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ANGULAR HYDROXYLATION OF POLYCYCLIC KETONES USING BENZENESELENINIC ANHYDRIDE[1]

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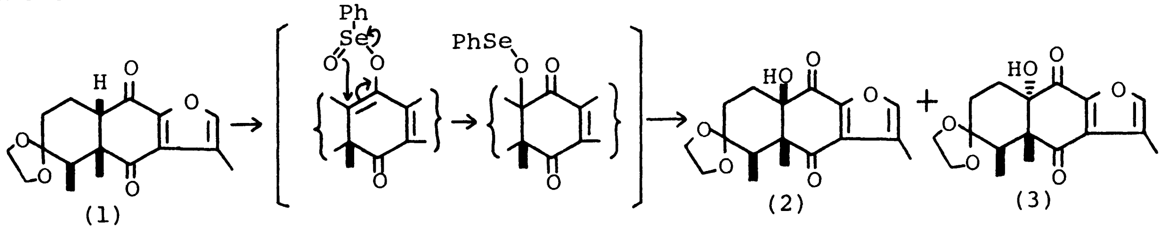
Introduction of a hydroxyl group into the angular position of tricyclic ketones (1, 4a, 4b, and 6) was accomplished by the use of benzeneseleninic anhydride, the products being obtained in a good yield.

Barton *et al.* reported *ortho*-hydroxylation of phenols using benzeneseleninic anhydride,[2] although a number of alicyclic alcohols were oxidised by this reagent to carbonyl derivatives in a high yield,[3] and the corresponding enones were obtained in some cases by further oxidation.[4] We report here that introduction of a hydroxyl group into the angular position of tricyclic ketones (1, 4a, 4b, and 6) by benzeneseleninic anhydride was accomplished, and the products were obtained in a good yield, without the formation of corresponding enones.

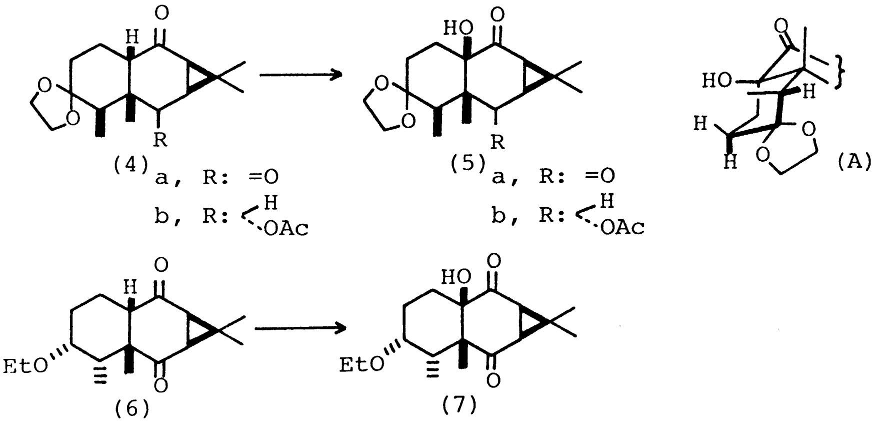
Scheme 1



A solution of 3,3-ethylenedioxy-6,9-dioxofuranoeremophilane[5] (1) and benzeneseleninic anhydride in toluene was heated under reflux for 4 hr to give 1, 2, and 3, in 24, 57, and 17% yield, respectively. Structure of the major product (2), mp 130-132°, was confirmed from its spectral data [MS: M^+ 320; IR: 3520 cm^{-1}; UV: λ_{max}^{EtOH} 243 and 304 nm; NMR δ: 1.17 (3H, d, J=7 Hz, 4-CH_3), 1.19 (3H, s, 5-CH_3), 2.30 (3H, 11-CH_3), 2.81 (1H, dq, J=7, 1 Hz, 4-H)]. In ^{13}C-NMR spectra of 1 and 2, a doublet signal of 10-C at δ 53.7 in 1 changed to a singlet signal at δ 80.6 in 2 due to introduction of a hydroxyl group. In ^{1}H-NMR spectrum of 2, 4-H appeared as a quartet signal at δ 2.81, with long-range coupling (J=1 Hz) with 2-H attributed to the "W" arrangement. From these data, the structure of 2 was found to be 3,3-ethylenedioxy-10β-hydroxy-6,9-dioxofuranoeremophilane, shown by the non-steroidal conformation (A). Structure of the minor product (3), mp 195-199°, was confirmed from its spectral data [MS: M^+ 320; IR: 3490 cm^{-1}; UV: λ_{max}^{EtOH} 243 and 302 nm; NMR δ: 1.16 (3H, d, J=7 Hz, 4-CH_3), 1.27 (3H, s, 5-CH_3), 2.25 (3H, 11-CH_3), 2.85 (1H, q, J=7 Hz, 4-H)].

A solution of tricyclic ketones (4a, 4b, and 6), which were prepared from the major adduct of 3-ethoxy-1,3-pentadiene and 3-carene-2,5-dione,[6] and benzeneseleninic anhydride in toluene, (for 4a in chlorobenzene),was heated under reflux for 4-5 hr. 10β-Hydroxy compounds, 5a, mp 148-150°, 5b, mp 170.5-172°, and 7, mp 155-157°, were obtained in 73, 80, and 70% yields(from converted 4a, 4b, and 6), respectively. Structures of 5a, 5b, and 7 were confirmed from their spectral data. Hydroxyl absorption band in IR spectra of 5a, 5b, and 7 appeared at 3450, 3450, and 3380 cm^{-1}, respectively. In ^{13}C-NMR spectra of 5a, 5b, and 7, the chemical shift of 10-C appeared as a singlet signal at δ 79.7, 78.1, and 79.9, respectively. In ^{1}H-NMR spectra of 5a and 5b, 4-H appeared as a quartet signal at δ 2.58 and 2.61, respectively, with long-range coupling with 2-H, attributed to the "W" arrangement. From these spectral data, the stereoformulae of 5a and 5b should be shown by the non-steroidal conformation (A) (Scheme 2).

Scheme 2



Benzeneseleninic anhydride is an effective reagent for angular hydroxylation of a variety of polycyclic ketones which are enoliziable in the angular position.

References and Note

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