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PHOTOCHEMISTRY OF GIBBERELLIN C;
SYNTHESIS OF HIGHLY STRAINED 8(7→11)-abeo-7.8-EPOXY-GIBBANES[1]

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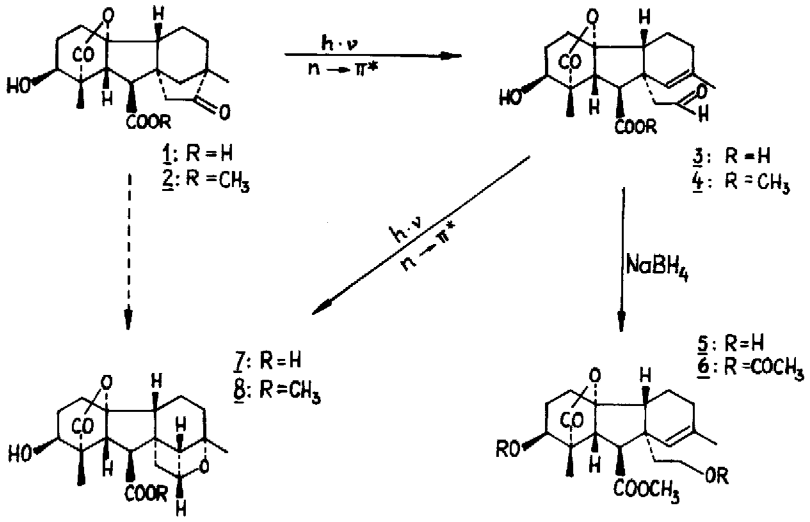
Recently, the Norrish type I photocleavage of 2-keto gibbanes[2] of the gibberellin A_1 series has been reported leading to $\Delta^{1(10a)}$-1.2-seco-2-aldehydes in high yields[3]. In this communication, we present results concerning the $n\rightarrow\pi^*$ photochemistry of gibberellin C (1)[4] and its methyl ester 2, respectively, characterized by Norrish I cleavage and subsequent intramolecular [2+2] cycloaddition of the formed secoaldehyde giving pentacyclic gibbane oxetanes of type 7.

Thus, gibberellin C (1, 200 mg) in ethyl acetate (100 ml) was irradiated under argon through pyrex at 25-30°C for 13 hrs using a 500 W high pressure mercury lamp. By SiO_2 chromatography besides starting ketone 1 the amorphous secoaldehyde 3 (40 mg), $[\alpha]_D^{26}$ +73.0° (c=0.229, ethanol) was obtained; MS m/e 348 (M^+); IR ν_{max}^{nujol} 3430 (OH), 1740 (C=O), 1643 cm^{-1} (C=C); UV λ_{max} (ε) 274 nm (480); 60 MHz ^{1}H-NMR $\delta_{HMDS}^{acetone-d_6}$ 1.10 (s, 1-CH_3), 1.55 (s, 7-CH_3), 2.78 (d, J=6 Hz, 10-H), 3.33 (d, J=6 Hz, 10a-H), 3.73 (2-H), 5.88 (11-H), 9.58 ppm (t, J=2.5 Hz, 8-H).

Under the same photolysis conditions 2 yielded 40% of the amorphous ester 4, $[\alpha]_D^{26}$ +70.5° (c=0.426) and m/e 362 (M^+) which is also available nearly quantitatively via CH_2N_2 methylation of the aldehyde acid 3. Compound 4 was reduced with $NaBH_4$ (0.5 hrs, methanol, 20°C) to give the corresponding diol ester 5, $[\alpha]_D^{25}$ +44.5° (c=0.495), and upon treatment with acetic anhydride/pyridine (20 hrs, 20°C) the diacetyl derivative 6, $[\alpha]_D^{26}$ +52.0° (c=0.301).

Upon further irradiation (48 hrs) of 4 and SiO_2 chromatography 66% of the oxetane 8, m.p. 223°C dec. (ether/hexane) and $[\alpha]_D^{26}$ +66.5° (c=0.350) has been isolated which was also obtained (58%) upon prolonged photolysis of starting ketone 2 via not isolated intermediate 4; MS m/e 362 (M^+); IR $\nu_{max}^{CHCl_3}$ 3628 (OH)



1770 (γ-lactone), 1730 (ester C=O), 946 cm^{-1} (oxetane); 100 MHz ^{1}H-NMR $\delta_{\mathrm{HMDS}}^{\mathrm{acetone}\text{-}d_6}$ 1.10 (s,1-CH_3), 1.33 (s,7-CH_3), 1.44 (dd, J=13 Hz, J'=2 Hz,9β-H), 2.60 (d, J=7 Hz,10-H), 2.74 (d, J=13 Hz,9α-H), 2.99 (d, J=7 Hz,10a-H), 3.50 (s,methylester-H_3), 3.68 (2-H), 3.81 (d, J=6 Hz,11-H), 3.96 ppm (dd, J=6 Hz, J'=2 Hz,8-H). The latter NMR correlations have been established by spin decoupling and INDOR experiments. The corresponding free oxetane acid 7 obtained upon prolonged irradiation (100 hrs) of 1 proved to be instable and was therefore transformed with CH_2N_2 to the methylester 8.

The oxetane formation is nonquenchable by oxygen and could be interpreted as a rapid exciplex generation between the $(n-\pi^*)S_1$ state of the aldehyde carbonyl and the neighbouring olefinic double bond followed by formation of a 1.4 biradical species as proposed recently for more simple model systems.[5]

References

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