

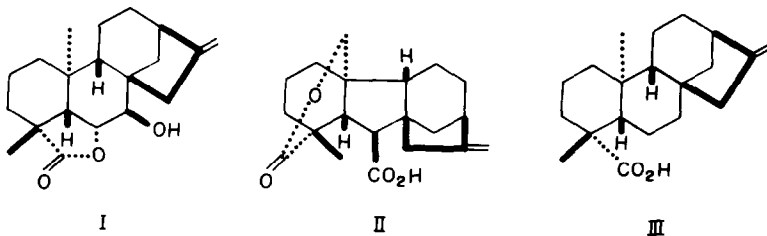
APPLICATION OF THE BARTON PHOTOCHEMICAL LACTONIZATION
IN DITERPENE FIELD*

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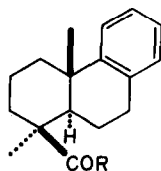
(Received 8 February 1966)

Recent discoveries of lactonic diterpenoids other than the C_{19} gibberellins from *Gibberella fujikuroi*, such as 7-hydroxykaurenolide (I)(1) and a C_{20} gibberellin (II)(2), prompted us to study an application of the Barton photochemical lactonization (3), which is the only method now available for converting saturated acids into lactones. This is a very promising method for the synthesis of the hydroxy lactone (I) from kaure-16-en-19-oic acid (III), of which racemate has been synthesized by us (4). This communication describes the results obtained with a simple model compound, (\pm)-desoxypodocarpic acid (IVa, R=OH)(5).

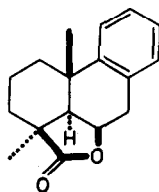
The acid in chloroform was treated with thionyl chloride to give the corresponding acyl chloride (IVb, R=Cl) which was added into ether saturated with dry ammonia to afford (\pm)-desoxypodocarpamide (IVc, R= NH_2), m.p. 175-176°, ν_{max} . (mujol) 3510, 3340, 3290, 3160, 1680, 1612, 763, 733 cm^{-1} , δ (



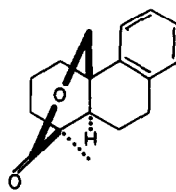
* Diterpenoid Total Synthesis - VI. Part V. K. Mori, M. Matsui, *Tetrahedron*, in press.



IV



V



VI

CDCl_3 , 100Mc, p.p.m. from TMS) 1.21 (s, CH_3), 1.31 (s, CH_3), Ca. 2.90 (m, PhCH_2), ca. 5.85 (broad, NH_2), 7.17-7.26 (m, C_6H_4 -).

The amide in benzene with lead tetracetate-iodine reagent was irradiated with a 8W low-pressure mercury lamp for 48 hrs. After alkaline hydrolysis, the product was separated into alkali-insoluble part and alkali-soluble part. The latter was boiled with dilute hydrochloric acid to effect lactonization. The neutral lactone fraction was chromatographed over alumina. Elution with ether-petroleum ether (1:9) afforded a γ -lactone (V) in 8-12% yield, m.p. 138-139°, ν_{max} . (nujol) 1768, 1195, 1178, 1114, 1040, 1005, 765, 735, (CHCl_3) 1772, 1184, 1118, 1044, 1006 cm^{-1} , δ (CDCl_3 , 100Mc, p.p.m. for TMS) 1.16 (s, CH_3), 3.12-3.65 (m, PhCH_2), ca. 5.13 (m, $-\text{CO}_2-\text{CH}-$), 7.21 (C_6H_4 -). Further elution with ether and then ethyl acetate gave a δ -lactone (VI) in 2-3% yield, m.p. 149-150°, ν_{max} . (nujol) 1734, 1164, 1143, 1135, 1120, 1040, 758, 742, (CHCl_3) 1732 (1724 sh.), 1165, 1160, 1145, 1138, 1125, 1045 cm^{-1} , δ (CDCl_3 , 100Mc, p.p.m. from TMS) 1.35 (s, CH_3), Ca. 2.96 (m, PhCH_2), 4.36 (s, $-\text{CO}_2-\text{CH}_2-$), 7.20-7.28 (m, C_6H_4). These two lactones were identified with the corresponding optically active lactones derived from abietic acid by a multi-step synthesis (6) through spectral comparisons. No product containing 4 \rightarrow 2 lactone bridge (phenanthrene numbering) was obtained.

It is interesting that both of the isolated lactones have their structural counterparts among the metabolites of *Gibberella fujikuroi*. It is also to be noted that the predominant product was not the δ -lactone (VI) but the γ -lactone (V), while photolysis of a resin acid azide is known to give a δ -lactam corresponding to (VI) as a major product (7).

Studies are in progress employing other resin acid analogs as starting materials.

Acknowledgment. We are indebted to Drs. A. Tahara and K. Hirao, Institute of Physical and Chemical Research, Tokyo, for carrying out the spectral comparisons of the lactones.

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