

PHOTOCHEMICAL REARRANGEMENT OF STEROIDAL HYDRAZONE AND
ACYLHYDRAZONE (1)

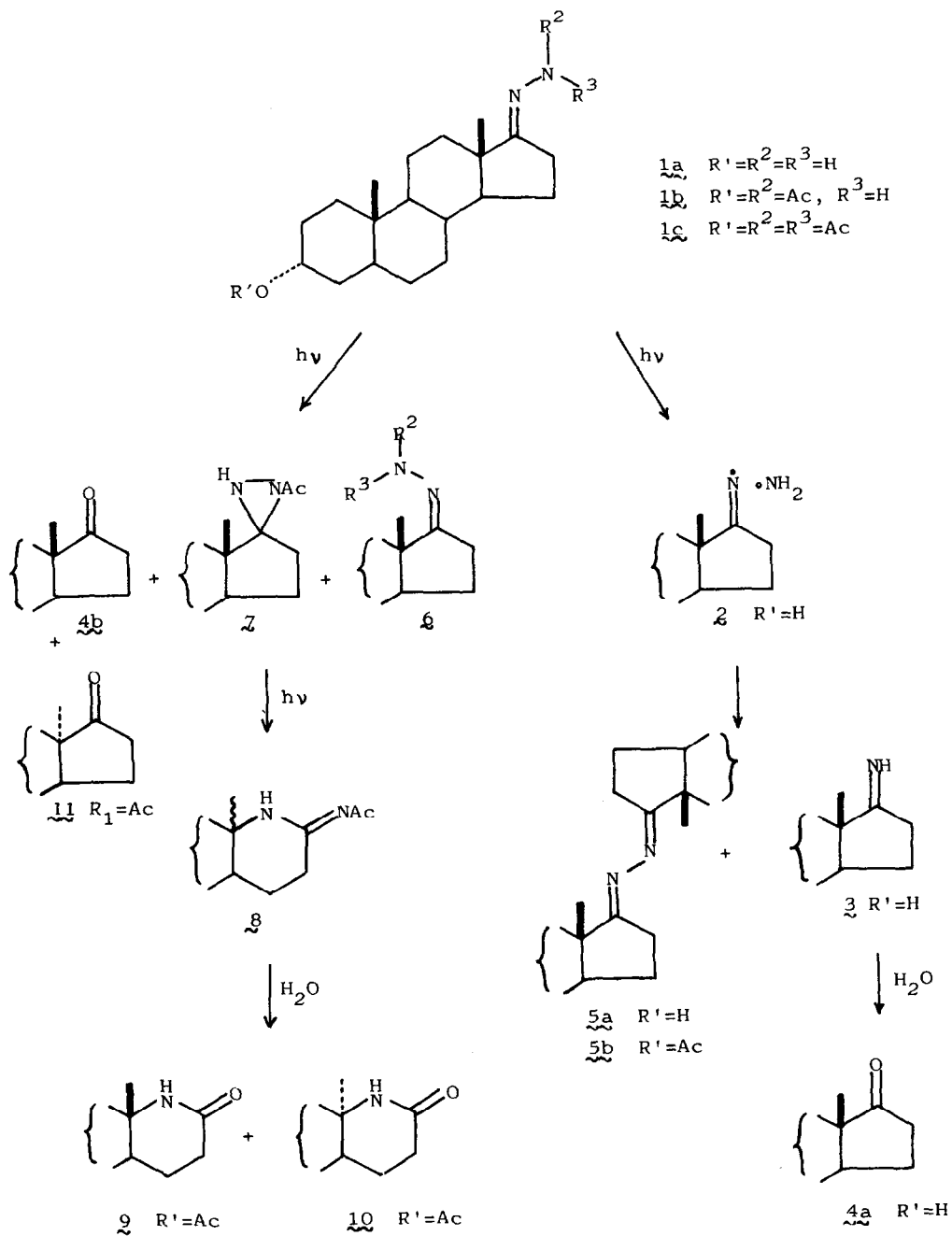
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Photochemical transformations of the hydrazones of aromatic ketones and aldehydes have been reported by Binkley. (2) We wish to report on the results of the photolyses of steroidal hydrazone and the N-acyl derivatives. It has been found that the latter underwent a new photoinduced rearrangement to lactams whereas the former afforded mainly the products due to the N-N bond homolysis. This distinct difference between the modes of the photolyses of hydrazone and its acyl derivatives is rather striking.

Androsterone hydrazone 1a, m.p. 230-231°C, (u.v. due to n, π^* ; λ_{\max} 198 nm, ϵ ; 3900, CH₃OH), prepared from androsterone (3.4 mmol) and an excess of hydrazine hydrate (10 ml) in ethanol (30 ml) under reflux, was photolyzed in dry dioxane (0.013 M) by a 15 W low pressure Hg arc lamp for 7 hours. The examination of the products by the tlc indicated the formation of at least 6 compounds apart from the recovery of 1a (18%), and the preparative tlc of the products afforded two major compounds, androsterone 4a (11%) and a new compound 5a, m.p. 247-248°C, (8%). The mass spectrum (M^+ 576) and the elemental analysis of 5a were in accord with the molecular formula C₃₈H₆₀O₂N₂ and 5a was confirmed to be the corresponding azine by the spectral data (n.m.r., CDCl₃ τ 9.22, 3H, S, 19-methyl, τ 9.14, 3H, S, 18-methyl, τ 6.02, 1H, S, 3 β -H; i.r., nujol, 1668 cm⁻¹, N=C, 3400 cm⁻¹, OH; u.v., methanol, λ_{\max} , 210 nm, ϵ ; 15000, 228 nm, ϵ ; 3700) and by direct comparison with azine prepared by the ground state reaction. (3)

On the other hand, N, O-diacetylandrosterone hydrazone, 1b, m.p. 218-220°C, (4) (u.v., due to n, π^* ; λ_{\max} 231 nm, ϵ ; 6200, CH₃OH) in dry dioxane (0.005 M)



Scheme

for 28 hours by a 15 W low pressure Hg arc lamp afforded the products (four compounds by tlc analysis), from which a mixture of O-acetylandrosterone 4b and O-acetyl-13 α -androsterone 5, (5) a compound 6, m.p. 232-234°C, O-acetyl-D-homo-5 α -17 α -aza-androsterone 9 and 3-O-acetyl-D-homo-5 α -17 α -aza-13 α -androsterone 10 were isolated in the yields of 23%, 26%, 11% and 19% by the preparative tlc. The latter two were confirmed by direct comparison with the authentic specimens obtained by the Beckmann rearrangements of 3-O-acetylandrosterone oxime and 3-O-acetyl-13 α -androsterone oxime. (6) The n.m.r. and u.v. spectra and the mass spectral fragmentation pattern of 6 were nearly identical with the starting 1b. However, the i.r. spectrum of 6 differs from that of 1b, and therefore 6 should be an isomer of 1b with respect to the C=N linkage, namely the NHAc group of 6 syn with respect to the C₁₃-C₁₇ bond.

The photolysis of N, N, O-triacetylandrosterone hydrazone, 1c, m.p. 151-153°C, (7) (u.v. due to n, π^* ; λ_{\max} 231 nm, ϵ ; 3000, CH₃OH) under the condition described above was found to proceed extremely slowly, and afforded only a mixture of ketones 4b and 11 and ill-defined products.

Mechanistic insight of these photoinduced reactions are under investigation, and on the basis of some preliminary results only brief comments will be made. Homolysis of the N-N bond of 1a in the solvent cage would generate an imino radical 2. The hydrogen abstraction of 2 from the solvent would lead to an imine 3 and this would be hydrolyzed to give 4a during photolysis (with a trace of H₂O) or in work-up stage. Dimerization of the imino radical 2 would afford the observed azine 5a. On the other hand, the lactams 9 and 10 would be formed via the photochemical formation of a diaziridine intermediate 7 followed by the rearrangement to e.g., 8 and hydrolysis during photolysis or work-up stage. Diaziridines in general are known to be isolatable species, and the ground state reaction of diaziridines are also known to lead to the compounds other than amides. (8) Therefore, rearrangement from the hypothetical diaziridine to the lactams would also seem to be photochemical.

Irradiation of 1b in dioxane by the monochromatic light of 233 \pm 4 nm (8.8 x 10⁻⁵ Mol) with or without oxygen caused a gradual decrease of the absorption maximum of 1b, and after ca. 2.5 hours the absorption at 231 nm of 1b

had vanished leaving only a weak absorption maximum at 212 nm, which remained unchanged on further irradiation by the monochromatic light of 212 nm. (9)

We regard these results as an evidence for the involvement of an excited singlet of 1b in the transformation from 1b into 7.

REFERENCES AND NOTES

- 1) Photoinduced transformations XXII. The previous paper, H. Suginome and T. Uchida, preceding paper.
- 2) R. W. Binkley, Tetrahedron Letters, 1893 (1969); 2085 (1970).
- 3) The azine 5a was obtained through the preparation of O-diacetylazine 5b, m.p. 238-240°C, from O-acetylandrosterone, (2.5 mmol), hydrazine hydrate (12 mmol) and HCl (0.3 ml) in ethanol (4 ml) at room temperature, followed by the hydrolysis.
- 4) Prepared by the usual method at room temperature.
- 5) These two isomeric ketones were readily distinguishable by the chemical shift differences of both the 18- and the 19-methyl groups.
- 6) preceding paper.
- 7) Prepared in the usual manner at ca. 60°C.
- 8) E. Schmitz, Angew. Chem. Internat. Edit., 3, 333 (1964).
- 9) Jasco CRM-FA spectro-irradiator was used in these experiments.

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