H), 6.3 (1H, s, -CH=C<), 2.1 (3H, s, -COCH $_3$).

Thus, the above photomigration of the N-acetylenamines of cyclic ketones would be an useful preparative means to synthesize 2-acetylketones from the corresponding ketones as mentioned by Yang (1).

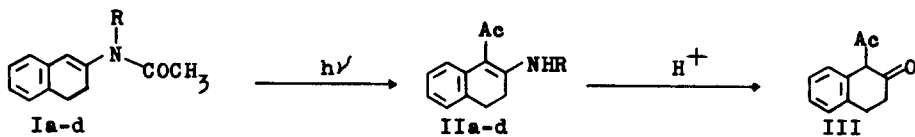


Table I

		Ia-d	IIa-d		III
	R	bp	m.p.	Yield(%)	Yield(%)
a	CH ₂ CH=CH ₂	133°/1mm	72.5~73.5°	60	70
b	CH ₃	123°/1mm	122~123.5°	67	65
c	CH ₂ Ph	160°/1mm	85~86°	46	55
d	C ₄ H ₉ -n	160°/1mm**	49.5~50.5°	50	60

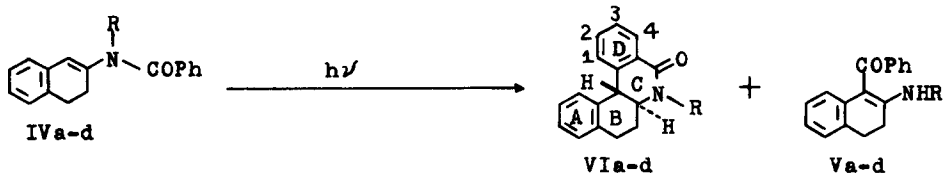
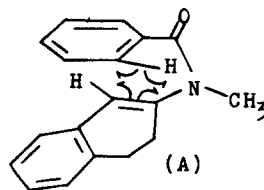
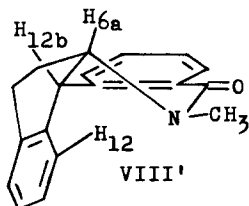
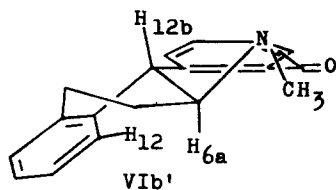
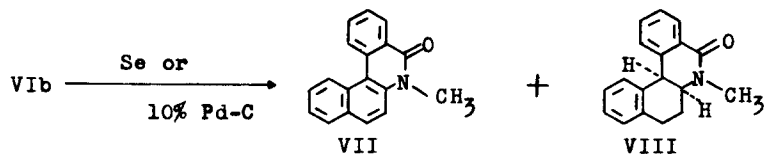


Table II

		IVa-d	VIa-d	
	R	bp	m.p.	Yield(%)
a	CH ₂ CH=CH ₂	185°/1mm**	180°/1mm*	71
b	CH ₃	172°/1mm	160~163°	40
c	CH ₂ Ph	190°/1mm	143~144°	47
d	C ₄ H ₉ -n	158°/1mm	113.5~114.5°	63



* b.p.
** bath temp.

Then, the N-benzoylenamines were also prepared and irradiated as above. Chromatography of the reaction mixture separated the expected benzoyl-migrated product (Vb) only as a minor product, but the major product was the cyclized compound (VIb), m.p. 160-163°C, which was homogeneous on TLC but gave three peaks on GLC at 250°C probably due to thermal decomposition, and exhibited IR_{max}^{Nujol}(cm⁻¹): 1650(s). NMR δ(CDCl₃): 8.08 (1H, m, C₄-H), 7.1-7.45 (7H, m, aromatic H), 4.26 (1H, d, J=11.3Hz, C_{12b}-H), 3.63 (1H, t(J=11.3Hz) of d(J=3.5Hz), C_{6a}-H), 3.2 (3H, s, N-CH₃), 2.7-3.0 (2H), 1.6-2.65 (2H).

Skeletal structure of VIb was established by dehydrogenation of VIb with 10 % Pd-C or selenium on heating to give the fully aromatized compound (VII), m.p. 121-122°C, which was identical with the sample prepared (7) on comparisons of their mixed melting point and other spectral data. And in addition, when VIb was dehydrogenated with selenium at 250°C for 3 hr, the compound (VIII), m.p. 175-178°C, with the same elemental composition with VIb, was obtained in 41 % yield and VIII was homogeneous both on TLC and GLC, and exhibited IR_{max}^{Nujol}(cm⁻¹): 1650. NMR δ(CDCl₃): 8.08 (1H, m, C₄-H), 7.1-7.3 (6H, m, aromatic H), 6.8 (1H, m, C₁₂-H), 4.47 (1H, d, J=5.5Hz, C_{12b}-H), 3.67 (1H, m, C_{6a}-H), 3.18 (3H, s, N-CH₃), 2.7-3.0 (2H), 1.66-2.1 (2H).

Comparisons of NMR spectra of VIb and VIII, particularly the coupling constants of C_{12b}-H and C_{6a}-H (J=11.3Hz in VIb and 5.5Hz in VIII)(9) and high field shift of an aromatic proton (C₁₂-H) of VIII by 0.38 ppm. due to the anisotropy of the another benzene ring (D)(8), which was not observed in VIb, and thorough inspection of Dreiding molecular model could unequivocally suggest the stereochemistry of these two compounds (VIb and VIII), as the B/C trans-junction in VIb and the cis-junction in VIII, shown by conformations (VIb' and VIII')(9). Therefore, the photochemical and the following reactions could be explained as follows; photochemical cyclization of Ia would proceed stereoselectively probably within the "cage" circumstance (A) to give the B/C trans-isomer (VI), which was, upon heating with selenium, abstracted two hydrogens from C_{12b} and C_{6a} forming Δ^{6a,12b}-dehydro intermediate, which was then partly dehydrogenated to the aromatized compound (VII) and partly reaccepted hydrogens from hydrogenated selenium, presumably through the mode of catalytic hydrogenation to give the B/C cis-isomer (VIII). This tendency of hydrogen transfer was observed also with Pd-C though in

lesser extent. Thus, a variety of the N-benzoylenamines (IVb-d) were similarly photocyclized to give the corresponding benzo(a)phenanthridine products (VIb-d) as shown in Table II.

Data so far obtained could suggest that the photochemical reaction of the N-aliphatic acylenamines undergoes the acyl migration giving l-acylenamines, whereas the N-benzoylenamines proceed either by migratory or cyclizational ways, in the latter case, forming nitrogen-containing polycyclic systems and this type of the photochemical reaction of the N-acylenamines are very useful in synthetic point of view. Further extensive study along this line are now under progress.

ACKNOWLEDGEMENT

The authors are grateful to Miss J. Uraoka for her collaboration.

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All m.p's and b.p's are uncorrected. Satisfactory analyses were obtained for all new compounds.

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