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ALICYCLIC TERPENOIDS FROM CYCLOCITRYL PHENYL SULFIDES. III.1)

A SYNTHESIS OF DIHYDROACTINIDIOLIDE AND TETRAHYDROACTINIDIOLIDES.

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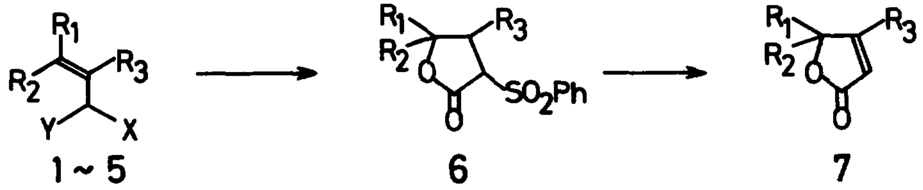
The development of convenient transformation of allylic alcohols to Δ^2-butenolides is an interesting subject for organic synthesis. Halolactonization of β,γ-unsaturated acid 5 followed by dehydrohalogenation2) is one of known routes to 7, but the method is not necessarily effective for polyolefinic carboxylic acid systems. Here, we describe an useful transformation of geraniol to dihydroactinidiolide 8 3) and tetrahydroactinidiolides 9 4) *via* double cyclization of α-sulfonyl carboxylic acid 11 to lactone 13 to demonstrate an example for a novel construction of Δ^2-butenolide 7 from 1 through 2, 3, 4, and 6 as shown in scheme 1.

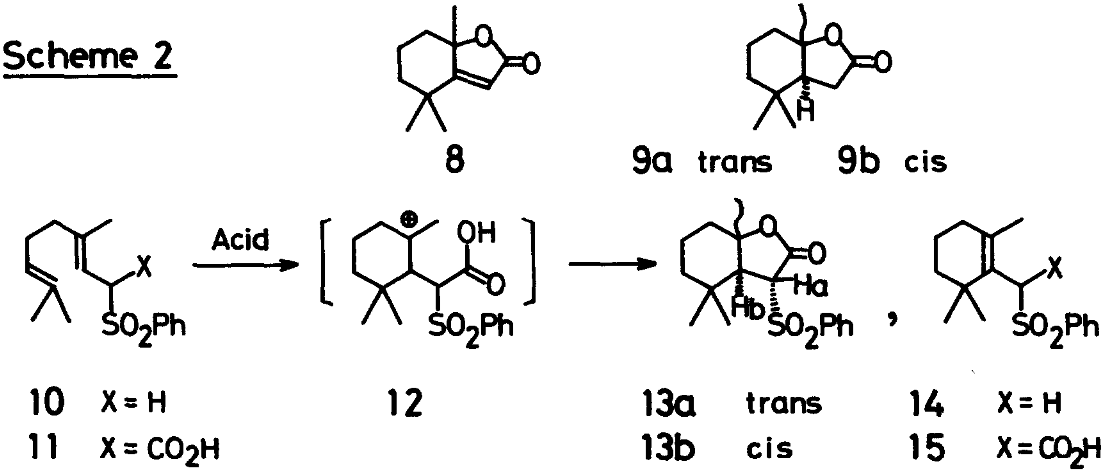
Scheme 1



(X, Y) ; 1 (OH, H), 2 (Br, H), 3 (SO_2Ph, H), 4 (SO_2Ph, CO_2H), 5 (CO_2H, H)

R_1, R_2, R_3 ; Alkyl, Alkenyl

Scheme 2



Carboxylic acid 11 was prepared quantitatively on treatment of 10[5] with 1 eq amount of BuLi in THF at -78° followed by the action of dry CO_2 at the temperature. Cyclization of 11 was performed with both protonic and Lewis acids[6]. Thus, treatment of 160 mg (0.5 mmol) of 11 with 2 mmol of BF_3 in 6 ml dry CH_2Cl_2 at refluxing temperature for 2 hr gave lactone 13 (75%, trans-13a: cis-13b = 2:5) and carboxylic acid 15[7] (20%). While, vigorous stirring 100mg (0.3 mmol) of 11 in 1.5 ml of concd. H_2SO_4 at 5-10° for 1 hr afforded cis-13b (75%) as a sole isolable product without contamination of trans-13a[8]. The ratio of 13a/13b varies depending on the reaction conditions. The isomers were separated through column chromatography over silica gel ; trans-13a : IR (Nujol) 1770 (C=O), 1585, 1305, 1145 (SO_2) cm^{-1}, NMR ($CDCl_3$) δ 8.00-7.30 (m, 5H, ArH), 4.17 (d, J=13Hz, 1H, Ha), 2.78 (d, J=13Hz, 1H, Hb), 2.05-1.75 (m, 6H, CH_2), 1.41 (s, 3H, CH_3), 1.34 (s, 3H, CH_3), 1.15 (s, 3H, CH_3), cis-13b : IR (Nujol) 1770 (C=O), 1585, 1317, 1150 (SO_2) cm^{-1}, NMR ($CDCl_3$) δ 8.07-7.35 (m, 5H, ArH), 4.02 (d, J=6Hz, 1H, Ha), 2.76 (d, J=6Hz, 1H, Hb), 2.00-1.31 (m, 6H, CH_2), 1.60 (s, 3H, CH_3), 1.14 (s, 3H, CH_3), 1.06 (s, 3H, CH_3).

The trans-lactone 13a was isomerized to the thermodynamically more stable cis-13b by stirring 13a in concd. H_2SO_4 (89%). Carboxylic acid 15 was converted smoothly to cis-13b on treatment of 15 with a 1:1 mixture of H_2SO_4 and AcOH. The formation of 15 and the successive cyclization of 15 to 13b suggest that the cyclization of 11 undergoes in a stepwise mechanism via 12.

Reductive desulfurization[9] of 13a and 13b by Raney Ni W-2 in refluxing ethanol afforded trans and cis-tetrahydroactinidiolide 9a (82%) and 9b (80%), respectively, whose IR and NMR spectra are consistent with those reported[4,10]. Finally, dihydroactinidiolide 8 was obtained (63%) by thermal desulfurization of 13a and 13b at 320-350°. The IR and NMR spectra of the lactone 8 are superimposable with those of authentic sample.[2]

Detailed studies for demonstrating the generality of the reaction scheme 1 are going on.

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