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5,5-DIMETHYL-2-THIOXO-3-PHENYLSPIRO(1,3-OXAZOLIDINE-4,2-[2H]CHROMENES)

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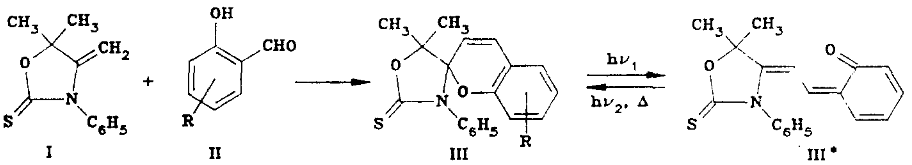
Proceeding from a stable methylene base – 2-thioxo-4-methylene-5,5-dimethyloxazolidine (I) [1] – via the scheme presented below we obtained new photochromic spiropyrans III in 70-90% yields:



IIIa. R=H; b R=5',6'-benzo; c R=6'-NO_2

The condensation was carried out by refluxing oxazolidinethione I and the corresponding o-hydroxy aldehydes II in a molar ratio of 1:1 in glacial acetic acid in the presence of catalytic amounts of $HClO_4$. The spirocyclic structure of the III obtained was confirmed by IR, UV, and PMR spectroscopic data.

The results of elementary analysis of IIIa-c were in agreement with the calculated values.

Compound IIIa. This compound was obtained in 71% yield and had mp 153-154°C (from ethanol). IR spectrum (mineral oil): 1746, 1646, 1600, 1587, 1309, 1256, 1237, 1157, 1100, 1029, 1009, 985, 960 cm^{-1}. PMR spectrum ($CDCl_3$): 1.48 [6H, s, $C(CH_3)_2$], 5.42 (1H, d, $^3J_{CH=CH}$ = 10 Hz, 3'-H), 6.55 (1H, d, $^3J_{CH=CH}$ =10 Hz, 4'-H), 6.75-7.38 ppm (9H, m, aromatic).

Compound IIIb. This compound was obtained in 86% yield and had mp 193-194°C (from ethanol). IR spectrum (mineral oil): 1730, 1660, 1633, 1580, 1302, 1266, 1237, 1100, 1075, 1036, 1009, 980, 960 cm^{-1}. PMR spectrum ($CDCl_3$): 1.55 [6H, s, $C(CH_3)_2$], 5.97 (1H, $^3J_{CH=CH}$ = 10.5 Hz, 3'-H), 7.05-7.93 ppm (12H, m ,4'-H, aromatic).

Compound IIIc. This compound was obtained in 81% yield and had mp 176-177°C (from ethanol). IR spectrum (mineral oil): 1761, 1646, 1612, 1573, 1304, 1256, 1232, 1107, 1100, 1075, 1011, 980, 951 cm^{-1}. PMR spectrum ($CDCl_3$): 1.53 [6H, s, $C(CH_3)_2$], 5.66 (1H, d, $^3J_{CH=CH}$ = 10.5 Hz, 3'-H), 6.65 (1H, d, $^3J_{CH=CH}$ =10.5 Hz, 4'-H), 6.94-8.20 ppm (8H, m, aromatic).

UV spectrum (in 2-propanol), λ_{max}, nm (log ε): IIIa 297 sh (3.29), 304 (3.52), 313 (3.24); IIIb 301 (3.73), 315 (3.87), 341 (3.60), 355 (3.63); IIIc 305 (3.84).

In the case of irradiation with UV light (with a DRSh-250 Hg lamp with λ_{max} 313 nm under steady-state conditions for 10-30 sec) solutions of spiropyrans III in 2-propanol ($c \approx 5 \cdot 10^{-5}$ mole/liter) at –50°C display reversible photochromic transformations associated with electrocyclic opening of the pyran fragment in the electronically excited state, which leads to isomerization of spirocyclic form III to valence-tautomeric o-quinoneallide form III*. The maxima of the long-wave absorption bands of the photoinduced III* forms were recorded in the electronic spectra: III* a 376 sh, 397, 511 sh; III*b 448; III*c 533 sh, 571 nm. Colored photoinduced form III*b is stable at room temperature ($\tau/2 \approx$ 250 sec at 20°C).

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HIGHLY EFFECTIVE DEHYDROGENATION OF STEROID ISOXAZOLINES

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We have previously described the synthesis of steroid derivatives Ia, b, which contain anisoxazolinyl substituent attached to the $C_{(20)}$ atom [1]. Various methods for the isoxazoline → isoxazole oxidative transformation are known; however, their application to derivatives of the I type does not lead to the desired results. We have established the formation of isoxazoles IIa, b as side products in the dehydration of 20-isoxazolinyl steroids with thionyl chloride in chloroform; the principal reaction products are olefins IIIa, b.

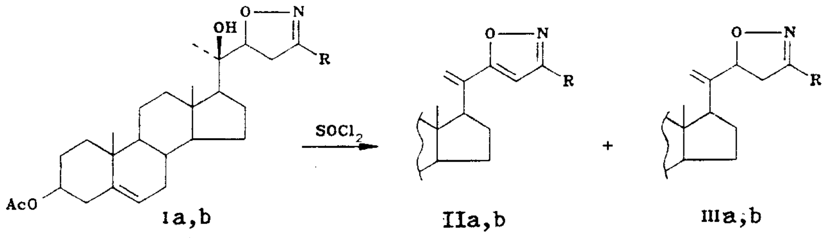
Replacement of chloroform by pyridine leads to the formation of II and III in equal ratios, while the use of DMF as the solvent makes it possible to obtain a single product, viz., isoxazoles IIa, b in up to 90% yields.

It was shown by special experiments that the formation of isoxazoles IIa, b does not occur in the reaction of thionyl chloride and isoxazolines IIIa, b in DMF. A steroid isoxazoline that does not have a 20-hydroxy group remains unchanged under the same conditions. These results constitute evidence that the observed dehydrogenation occurs in the step involving the dehydration itself of starting alcohols Ia, b, while the mechanism of the dehydrogenation that we observed probably includes participation of the 20-hydroxy group.

A 0.27-mmole sample of thionyl chloride was added with stirring to a solution of 0.18 mmole of Ia, b in 1 ml of DMF, after which the mixture was stirred for 1 h at 20°C and then poured into 10 ml of saturated Na_2CO_3 solution. The resulting mixture was extracted with ether, the extract was dried with Na_2SO_4, and the solvent was evaporated in vacuo. The residue was chromatographed on silica gel [elution with ether–hexane (1:10)] to give IIa, b.

The results of elementary analysis of IIa, b were in agreement with the calculated values.

3β-Acetoxy-20(3-isopropyl-5-isoxazolyl)pregna-5,20(21)-diene (IIa). This compound was obtained in 90% yield and had mp 140-142°C. PMR spectrum ($CDCl_3$): 5.33 and 5.81 (2H, two s, 21-H), 6.08 ppm (1H, s, 4'-H). Mass spectrum, m/z: 451 (M^+), 391 $(M - AcOH)^+$.



I–III a $R=CH(CH_3)_2$; б $R=COOC_2H_5$

3β-Acetoxy-20(3-carbethoxy-5-isoxazolyl)pregna-5,20(21)-diene (IIb). This compound was obtained in 85% yield and had mp 168-170°C. PMR spectrum ($CDCl_3$): 5.44 and 5.96 (2H, two s, 21-H), 6.63 ppm (1H, s, 4'-H). Mass spectrum, m/z: 481 (M^+), 421 $(M - AcOH)^+$.

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