# Photochemical Interconversion between Norfriedelin and $5\alpha$-Vinyl-$10\beta$-formylmethyl-des-A-friedelane

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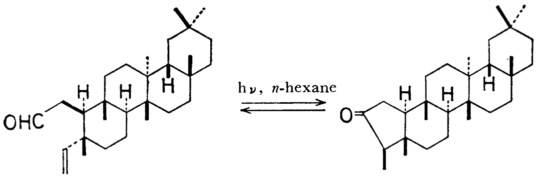
The photochemical reaction of aldehyde in the presence of olefin to saturated ketone has already been reported.[1,2] We now wish to describe a photochemical reaction of $5\alpha$-vinyl-$10\beta$-formylmethyl-des-A-friedelane (I) in *n*-hexane to yield norfriedelin (II)[3] (path A). This would be the first instance of the intramolecular ketone formation reaction of an olefinic aldehyde. As I was formed on irradiation of II in the same solvent (path C), it is noteworthy that the photochemical interconversion between I and II took place.



(I) (II)

Fig. 1

Norfriedelin (II, 1.00 g) in *n*-hexane (700 m*l*) was irradiated with a high pressure mercury lamp for 50 hr. Dry column chromatography and recrystallization afforded I [223 mg, mp 162.5—163.5°C, IR (Nujol) 3075, 1625, 907 ($CH=CH_2$), 2700, 1715 $cm^{-1}$ (CHO), NMR (in $CDCl_3$, $\delta$; an internal standard: TMS) 9.70 ($-CH_2\underline{C}HO$, t, $J=2$—3 Hz), MW(mass) $M^+$ 412].

A solution of I, (35 mg) was heated under reflux with bubbling of argon for 1 hr. The solution was then irradiated with a high pressure mercury lamp at room temperature for 30 hr.

The solvent was distilled off and the reaction products were separated with silica gel dry column chromatography. Elution with petroleum ether-benzene (10 : 1) gave hydrocarbon mixture (~6 mg), and the starting material (13 mg) was then recovered.

Norfriedelin (II) was eluted with benzene and weighed about 2 mg. The IR spectrum ($\nu_{C=O}$ 1750 $cm^{-1}$), mass spectrum ($M^+$ 412) and $R_f$ value on TLC were identical with those of the authentic sample. In gas chromatographic examination, however, two peaks appeared at $t_R=$ 31.5 and 28.9 min in the case of Diasolid H-523 at 250°C and $t_R=12.0$ and 11.0 min in the case of OV-17 at 290°C. The peak with longer $t_R$ was predominant and was shown to be due to norfriedelin (II) and the other due to 4-epinorfriedelin (II′). However, no isolation of II′ has yet been achieved.

Formation of norfriedelin (II) from the olefinic aldehyde (I) could be interpreted by the following mechanism (path A). Intermediate radical (III) may attack either $C_4$ or $C_{23}$ carbon atom of the double bond, giving rise to IV or V, respectively. Radical (IV) is converted immediately to tertiary radical (VI) by migration of hydrogen atom at $C_4$ to $C_{23}$. As hydrogen must attack the resulting radical (VI) from both sides, norfriedelin (II) is accompanied with its $4\alpha$-methyl epimer (II′). A part of II′ could be also formed from photochemical isomerization of II. As no cyclohexane derivative was formed, the process leading to radical (V) (path B, or *via* IV) is considered unfavourable under the above conditions. These findings are in accord with the observation that cyclopentane formation is a kinetically favoured process for free radical cyclization.[4]

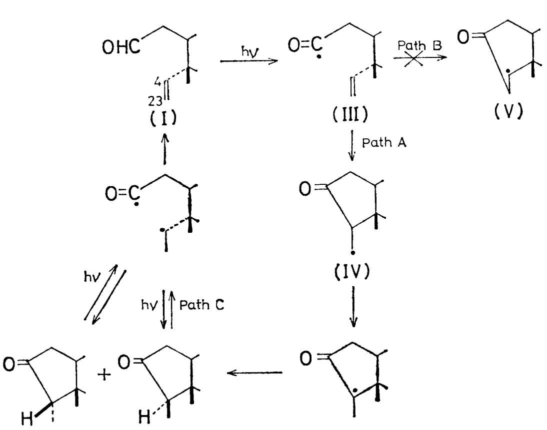


Fig. 2

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