

147. Photochemical Reactions. VI. Photo-*Beckmann* Rearrangement with Vinyl Migration¹⁾

Preliminary Communication

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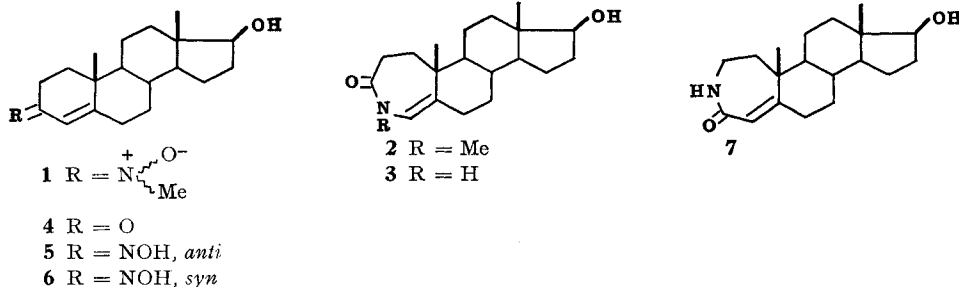
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(31. III. 76)

Summary. The carefully controlled UV. irradiation of 3-hydroxyimino- Δ^4 - and 3-hydroxyimino- Δ^4, Δ^6 -steroids yield as a result of vinyl and alkyl migration, lactams besides products expected.

Rearrangement of conjugated steroidal ketonic nitrones yields N-substituted lactams as a result of vinyl migration (**1** $\rightarrow$ **2**) [2]. Synthesis of the analogous N-non-substituted compounds **3** seems not to be feasible: The *Beckmann* rearrangement of the appropriate oximes gives only the alkyl migration isomers (e.g. **5** and **6** $\rightarrow$ **7**) [3], and by irradiation **5** and **6** or similar unsaturated oximes show either a remarkable lack of reactivity [4], or *syn-anti* isomerization and fragmentation to ketone, followed by a slow and extensive decomposition [4] [5]. In no case have the least mentioned authors reported the formation of lactams as a result of a photo-*Beckmann* rearrangement.

Scheme 1



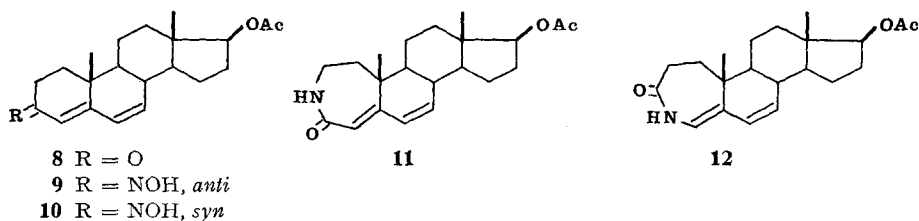
Nevertheless, from our previous work, a) the isolation of a lactam after UV. irradiation of 3-hydroxyimino-17 β -acetoxy-androsta-1,5-diene [6], and b) the photolability of conjugated lactams to give mainly dimers [7], suggest that the photo-*Beckmann* rearrangement of **5** or **6** and of analogous oximes may take place, the primarily formed lactamic products not being detected owing to their further photochemical reaction.

A systematic study was therefore undertaken and the following were found to be the most suitable conditions for photo-rearrangement: 1) Use of a medium pressure Hg lamp without filter, short irradiation time (~ 30 min), and low concentration ($\sim 0.1\%$) ensure that the photo-*Beckmann* rearrangement takes place quickly, and secondary reactions (dimerization) are minimized; 2) use of a hydroxylic solvent,

¹⁾ For part V, see [1].

wich corroborates previous observations [8], suggesting either a protonation at some step or the formation of the intermediate oxaziridine proceeding *via* a polarized excited state [9]; 3) use of thin irradiation layers (~ 1 cm), suggesting a possible wall effect²⁾. These conditions were applied to the testosterone oximes (**5** and **6**) [10] and to those of 17 β -acetoxy-androsta-4,6-dien-3-one (**9** and **10**), obtained from the corresponding ketones **4** and **8**, respectively; in each case the geometrical isomers were separated by column chromatography³⁾. It was found that the SOCl_2 induced *Beckmann* rearrangement of the four isolated oximes gave only the lactams involving alkyl migration $5 \rightarrow 7 \leftarrow 6$ and $9 \rightarrow 11 \leftarrow 10$ (**7**: m.p. 282–285°; NMR.: $\delta = 5.74$ (br. s, H-C(4a)); 6.46 (br., NH); after D_2O addition the signal at 5.74 sharpens and the one at 6.46 vanishes. **11**: m.p. 254–256°; NMR.: $\delta = 5.75$ ($d \times d$, $J_{6,7} = 10$, $J_{6,8} = 2$, H-C(6)); 5.90 (br. s, H-C(4)); 6.04 ($d \times d$, $J_{7,8} = 2$, H-C(7)); 7.10 (br., NH); after D_2O addition the signal at 7.10 vanishes).

Scheme 2



On irradiations each of the four oximes undergoes *syn-anti* isomerization ($5 \rightleftharpoons 6$, $9 \rightleftharpoons 10$), and fragmentation to the ketone ($5 \rightarrow 4 \leftarrow 6$, $9 \rightarrow 8 \leftarrow 10$). In addition, each oxime yields the lactam by alkyl migration ($5 \rightarrow 7 \leftarrow 6$, $9 \rightarrow 11 \leftarrow 10$), and in higher proportion the isomer by vinyl migration ($5 \rightarrow 3 \leftarrow 6$ and $9 \rightarrow 12 \leftarrow 10$) (**3**: m.p. 268–269°; NMR.: $\delta = 5.52$ ($d \times d$, $J_{4,4a} = 6$, H-C(4a)); 6.88 (br., NH); after D_2O addition the signal at 6.88 vanishes and the one at 5.52 becomes a br. s; $J_{4a,6} = 2$. **12**: m.p. 300–305°; NMR.: $\delta = 5.48$ ($d \times d$, $J_{6,7} = 10$, $J_{6,8} = 2$, H-C(6)); 5.61 (d , $J_{4,4a} = 6$, H-C(4a)); 5.90 ($d \times d$, $J_{7,8} = 2$, H-C(7)); 7.28 (br., NH); after D_2O addition the signal at 7.28 vanishes and the one at 5.61 becomes a s).

The lactams are formed in expected low yield (4 to 10%), since the *syn-anti* isomerization is usually the main route for energy degradation on irradiation of oximes [11]. Nevertheless, these results support a generalization of the photo-*Beckmann* rearrangement, legitimately considered doubtful [4] [5]. They also provide a mode of synthesis for isomeric lactams resulting from vinyl migration, which, to our knowledge, are not obtained by non-photochemical *Beckmann* rearrangement of the appropriate unsaturated oximes (*vide supra*).

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- ²⁾ We thank Prof. Dr. G. O. Schenck, Institut für Strahlenchemie, Max-Planck-Institut für Kohlenforschung, Mülheim, for raising this point.
- ³⁾ The structures of all new compounds are supported by IR., UV., NMR. and mass spectral data, as well as quantitative elemental analysis. We thank Dr. H. Wehrli, ETH, Zürich, for his help in the analyses and for his kind interest in our work.

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148. Structure of 1-*exo*-Phenylbicyclo[2.1.0]pentane-5-carboxylic acid by X-Ray Analysis

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Dedicated to Professor *V. Prelog* on the occasion of his 70th birthday.

(16. III. 76)

Summary. The title compound ($C_{12}H_{12}O_2$) crystallizes in the monoclinic space group $P2_1/c$. The structure was solved by direct methods, and the positions of all the hydrogen atoms were obtained from a difference synthesis. The final R_w was 0.04. Current MO theories of the interaction of unsaturated groups with small ring systems are consistent with the bond length variations encountered in the present substituted bicyclo[2.1.0]pentane skeleton with respect to the unsubstituted hydrocarbon.

1-Phenylbicyclo[2.1.0]pentane-5-carboxylic acids were prepared by *Schaffner et al.* in connection with a mechanistic study of the triplet oxa-di- π -methane photorearrangement of β,γ -unsaturated ketones [1]. The synthesis involved $CuSO_4$ -catalysed addition of ethyl diazoacetate to 1-phenylcyclobutene. Hydrolysis of the two resulting isomeric ethyl bicyclopentane-carboxylates afforded the acids. The present structure determination was carried out to confirm the *exo* configuration deduced from NMR. data for the isomer of m.p. 131° .

