

PHOTOCHEMICAL REACTION OF FRIEDELIN WITH ACETONE

Hidekazu Shirasaki, Takahiko Tsuyuki, and Takeyoshi Takahashi

Department of Chemistry, Faculty of Science,  
The University of Tokyo, Bunkyo-ku, Tokyo, Japan

and

Robert Stevenson

Department of Chemistry, Brandeis University  
Waltham, Massachusetts, 02154 U.S.A.

(Received in Japan 1 April 1975; received in UK for publication 19 May 1975)

The photochemical reaction of friedelin (1) in various organic solvents has been reported.<sup>1)</sup> In this communication, we present a new reaction between a photochemically produced ketene and a ketyl radical in the photo-irradiation of friedelin (1) in ether containing acetone.

Friedelin (1; 86 mg) in ether (30 ml) containing acetone (0.5 ml) was irradiated with a high pressure mercury lamp for 2 hr under a nitrogen atmosphere in a quartz vessel.

By column chromatography, a hydroxycarbonyl compound (2; 12 mg) has now been isolated, m.p. 180.5-181.5 °C (crystallized from light petroleum); IR (Nujol) 3500, 1705, and 1140  $\text{cm}^{-1}$ ; PMR ( $\text{CDCl}_3$ )  $\delta$  ~0.80 (6H, s and t overlapped), 0.89, 0.95, 1.03, 1.18 (each 3H, s), 1.00, 1.37 (each 6H, s), 2.40-2.75 (2H, m), and 3.77 (1H, s; disappeared on addition of  $\text{D}_2\text{O}$ ); ( $\text{CD}_3\text{COCD}_3$ )  $\delta$  4.18 (1H, s; disappeared on addition of  $\text{D}_2\text{O}$ ); mass spectrum  $m/e$  486 ( $\text{M}^+$ ), 471, 457, 453, 443, 430, 428, 413, 319, 307, 301, 275, 274, 273, and 205 (base peak); Found: C, 81.57; H, 12.07 %. Calcd for  $\text{C}_{33}\text{H}_{58}\text{O}_2$ : C, 81.42; H, 12.01 %. The molecular formula showed an increment of  $\text{C}_3\text{H}_8\text{O}$  in comparison with that of friedelin ( $\text{C}_{30}\text{H}_{50}\text{O}$ ).

Conversion of this hydroxycarbonyl compound (2) to the known 10 $\beta$ -(2-carboxyethyl)-5 $\alpha$ -ethyl-des-A-friedelane (5)<sup>1b,d)</sup> by successive LAH reduction,  $\text{Pb}(\text{OAc})_4$

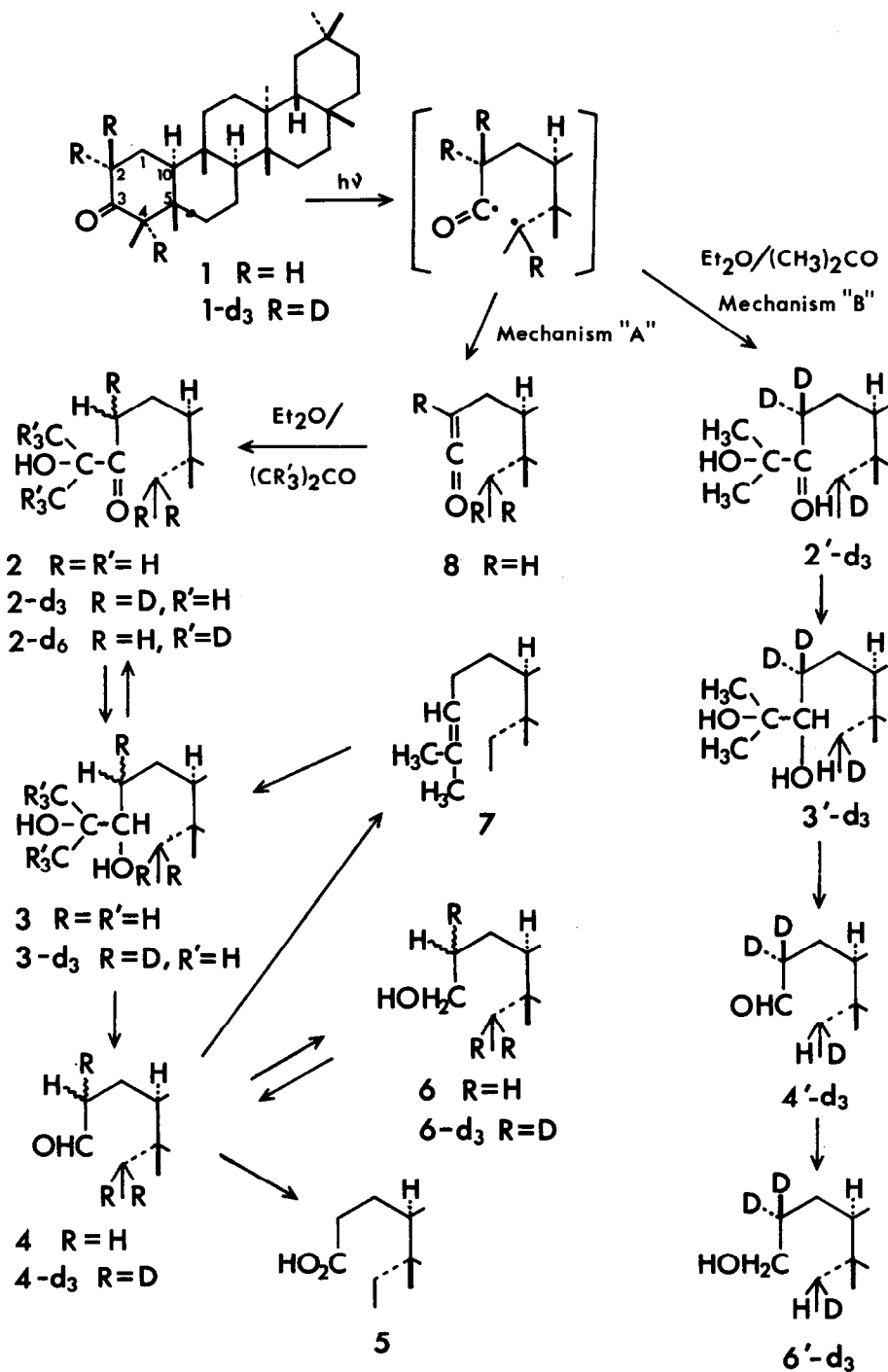
oxidation and  $\text{Ag}_2\text{O}$  oxidation indicated that it had the structure 5 $\alpha$ -ethyl-10 $\beta$ -(4-hydroxy-4-methyl-3-oxopentyl)-des-A-friedelane (2). This was confirmed by the following synthesis.

5 $\alpha$ -Ethyl-10 $\beta$ -(2-formylethyl)-des-A-friedelane (4), prepared from 5 $\alpha$ -ethyl-10 $\beta$ -(3-hydroxypropyl)-des-A-friedelane (5),<sup>1d</sup> was treated with isopropyltriphenylphosphonium bromide. The resulting isopropylidene derivative (7) was oxidized with  $\text{OsO}_4$  to give a mixture of epimeric diols (3), which on oxidation with  $\text{CrO}_3$  yielded the hydroxycarbonyl compound identical with the photo-irradiation product.

The structure of 2 indicated a participation of acetone and a mechanism involving the addition of the acetone-derived ketyl radical (2-hydroxy-2-propyl radical) followed by abstraction of a hydrogen atom, would reasonably account for the formation of 2. This was substantiated by the following experiments. When friedelin (1) was photolyzed for 3 hr in ether without addition of acetone, no hydroxycarbonyl compound (2) was obtained. When acetone- $\text{d}_6$  (1 ml) was added to a solution of 1 (317 mg) in ether (150 ml) and the solution was irradiated for 5 hr, the resulting hydroxycarbonyl compound (2- $\text{d}_6$ ; 45 mg) showed the expected molecular ion peak at  $m/e$  492.

2,2,4-Trideuteriofriedelin (1- $\text{d}_3$ ; 101 mg) was subjected to the photochemical reaction for 6 hr in ether (70 ml) containing acetone (0.7 ml) to give a trideuteriated hydroxycarbonyl compound (2- $\text{d}_3$ ; 11 mg), which showed the molecular ion peak at  $m/e$  489. Reduction of the trideuteriated product (2- $\text{d}_3$ ) with LAH in ether yielded a mixture of the epimeric diols (3- $\text{d}_3$ ), which on treatment with  $\text{Pb}(\text{OAc})_4$  in benzene gave an aldehyde (4- $\text{d}_3$ ) with the molecular ion peak at  $m/e$  431. A doublet signal ( $\delta$  9.73,  $J=2$  Hz) due to the aldehydic proton in the PMR spectrum of 4- $\text{d}_3$  indicates that an  $\alpha$ -carbon atom adjacent to the carbonyl group bears one deuterium atom and moreover that the remaining two deuterium atoms attach to the  $\text{C}_{(4)}$ -atom. This was confirmed by the PMR spectrum of the alcohol (5- $\text{d}_3$ ), using  $\text{Eu}(\text{dpm})_3$  as a shift reagent, in which a signal due to the methyl group attached to the  $\text{C}_{(4)}$ -atom was observed as a singlet.

These observations lead to the conclusion that the 2-hydroxy-2-propyl



radical attacked the carbonyl carbon atom of a ketene (8) to form a carbon radical which abstracted a hydrogen from the solvent (mechanism "A"). An alternative pathway (mechanism "B") involving an initial attack of the 2-hydroxy-2-propyl radical on the acylalkyl biradical formed by  $\alpha$ -cleavage of friedelin (1) and a subsequent hydrogen abstraction from the solvent has been excluded. In an experiment using 2,2,4-trideuteriofriedelin ( $1-d_3$ ) in ether containing acetone, the degradation of the product ( $2'-d_3$ ) would give an aldehyde ( $4'-d_3$ ) whose aldehydic proton should resonate as a singlet in the PMR spectrum. Similarly, a signal due to a methyl group at C<sub>(4)</sub> of an alcohol ( $6-d_3$ ) would appear as a doublet. These predictions were in fact contrary to observation.

The presence of pinacol in the photolysate was demonstrated by glc examination further supporting the involvement of the 2-hydroxy-2-propyl radical in the photolysis of friedelin (1) in ether containing acetone.

#### REFERENCES

- 1) -a. F. Kohen and R. Stevenson, Chem. and Ind., 1966, 1844. -b. T. Tsuyuki, S. Yamada, and T. Takahashi, Bull. Chem. Soc. Japan, 41, 511 (1968). -c. T. Tsuyuki, R. Aoyagi, S. Yamada, and T. Takahashi, Tetrahedron Letters, 1968, 5263. -d. F. Kohen, A. Samson, and R. Stevenson, J. Org. Chem., 34, 1355 (1969). -e. M. Takai, R. Aoyagi, S. Yamada, T. Tsuyuki, and T. Takahashi, Bull. Chem. Soc. Japan, 43, 972 (1970). -f. R. Stevenson, T. Tsuyuki, R. Aoyagi, and T. Takahashi, ibid., 44, 2567 (1971). -g. R. Aoyagi, T. Tsuyuki, T. Takahashi, and R. Stevenson, Tetrahedron Letters, 1972, 3397. -h. R. Aoyagi, S. Yamada, T. Tsuyuki, and T. Takahashi, Bull. Chem. Soc. Japan, 46, 959 (1973). -i. R. Aoyagi, T. Tsuyuki, M. Takai, T. Takahashi, F. Kohen, and R. Stevenson, Tetrahedron, 29, 4331 (1973). -j. H. Shirasaki, R. Aoyagi, T. Tsuyuki, T. Takahashi, and R. Stevenson, Bull. Chem. Soc. Japan, 48, 1073 (1975).