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THALLIUM(III) SALT-INDUCED OLEFINIC CYCLIZATION OF o-PRENYLPHENOLS

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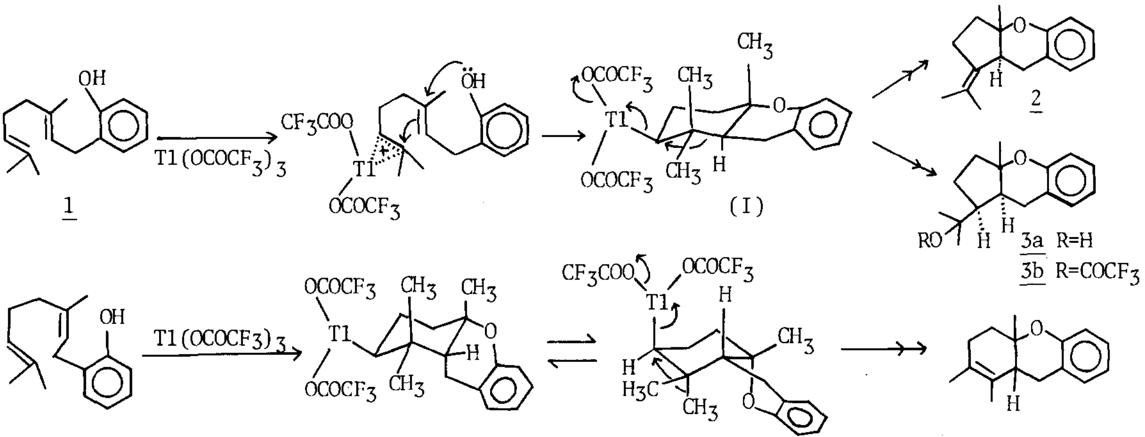
Summary Olefinic cyclization of o-prenylphenols (1), (4) and (6) induced by thallium(III) trifluoroacetate was performed.

In our previous reports on the thallium(III) salt-induced cyclization of acyclic monoterpene 1,5-dienes (geraniol[1], nerol[2] and citral[3]), we have found that the cyclization was effected by an initial intramolecular attack of a nucleophilic group (carbon-carbon double bond or oxygen function) to the carbon-carbon double bond activated by thallium(III) salt, followed by oxidative cleavage of the carbon-thallium bond to give various types of the cyclization products. These studies also demonstrated that the mode of cyclization was exceedingly influenced by both the kind of the oxygen function and the stereochemistry of the carbon-carbon double bond of the 1,5-dienes. These results led us to expect that a phenolic oxygen of o-prenylphenols could participate the cyclization with thallium(III) salt and the geometry of the carbon-carbon double bond also affects the course of the cyclization. Here we wish to describe thallium(III) salt-induced cyclization of o-prenylphenols, o-geranylphenol (1), o-nerylphenol (4) and o-farnesylphenol (6), giving the cyclization products which are dependent on the geometry of the carbon-carbon double bond of the o-prenylphenols used.

Thallium(III) trifluoroacetate (TTFA)(8.75 g) was added to a solution of 1(2.7 g) in methylene chloride (270 ml) and the mixture was vigorously stirred at room temperature for 2 hrs. The crude product[4] was further hydrolyzed with ethanolic sodium hydroxide to give two crystalline products (2) (mp 53-54°C)[5,6] and (3a) (mp 103-104.5°C)[5,6] in 38 % and 35 % yield, respectively. Dehydration of 3a with p-toluenesulfonic acid gave quantitatively the olefin (2).

Remarkable difference was observed when o-nerylphenol (4), a geometrical isomer of 1, was examined for the reaction. Treatment of 4 with TTFA at -5°～ -10°C for 2 hrs followed by base treatment gave exclusively a cyclization product (5)[5,6] as an oily substance in 73 % yield.

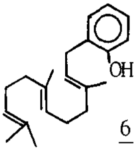
Possible reaction path ways for these cyclizations are shown in the Scheme. In both cases, 1 and 4, the carbon-carbon double bond is initially activated by thallium(III) salt to give a π-complex intermediate. Nucleophilic attack of the remaining carbon-carbon double bond to the π-complex center followed by the trap of the resultant cationic center by the phenolic oxygen gives the tricyclic



Scheme

intermediate (I) and (IIa), respectively. In the case of (I) having a trans ring junction derived from E-type geometry of the carbon-carbon double bond in 1, oxidative cleavage of the carbon-thallium bond followed by rearrangement in a trans-anti-parallel manner leads to the ring-contracted products (2) and (3b). On the other hand cis-fused intermediate (IIa) comes to equilibrate with another conformer (IIb), which leads to 5 by the rearrangement of the methyl group.

Similar reaction of o-farnesylphenol (6) with TTFA also gave the cyclization products (7)(mp 105-106°C)[5] and (8)(oil)[5], though in poor yield.



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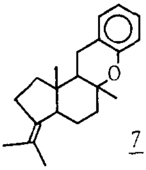

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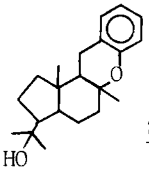

8

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4. The IR spectrum showed the presence of a trifluoroacetate in the products.
5. Satifactory elemental analyses or high resolution mass spectra were obtained for these new compounds. The following spectral data are also satisfactory for their structures.
   2: UV(EtOH) 264, 272 nm; ^{1}H-NMR(100 MHz,CDCl$_3$) δ_{ppm} 1.02(3H,s), 1.64(3H,brs), 1.78(3H,brs), 2.16-2.64(2H,m), 3.28(1H,dd,J=14,5 Hz), 6.7-7.2(4H,m).
   3a: IR(CHCl$_3$) 3590 cm^{-1}; UV(EtOH) 264, 272 nm; ^{1}H-NMR(100 MHz,CDCl$_3$) δ_{ppm} 1.16(1H,s,OH), 1.22(6H,s), 1.34(3H,s), 1.68-2.00(4H,m), 2.18-2.42(2H,brs),2.90-3.18(2H,m),6.6-7.1(4H,m).
   5: UV(EtOH) 276, 283 nm; ^{1}H-NMR(100 MHz,CDCl$_3$) δ_{ppm} 1.36(3H,s), 1.70(3H,brs), 1.9-2.2(3H,m), 2.53(1H,dd,J=16,10 Hz), 2.98(1H,dd,J=16,6 Hz), 6.6-7.1(4H,m), 1.60(3H,s).
   7: UV(n-hexane) 276, 283 nm: ^{1}H-NMR(100 MHz,CDCl$_3$) δ_{ppm} 0.67(3H,s), 1.24(3H,s), 1.5-3.0(12H), 1.61(3H,brs), 1.76(3H,q,J=2 Hz), 6.7-7.2(4H,m).
   8: IR(CHCl$_3$) 3580 cm^{-1}; ^{1}H-NMR(100 MHz,CDCl$_3$) δ_{ppm} 0.86(3H,s), 1.20(3H,s), 1.23(3H,s), 1.25 (3H,s), 1.0-3.0(14H), 6.6-7.2(4H,m).
6. The trans nature of the ring junction of 2 and 3a was determined by the fact that the ketone obtained by ozonolysis of 2 easily epimerized to the stable cis-fused ketone. The stereochemistry of 5 was suggested by the ^{1}H-NMR decoupling experiments.

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