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SYNTHESES OF PERILLENE AND ROSEFURAN FROM COMMON STARTING MATERIALS

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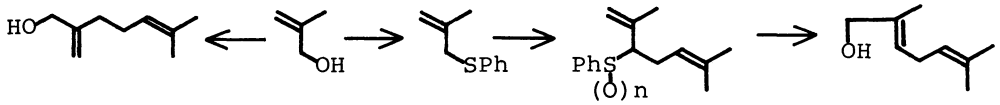
Two structurally isomeric furanomonoterpenes perillene and rosefuran have been synthesized using methallyl alcohol and prenyl chloride as common starting materials.

Both 3- and 2,3-substituted furans are widely distributed in nature. Perillene (1a), a 3-substituted furan isolated from an animal[1] and a plant,[2] and rosefuran (1b), a 2,3-disubstituted furan isolated from Bulgarian rose oil,[3] are simple monoterpenoid examples of such furanoid compounds. We report here new syntheses[4] of these isomeric furanomonoterpenes using methallyl alcohol (2) and prenyl chloride as common starting materials by employing the Payne rearrangement[5] as a key stage.

The allyl alcohol (3a) leading to perillene (1a) was prepared in 30% yield by treating methallyl alcohol (2) with n-butyllithium (2.0 equiv.) in the presence of excess N,N,N',N'-tetramethylethylenediamine followed by prenyl chloride (THF, -20 °C).[6] On the other hand, the isomeric allyl alcohol (3b) leading to rosefuran was prepared in 19% overall yield from 2 via a four step sequence of reactions. Thus, upon treatment with diphenyl disulfide (1.5 equiv.) and tri-n-butylphosphine (1.5 equiv.) (pyridine, 0 °C),[7] 2 afforded the sulfide (4), in 68% yield, which was then treated with prenyl chloride (2 equiv.) in the presence of n-butyllithium (1.1 equiv.) (THF, -78 °C) to give the alkylated compound (5) in 55% yield. Oxidation of 5 with m-chloroperbenzoic acid (1.0 equiv.) (methylene chloride, -20 °C) gave the sulfoxide (6) which was then treated with trimethyl phosphite (2.5 equiv.)[8] or diethyl amine (3.0 equiv.)[9] (methanol, reflux) to give the desired allyl alcohol (3b) in about 50% yield from 5 via [2,3]-sigmatropic rearrangement and concurrent reduction.

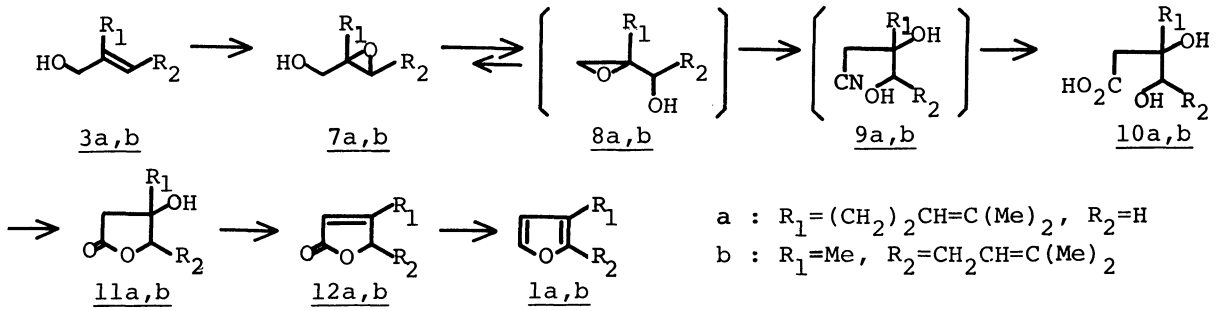


3a 2 4 5 : n=0 6 : n=1 3b

Scheme 1.

Conversion of the isomeric allyl alcohols (3a and b) into the corresponding natural products was achieved in the same way via the known butenolide

intermediates (12a and b), respectively. Oxidation of 3a with t-butyl hydroperoxide (2.0 equiv.) in the presence of vanadyl acetylacetonate (2 mol%) (methylene chloride, 0 °C)[10] gave the epoxide (7a) in 83% yield. Treatment of the epoxide (7a) with sodium cyanide (5.0 equiv.) in 60% ethanol for 16 h at reflux temperature allowed concurrent sequential reactions-----i) Payne rearrangement, ii) substitution at primary center, and iii) hydrolysis-----to give the dihydroxy acid (10a), which was azeotropically refluxed in toluene to give the hydroxy lactone (11a) in 65% yield from 7a. Reaction of 11a with methanesulfonyl chloride (1.2 equiv.) in the presence of triethylamine (2.4 equiv.) (methylene chloride, 0 °C) afforded the known 3-substituted butenolide (12a),[11] in 92% yield, which on reduction with diisobutylaluminum hydride (toluene, -15 °C) gave perillene (1a) in good yield as reported.[11] In the same way, the isomeric allyl alcohol (3b) was in turn transformed into the epoxide (7b) (85% yield), the hydroxy lactone (11b) (56% yield from 7b), and the known 3,4-substituted butenolide (12b)[12] (100% yield) without difficulty. As reported 12b afforded rosefuran (1b) in good yield on reduction with diisobutylaluminum hydride (toluene, -15 °C).[12]



Scheme 2.

Although syntheses of two simple 3- and 2,3-substituted furanomonoterpenes have been exemplified in this report, the method may be extended to synthesize more complex terpenoid analogues as well as 2,4-, 2,5-, 3,4-disubstituted and 2,3,4-trisubstituted furan derivatives from appropriate allyl alcohol precursors.

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