SHORT COMMUNICATIONS

Friedelin and Related Compounds. Part XI.[1] Identification of a Saturated Nor-Aldehyde from Ultraviolet Irradiation of Friedelin

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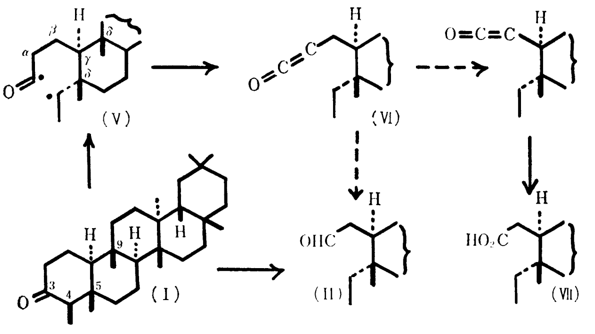
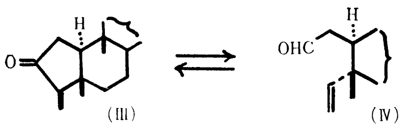
In previous works,[2,3] it was reported that the ultraviolet irradiation of friedelin (I) in diethyl ether solution yields a mixture of hydrocarbons, an unidentified aldehyde, ketones,[4,5] and hydroxycarbonyl compounds.

In this communication, we present evidence that the aldehyde has the structure 5α-ethyl-10β-formylmethyl-des-A-friedelane (II). Isolation of a *saturated nor*-secoaldehyde by photochemical degradation of a cyclic ketone is apparently unprecedented.

A solution of friedelin (1.0 g) in diethyl ether (1 *l*) was irradiated at room temperature under a nitrogen atmosphere for 2.25 hr with a high pressure quartz mercury vapour lamp (Hanovia 8A-36). This procedure was repeated and the combined residue, after solvent removal, was chromatographed on silica gel (300 g, Merck). The crude aldehyde fraction (84 mg) was then purified by further chromatography on alumina (Woelm, neutral, 15 g, then repeated on 20 g), and then crystallized from ether to give *5α-ethyl-10β-formylmethyl-des-A-friedelane* (II) as needles (18 mg), mp 182°C. The empirical formula, $C_{29}H_{50}O$, was confirmed by mass spectrum determination (*m/e*, relative intensity %): 414 (65%, M^+), 399 (29, M−15), 386 (21, M-28; aldehyde), 385 (8, M-29), 371 (10, M-43; loss of $-CH_2CHO$), 358 (8, M-56; 3,4-seco-friedelane), 273 (69), 261 (18), and 205 (100). Other analytical and spectroscopic data were as previously reported.[3]

The proposed structure (II) was confirmed by comparison (IR, NMR, mass spectrum, analytical TLC) with a specimen, mp 181—181.5°C, prepared by catalytic hydrogenation (palladium-carbon, ethanol) of 5α-vinyl-10β-formylmethyl-des-A-friedelane (IV) produced by photo-irradiation of *nor*-friedelin (III) in hexane.[6]





The pathway for the well-documented photo-cleavage of cyclohexanones to yield *δ-unsaturated* aldehydes by α-cleavage followed by transfer of a hydrogen atom from a δ-carbon atom (six-membered transition state) is unavailable for friedelin (quaternary C-5 and C-9). It seems probable, consequently, that the initial diradical species (V) is stabilized by hydrogen transfer from C-2 to the alkyl radical (six-membered transition state) to yield the ketene (VI) which undergoes the unusual degradation to the *nor*-seco aldehyde (II). It is of interest, in this connexion, that a *nor*-seco carboxylic acid (VII) was identified as a product of irradiation of friedelin in hexane.[7] Experiments aimed at elucidation of the mechanism of formation of II and VII are in progress.[8]

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[1] Part X. Ref. 2.

[2] F. Kohen and R. Stevenson, *Chem. Ind.* (London), **1966**, 1844.

[3] F. Kohen, A. S. Samson, and R. Stevenson, *J. Org. Chem.*, **34**, 1355 (1969).

[4] T. Tsuyuki, S. Yamada, and T. Takahashi, This Bulletin, **41**, 511 (1968).

[5] T. Tsuyuki, R. Aoyagi, S. Yamada, and T. Takahashi, *Tetrahedron Lett.*, **1968**, 5263.

[6] R. Aoyagi, T. Tsuyuki, and T. Takahashi, This Bulletin, **43**, 3967 (1970).

[7] M. Takai, R. Aoyagi, S. Yamada, T. Tsuyuki, and T. Takahashi,This Bulletin, **43**, 972 (1970).

[8] In this connexion, it is significant that the saturated nor-aldehyde (II) is *not* detected on similar irradiation of nor-friedelin (III).