ELECTROCYCLIZED RETINAL

Kiyoshi Tsukida, Masayoshi Ito, and Akiko Kodama¹

Kobe Women's College of Pharmacy Motoyama-kitamachi, Kobe 658, Japan

During our studies on (Z)–(E) isomerization of retinals (I) directed towards clarifying early stages of the visual process, we noticed the formation of a heretofore unknown photoproduct in the irradiated mixture of all-(E)-retinal (I) in an acetonitrile solution. We describe here the direct irradiation of I and of all-(E)- β ionylidenecrotonaldehyde (II) to give the first example of the 6e-electrocyclized conjugated polyenal, (III) or (IV), respectively.

Thus, a solution of I (0.0027 M) in acetonitrile was irradiated with a 300 W high-pressure Hg lamp through a Pyrex filter under N2-bubbling and water-cooling for 5 hr. The major photoproduct other than (Z)-(E) retinal isomers was obtained in a pure state by employing column chromatography and subsequent preparative thin-layer chromatography (yield, ca. 7%): M⁺ 284.2142 (calcd. for $C_{20}H_{28}O$, 284.2140); colorless oil; UV (nm, EtOH) 280 (ε 15,000), +NaBH₄ \rightarrow 235 and IR (cm⁻¹, CHCl₃) 1660, 1628 [aliphatic conjugated dienal]; ¹H-NMR (δ, CDCl₃, 90 MHz) 0.97, 1.12 and 1.23 (s and 3H each, 3 × Me), 1.72 (s, 3H, C-9-Me), 2.10 (s, 3H, C-13(Z)-Me), 1.2-2.2 (m, 6H), 2.87 (d, J=11.0, 1H, C-10-H), 5.84 (s-like, C-7- and C-8-H) and 5.87 (d, J=8.0, C-14-H) (3H in total), 6.28 (dd, J=15.0 and 11.0, 1H, C-11(E)-H), 7.16 (d, J=15.0, 1H, C-12-H) and 10.2 (d, J=8.0, 1H, CHO); ¹³C-NMR (d, CDCl₃, 22.6 MHz) 190.2 (d, CHO), 154.4 (s, C-13), 142.9 (s, C-6), 139.2 (d, C-11), 133.4 (s, C-9), 128.7 (d, C-12), 127.7 (d, C-14), 120.7 (d, C-7), 117.7 (d, C-8) [1 C=O and 4 C=C] and peaks due to the additional 11 sp³-C. All spectral data mentioned above are consistent with the 6e-electrocyclized $(5\rightarrow 10)$ structure (III) for the photoproduct. Further, from the conrotatory photocyclization mode the stereochemistry about the new bond is believed to be cis. Tricyclodecene structures based on a $[\pi^4 + \pi^2]$ photo-Diels-Alder reaction and the retro- γ -structure (V) derived from a signatropic hydrogen migration can be clearly excluded. Similar irradiation of II, synthesized by partial reduction of β -ionylidenecrotononitrile by diisobutylaluminum hydride, afforded the corresponding electrocyclized product (IV).

In the retinal series, it was recently claimed as an extension of the irradiation studies on the trienal (VI) and the tetraenone (VII) that the only identifiable photoreaction in this series was geometric isomerization, and 7-(Z)-isomers of retinal

¹月田 潔, 伊藤允好, 小玉晶子



were predicted not to be present in significant amounts in the photo-stationary stable mixture derived from all-(E)-retinal (2-4). However, considering our own results that both retinal and β -ionylidenecrotonaldehyde do produce the corresponding photo-electrocyclized product, a possibility that the 7-(Z)-stereostructure would be intermediary during the irradiation of conjugated polyenals is now strongly suggested. In our previous paper (1), a typical aprotic solvent acetonitrile was reported to be the most effective media for obtaining the hindered 11-(Z)isomer from all-(E)-retinal. Then, the formation of the 7-(Z)-isomer from all-(E)-retinal would also be expected in acetonitrile solution, since 7-(Z)-retinal is known to have a similar excited state potential curve to the 11-(Z)-isomer mentioned above. Although the formation of 7-(Z)-isomers was not observed in our experiments, this apparent absence could be well explained by probable instantaneous transformation of these isomers to the electrocyclized structure in the solution. It is also obvious from our results that the preferred direction of photochemical reaction other than (Z)-(E) isomerization is 6e-electrocyclization upon direct irradiation of all-(E)-retinal, while neither sigmatropic rearrangement nor photo-Diels-Alder reaction proceed in any instance.

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