The Photochemical Cleavage of Friedelin

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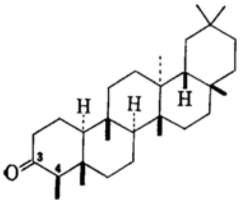
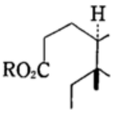
We wish to report the formation of a series of compounds (II—VI) on the photolysis of friedelin.

A boiling solution of friedelin[1] (I; 1.00 g) in ethanol was irradiated with a high pressure mercury lamp under a nitrogen atmosphere for 9 hr. The reaction products were separated by preparative thin layer chromatography (TLC). The main product was 3, 4-seco-ester[*1] (II, R=Et; 732 mg). The formation of 4-isofriedelin[*1] (III; 49 mg), 3β-friedelanol[1] (IV; 11 mg), 3α-friedelanol[2] (V; 86 mg) and 3, 4-seco-acid[*1] (II, R=H; 2 mg) was confirmed. A hydrocarbon (VI; 25 mg) was also isolated besides friedelin (I; 135 mg). The hydrocarbon (VI) showed two peaks on gas-liquid chromatography (GLC), though this compound gave only one spot on TLC (silica gel-silver nitrate). One of the peaks was shown to be due to 3-norfriedelane[*1] (VIa) and the other would be due to 3-nor-4-isofriedelane (VIb) (*Cf.* Experimental). However, no isolation of VIb has yet been furnished. The structure III was confirmed by alkaline isomerization to I.



(I)



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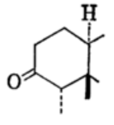

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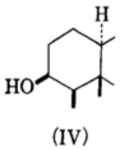

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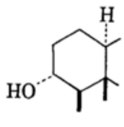
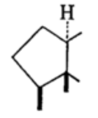
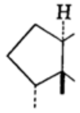


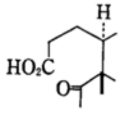
(V)



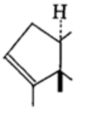
(VIa)



(VIb)



(VII)



(VIII)

Friedelin (I; 1.00 g) in acetic acid-water (9 : 1) was heated under reflux and was photolyzed under the same condition as above for 27 hr. The product was mainly the acid (II, R=H; 883 mg) accompanied with the hydrocarbon mixture (VIa and VIb: 20 mg) and friedelin (I; 28 mg).

In ethanol solution, the formation of II (R=Et and H) and of hydrocarbons (VIa and VIb) could be interpreted by the known photochemical reaction processes.[3] The formation of III would be explained by recombination of a diradical formed by α-cleavage (between positions 3 and 4) of I. A part of recovered friedelin (I) should be resulted from diradical recombination of alternative fashion. Furthermore, the photoreduction was concomitant to form a pair of friedelanols (IV and V).[4] In the aqueous acetic acid solution, the formation of II (R=H) was predominant.

Experimental

Photochemical Cleavage of Friedelin in Ethanol. The suspension of friedelin (1.00 g) in ethanol (600 m*l*) was heated under reflux with bubbling of nitrogen for 30 min. The solution was then irradiated with a high pressure mercury lamp (100 W) under a nitrogen atmosphere for 9 hr. Repeated separation of the products by preparative TLC (SiO_2 and SiO_2-$AgNO_3$) afforded the compounds (I)—(VI).

3, 4-Seco-ester (II, R=Et). 3, 4-Seco-ester was recrystallized from ethanol and then from acetone, mp 116.0—116.7°C.

Found: C, 81.40; H, 11.85%. Calcd for $C_{32}H_{56}O_2$: C, 81.29; H, 11.94%. This material was identical with the authentic sample in mp, TLC and IR spectrum. The authentic sample was obtained from friedonic acid (VII).[2b,5] Huang-Minlon reduction of VII yielded 3, 4-seco-acid (II, R=H), mp 211°C.

Found: C, 80.77; H, 11.78%. Calcd for $C_{30}H_{52}O_2$: C, 81.02; H, 11.79%.

Esterification (EtOH-H_2SO_4) and recrystallization from ethanol and then from acetone gave the ester (II, R=Et), mp 116.3°C.

4-Isofriedelin (III). 4-Isofriedelin was recrystallized from petroleum ether, mp 257.5°C, $\nu_{C=O}$ 1706 cm^{-1}. The solution of III in dioxane was heated under reflux with sodium methoxide in methanol under a nitrogen atmosphere for 6 hr. GLC examination (Diasolid

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1) E. J. Corey and J. J. Ursprung, *J. Am. Chem. Soc.*, **78**, 5041 (1956), and related papers.

2) a) N. L. Drake and S. A. Shrader, *ibid.*, **57**, 1854 (1935). b) N. L. Drake and W. P. Campbell, *ibid.*, **58**, 1681 (1936).

[*1] Refers to a new compound.

3) *Cf.* R. O. Kan, "Organic Photochemistry," McGraw-Hill, New York (1966), pp. 71—93, 222—223.

4) *Cf.* G. Quinkert, B. Wegement, F. Homburg and G. Cimbollek, *Chem. Ber.*, **97**, 958 (1964).

5) L. Ruzicka, O. Jeger and P. Ringnes, *Helv. Chim. Acta*, **27**, 972 (1944).

H-523, 240°C) revealed that the most of III (t_R=36.6 min) isomerized to I (t_R=41.1 min). The isomerized product was purified by preparative TLC and recrystallization from petroleum ether. The IR spectrum, mp, mixed mp and R_f value on TLC were identical with those of friedelin (I).

3-Norfriedelane (VIa) and 3-Nor-4-isofriedelane (VIb). The hydrocarbon fraction was recrystallized from chloroform-methanol, mp ~210°C.

Found: C, 87.11; H, 12.49%. Calcd for $C_{29}H_{50}$: C, 87.36; H, 12.64%. The IR spectrum and R_f value on TLC (SiO_2-$AgNO_3$) were identical with those of the authentic 3-norfriedelane. However, two peaks appeared at t_R=12.5 and 13.4 min on GLC (Diasolid H-523, 240°C). The authentic 3-norfriedelane (VIa) was prepared as follows: Hydrogenation (5% Pd-C/AcOEt) of 3-norfriedelene[2b] (VIII) proceeded mainly from α-side to afford the sole product, 3-norfriedelane*[1] (VIa), mp 224°C (Found: C, 87.15; H, 12.41%. Calcd for $C_{29}H_{50}$: C, 87.36; H, 12.64%), which gave a single peak at t_R=13.4 min on GLC under the same condition, described above.

Photochemical Cleavage of Friedelin in Aqueous Acetic Acid. Friedelin (1.00 g) in acetic acid-water (9 : 1) (600 m*l*) was irradiated at reflux temperature under nitrogen with a high pressure mercury lamp (100 W) for 27 hr. Working up as before and 883 mg of the 3, 4-seco-acid (II, R=H), mp 214.5—215.0°C, 20 mg of the hydrocarbon mixture (VIa and VIb), mp ~212°C, (Found: C, 87.40; H, 12.77%. Calcd for $C_{29}H_{50}$: C, 87.36; H, 12.64%) and 28 mg of friedelin (I) were obtained.