

FORMATION OF 3,4-SECO-3-NOR-FRIEDELIN-2-AL FROM FRIEDELIN

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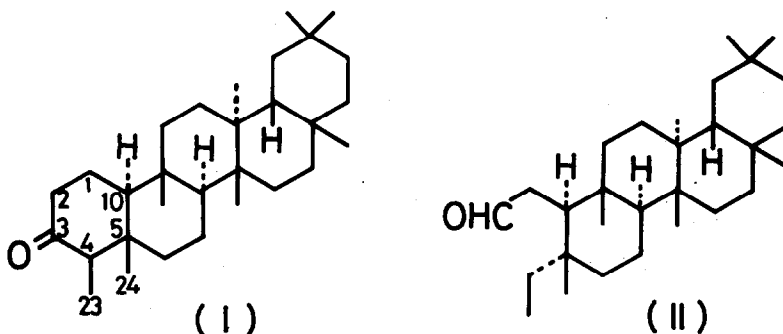
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Previously we reported the isolation of 3,4-seco-3-nor-friedelin-2-al (5 α -ethyl-10 β -formylmethyl-des-A-friedelane) (II)¹⁾ as well as hydrocarbons, carbonyl and hydroxycarbonyl compounds^{2,3,4,5)} by photoreaction of friedelin (I) in diethyl ether or n-hexane. Such cleavage of a cyclohexanone to yield an aldehyde with one less carbon atom is highly unusual, and we now wish to communicate further results which permit formulation of a mechanism for this transformation.



A solution of 2 α ,2 β ,4 α -trideuteriofriedelin (I-d₃, 330 mg, prepared from friedelin (I) and NaOD) was irradiated with a high pressure mercury lamp in n-hexane (500 g) for 27 hr under a nitrogen atmosphere. The reaction products

were separated by silica gel column chromatography. The aldehyde fraction (about 40 mg) was crystallized from diethyl ether to give II-d₃ (19.1 mg), the presence of three deuterium atoms being established by mass spectrometric determination. The locations of the deuterium atoms were determined by PMR spectral measurement. A signal at δ 9.78 (t, $J = 2.5$ Hz, 1 H) due to an aldehydic proton of II was absent in II-d₃ and a multiplet centered at δ 2.32 (C-1 methylene) of II appeared as a doublet at δ 2.32 ($J = 5.3$ Hz, 2H) in the deuteriated aldehyde (II-d₃). It is obvious that one of three deuterium atoms of II-d₃ is placed at aldehydic position (C-2) and that C-1 atom carries two hydrogen atoms. The reduction of the deuteriated aldehyde (II-d₃) with lithium aluminum hydride afforded an alcohol (III-d₃), which gave M^+ at m/e 419. The PMR experiments using Eu(dpm)₃ as shift reagent showed that a triplet signal due to C-23 methyl group of non-labelled alcohol (III) appeared as a singlet in the case of III-d₃. This indicates that the methylene group of the 5 α -ethyl group was labelled with two deuterium atoms. It may be concluded that the C-2 and C-4 atoms have been retained, that the C-3 atom has been extruded, and that the deuteriated aldehyde should be formulated as 2,4,4-trideuterio-3,4-seco-3-nor-friedelan-2-al (II-d₃).

These findings are rationalized by the mechanistic pathway (Fig. 1) involving

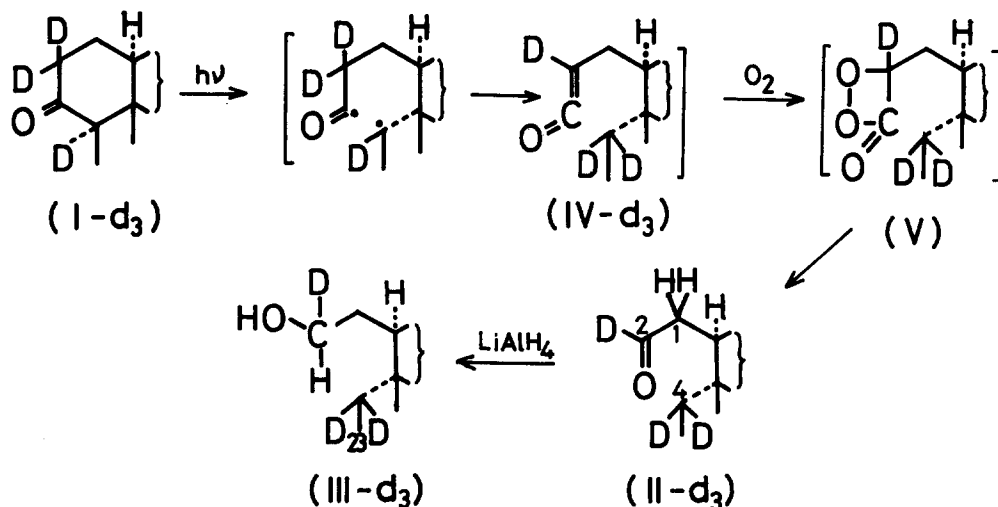


Fig. 1

autoxidation of the ketene (IV-d₃). Although Staudinger et al.⁶⁾ have proposed that a ketene may decompose through an oxygen-adduct such as V to give an aldehyde and carbon dioxide, mechanistic proof is lacking. The ketene (IV) produced photochemically suffered autoxidation in the subsequent separation procedure to give the seco-nor-aldehyde (II) with elimination of the carbon atom (C-3).

Further support (Fig. 2) was obtained by a study of the irradiation of friedelin-¹⁸O. A solution of 3-nitriminofriedelane (VI, 400 mg)⁷⁾ in water containing 5% of H₂¹⁸O (1 ml) and dioxan (40 ml) was heated under reflux for 30 hr.

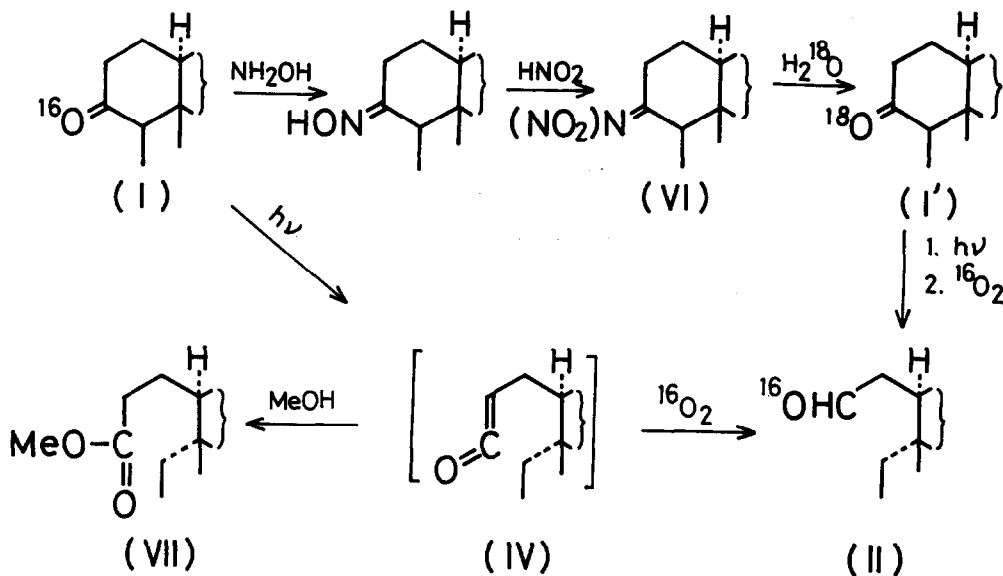


Fig. 2

After column chromatographic separation and recrystallization, 221 mg of friedelin containing friedelin-¹⁸O (I') was obtained; the ¹⁸O-isotopic abundance was determined by mass spectrometry by comparison (Table) with the relative intensities of peaks at m/e 428, 427 and 426 of I. In the mass spectrum of I', the percentage increase (4.8%) in relative intensity of the peak at m/e 428 corresponded to the isotopic content of ¹⁸O-atom in I' (Table).

Photoirradiation of I' under the same conditions yielded the aldehyde which on mass spectrometric examination (Table) was shown to contain no ¹⁸O-atom.

Table

m/e	428	427	426	m/e	416	415	414
I	5.8	34.2	100	II(from I)	5.6	32.9	100
I'	10.6	34.7	100	II(from I')	5.8	33.4	100

(Relative intensity in %)

The formation of the intermediate ketene (IV) was demonstrated as follows. On completion of irradiation of I, oxygen-free methanol was immediately added to the reaction mixture under a nitrogen atmosphere, solvents were removed under reduced pressure and the residue examined by TLC and mass spectrometry. The presence of the aldehyde (II) was scarcely detectable and the main reaction product was methyl 3,4-seco-friedelan-3-oate (VII).

The formation of the seco-nor-aldehyde (II) was, therefore, explicable by the autoxidation of the ketene (IV). After the photoreaction of I (500 mg) under the same conditions, dry air was introduced for 8.5 hr in the dark, followed by addition of methanol (30 ml). The seco-nor-aldehyde (II) was obtained as much as 35 mg (7 %). On the contrary the yield of the seco-ester (VII) was exceedingly reduced.

These observations support the conclusion that the seco-nor-aldehyde(II) is an autoxidation product of the ketene (IV), during work-up.

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