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ANOMALOUS BIRCH REDUCTION PRODUCTS OF 1,1,4aβ-TRIMETHYL-2β-HYDROXY-8-METHOXY-1,2,3,4,4a,9-HEXAHYDROPHENANTHRENE AND UNUSUAL REACTIVITIES OF THE PRODUCTS

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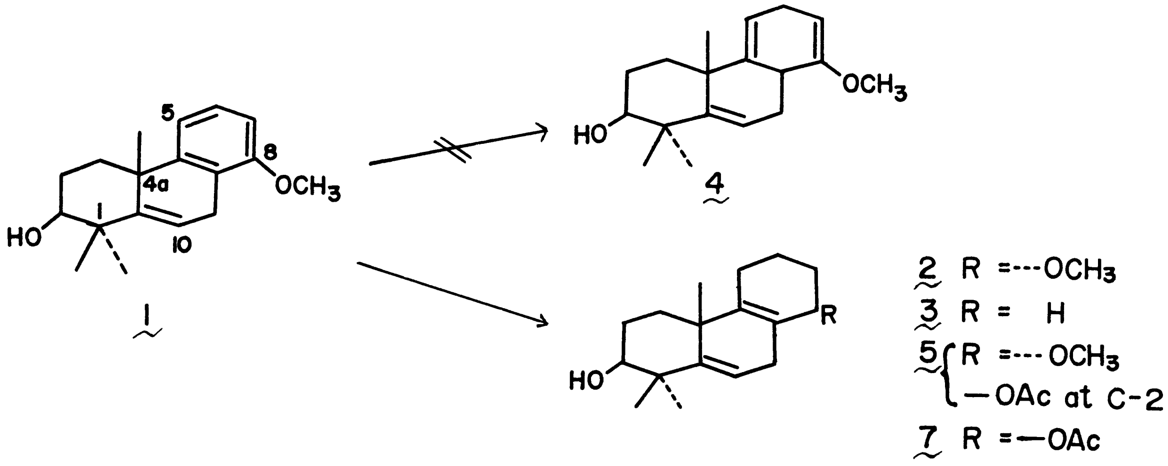
Birch reduction of the title compound 1 afforded a tetrahydroanisole 2 and its hydrogenolysis product 3. The methoxyl group of compound 2 is readily displaced by acetoxyl group with inversion of configuration by warming in acetic acid. Compound 3 is highly sensitive to oxygen; it is autooxidized to 8 on exposing to the air.

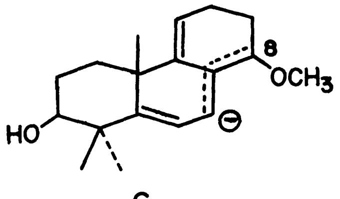
Treatment of the title compound 1[1)] (2.0 g) with Li (6.0 g) in a mixture of dioxane (30 ml)-liq. NH_3 (300 ml)-t-BuOH (280 ml) afforded two crystalline products 2, $C_{18}H_{28}O_2$, mp 162-164°, and 3, $C_{17}H_{26}O$, mp 135-137°, in 25 and 15% yields respectively.[2,3)]



Compound **2** contained hydroxyl group (3440 cm^{-1}) and was sparingly soluble in common NMR solvents. Acetylation under basic conditions (Ac$_2$O, pyridine) of **2** afforded monoacetate **5**, mp 112-114°, NMR and IR spectra of which showed the presence of following groups; three tert-methyls (δ4) 1.07, 1.13 and 1.17), equatorial sec-acetoxyl (δ 2.03, 3H, s, 4.45, 1H, t, J = 8 Hz; 1740 cm^{-1}), sec-methoxyl (δ 3.30, 3H, s, 3.57, 1H, m, W_H = 8 Hz), trisubstituted ethylene (δ 5.76, 1H, q, J = 2 + 6 Hz) and C-9 methylene group (only inner peaks of AB system were observed at δ 2.88, b.d, J = 6 Hz and at 2.52, b.s, W_H = 5 Hz). These data, coupled with molecular formula, indicate the product to be expressed as 1,2,3,4-tetrahydroanisole structure **2**, except for the orientation of the methoxyl group. The full stereostructure **2** with α-axial methoxyl group was elucidated by the X-ray methods.5)

Elemental composition of the second product **3** suggested that it would be a hydrogenolysis product of **2**. Spectral data of **3** (δ 1.15, 3H x 2 and 1.19, 3H, tert-methyls, 2.53, 2H, m, allylic methylene, 3.28, 1H, t, J = 8 Hz and 3400 cm^{-1}, C-2 sec-hydroxyl group, 5.75, 1H, t, J = 4 Hz, C-10 olefinic proton) are completely in agreement with this formulation.

Although a few examples of formation of 2,3,4,5-tetrahydroanisoles (vinyl ethers) and hydrogenolyzed materials as minor Birch products have already been described,6) ready formation of anomalous products **2** and **3** in moderate yields in this particular case could be ascribed to the presence of allylic double bond with respect to benzene ring in the starting material. The double bond would facilitate generation of the anion **6** from the normal primary product **4** and protonation at C-8 of **6** followed by 1,4-reduction would lead to the observed product **2**.



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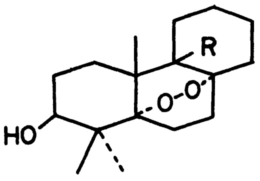


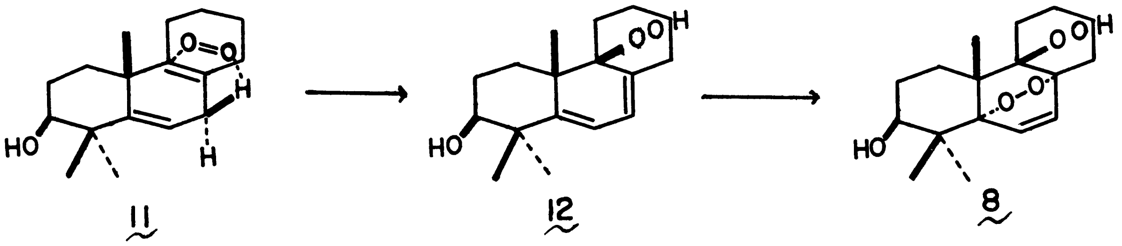
8 R = OOH

9 R = OOAc OAc at C-2

10 R = OH

The methoxyl group of compound **2** is remarkably reactive and readily displaced by acetoxyl group to afford acetoxy compound **7**, mp 146-147°, $C_{19}H_{28}O_3$, (δ 2.05, 3H, s, and 5.15, 1H, m, W_H = 8 Hz, in place of the peaks due to sec-methoxyl group) on warming in acetic acid at 45° for 3 hr in almost quantitative yield. The orientation of the acetoxyl group was shown unambiguously to be β, i.e. inverted, by X-ray crystallographic analysis of **7**.5) To our knowledge no example of such a ready displacement of methoxyl group by acetoxyl group with inversion of configuration seems to have been reported.

In contrast to **2** and **7**, which are stable to oxygen, the hydrogenolysis product **3** is readily oxidized on exposure to the air7) to give an amorphous product **8** in 40% yield. Crystalline diacetate (Ac_2O, pyridine) **9**, mp 128-129°, of **8** was analyzed for $C_{21}H_{30}O_7$ and exhibited NMR spectral data indicating the presence of three methyls (δ 1.10, 1.08, gem-dimethyl and 1.49, angular methyl), two acetoxyls (δ 2.03 and 2.12), axial C-2 proton (δ 5.10, 1H, t, J = 8 Hz) and vic-olefinic protons (δ 6.15 and 6.58, ABq, J = 12 Hz). Reduction of **8** with $NaBH_4$ gave diol **10**, mp 126-127°, $C_{17}H_{26}O_4$ (M^+ 294; δ 1.01, 1.08, gem-dimethyl and 1.25, angular methyl, 6.04 and 5.14, ABq, J = 10 Hz). Taking into account of the mechanism of formation of hydroperoxide-endoperoxide by singlet oxygen8) (**11**→**12**→**8**) above spectral and analytical data are best explained by assigning the formula **8** for the oxygenation product. Comparison of δ values of methyl groups and olefinic protons in **9** and **10** (see above data) indicates spacial closeness of oxygen function at C-4b, methyl group and double bond in these compounds and supports the formula **8**.



Anomalous reactivities of **2** and **3** are quite puzzling at present and seem to deserve further study.

REFERENCES AND NOTES

1) R. E. Ireland and P. W. Schiess, J. Org. Chem., **28**, 6 (1962).

2) Yields are not optimized. Absence of a moderate amount of the normal product **4** and other vinyl ethers in the crude mixture was indicated by the IR spectrum of acid hydrolysis product of the crude material. Use of less than 30 equiv. of Li lowers yields of **2** and **3** giving the starting compound unchanged.

3) Normal Birch reduction of 2-deoxy-dihydro compound of **1** has been reported; R. B. Turner, K. H. Gänshirt, P. E. Shaw, and J. D. Tauker, J. Amer. Chem. Soc., **88**, 1776 (1966).

4) All NMR data were obtained in $CDCl_3$ solutions. TMS was used as the internal standard.

5) The outline of the analysis is described in the accompanying paper.

6) A. P. Krapcho and A. A. Bothner-By, J. Amer. Chem. Soc., **81**, 3658 (1959); A. L. Wilds and N. A. Nelson, J. Amer. Chem. Soc., **75**, 5360 (1953); W. S. Johnson, B. Bannister, and R. Pappo, J. Amer. Chem. Soc., **78**, 6331 (1956).

7) The reaction seems to be photosensitized by a minute amount of colored impurities in the crude product. Pure specimen is oxidized rather slowly in the dark place.

8) C. S. Foote, Acc. Chem. Res., **1**, 104 (1968).

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