147. Photochemical Reactions. VI. Photo-*Beckmann* Rearrangement with Vinyl Migration[1])

Preliminary Communication

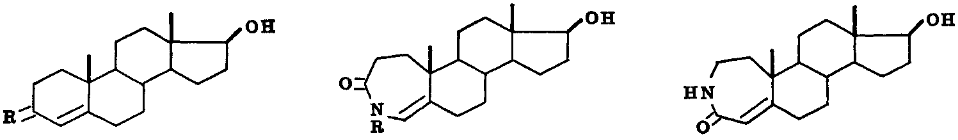
by **Miguel Armengol, Esperanza Coll, María Reixach, José M. Ribalta, José Repollés** and **Juan-Julio Bonet**
Instituto Quimico de Sarriá, Barcelona-17, Spain

(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** → **2**) [2]. Synthesis of the analogous N-non-substituted compounds **3** seems not to be feasible: The *Beckmann* rearrangement of the appropiate oximes gives only the alkyl migration isomers (*e.g.* **5** and **6** → **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



1 R = $\overset{+}{N}{<}^{O^-}_{Me}$

4 R = O

5 R = NOH, *anti*

6 R = NOH, *syn*

2 R = Me

3 R = H

7

Nevertheless, from our previous work, a) the isolation of a lactam after UV. irradiation of 3-hydroxyimino-17β-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 (~0.1%) ensure that the photo-*Beckmann* rearrangement takes place quickly, and secondary reactions (dimerization) are minimized; 2) use of a hydroxylic solvent,

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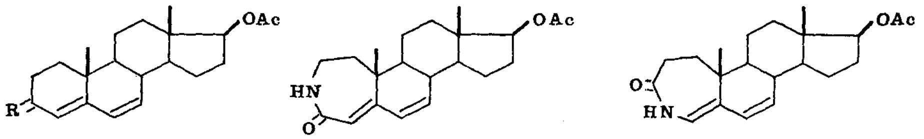
[1]) For part V, see [1].

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 effect[2]). These conditions were applied to the testosterone oximes (**5** and **6**) [10] and to those of 17β-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 chromatography[3]). It was found that the $SOCl_2$ induced *Beckmann* rearrangement of the four isolated oximes gave only the lactams involving alkyl migration $\mathbf{5} \rightarrow \mathbf{7} \leftarrow \mathbf{6}$ and $\mathbf{9} \rightarrow \mathbf{11} \leftarrow \mathbf{10}$ (**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



8 R = O
9 R = NOH, *anti*
10 R = NOH, *syn*

11

12

On irradiations each of the four oximes undergoes *syn-anti* isomerization ($\mathbf{5} \rightleftharpoons \mathbf{6}$, $\mathbf{9} \rightleftharpoons \mathbf{10}$), and fragmentation to the ketone ($\mathbf{5} \rightarrow \mathbf{4} \leftarrow \mathbf{6}$, $\mathbf{9} \rightarrow \mathbf{8} \leftarrow \mathbf{10}$). In addition, each oxime yields the lactam by alkyl migration ($\mathbf{5} \rightarrow \mathbf{7} \leftarrow \mathbf{6}$, $\mathbf{9} \rightarrow \mathbf{11} \leftarrow \mathbf{10}$), and in higher proportion the isomer by vinyl migration ($\mathbf{5} \rightarrow \mathbf{3} \leftarrow \mathbf{6}$ and $\mathbf{9} \rightarrow \mathbf{12} \leftarrow \mathbf{10}$) (**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 appropiate unsaturated oximes (*vide supra*).

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[2]) We thank Prof. Dr. *G. O. Schenck*, Institut für Strahlenchemie, Max-Plank-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

by **Gérald Bernardinelli, Jean-Jacques Combremont** and **Raymond Gerdil**

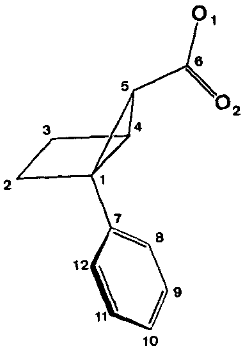
Département de Chimie Organique et Laboratoire de Cristallographie aux Rayons X,
Université de Genève, 30 quai Ernest Ansermet, 1211 Genève 4

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_ω 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°.



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