Unusual KMnO₄ oxidation product of β-ionone

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K MnO₄ oxidation of β-ionone has been reinvestigated. The structure proposed for the hydroxyionolactone 3 obtained in this reaction is supported by MS, UV, IR, ¹H and ¹³C NMR data and further confirmed by single crystal X-ray diffraction studies of the bromolactone 8.

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The hydroxyionolactone obtained¹ by KMnO₄ oxidation of β-ionone 1 was formulated² as β-lactone 2 which was further revised³ to structure 3 on the basis of its elemental analysis, UV and IR spectral data. However, no mass, ¹H and ¹³C NMR spectra were recorded which would support the structure 3. Moreover, formation of 3 by KMnO₄ oxidation of 1 seemed interesting from the mechanistic point of view. Therefore, we repeated the KMnO₄ oxidation of 1 and obtained hydroxyionolactone as a crystalline solid, m.p. 122°C.

All the structural features of 3 including the conjugated enol lactone butenolide part are consistent with the UV, IR, ¹H and ¹³C NMR data. Its ¹H NMR showed three singlets (δ 1.19, 1.46, 1.53), each integrating for three protons corresponding to two tertiary methyl groups (gemdimethyl) at C₄ and a tertiary methyl at C₇α respectively. The three methylene Hs appeared as multiplets in the region δ 1.5-2.27. The ¹³C NMR signals for all the eleven carbons fully support the structure 3. The DEPT and H decoupled ¹³C NMR spectra exhibited three sp³ methyls (δ 25.24, 25.66, 29.67), three sp³ methylenes (δ 19.94, 39.03, 41.6) and five quaternary carbons (δ 35.81, 85.13, 133.39, 141.27, 170.07). The high resolution CIMS showed M⁺ peak at m/z 219 (100% M⁺ + Na) and 196 (M⁺), corresponding to the molecular formula C₁₁H₁₆O₃. The genesis of the major fragment ions is presented below in Scheme I.

Although Brooks and co-workers³ have suggested the formation of 3 through the intermediate α-keto acid 4, it is not clear how 4 is formed. We believe that, the initially formed manganate ester 5 undergoes a cleavage* to give the α-keto aldehyde 7 via the Mn(III) complex 6. Further oxidation of 7 to the α-keto acid 4 followed by cyclization gives 3 (Scheme II).

Hydroxyionolactone 3 is reported¹ to form a bromolactone 8 on treatment with hydrobromic acid under unstated¹ conditions and by the addition of bromine to the aqueous solution of the lactone 3 (ref 3). However, the bromolactone obtained using these methods melted over a range (166-73°C) and was considered to be a mixture of stereoisomers³. The bromolactone 8 was prepared in 92% yield by generating bromine in-situ using potassium bromate and hydrobromic acid in glacial acetic acid⁵ (Scheme III).

Compound 8, a pale yellow crystalline solid that melted at 214°C with decomposition was analyzed for C₁₁H₁₅O₃Br (MS). The IR spectrum showed the presence of carbonyl band at 1790 cm⁻¹ and the absence of the hydroxyl functionality. The ¹H NMR spectrum of 8 could nicely account for all the 15 H present as 3 methyls (9 H) and 3 methylenes (6 H) as follows: δ 1.29 (s, 3H, C₄-H), 1.46 (s, 3H, C₄-H), 1.53-1.75 (m, 4H, C₅ and C₆-H), 1.79 (s, 3H, C₇-H), 2.48 (m, 1H, C₇-H), 2.52 (m, 1H, C₇-H). The H decoupled ¹³C NMR spectrum of 8 showed distinct 11 signals. Further support to the structure was found in

Note

*A similar cleavage without participation of the carbonyl group has been reported earlier⁴.
Scheme I — Mass spectral fragmentation of 3

Scheme II
the mass spectral data. The characteristic feature of EIMS is the fragment ions $m/z$ 202, 204 and 187, 189 obviously indicating the presence of bromine atom in these fragment ions.

Although, the spectral data of 8 obtained by our method is in agreement with the structure, the melting point (214 °C) does not tally with that reported by earlier workers (166-73 °C) and is attributed to the presence of only the cis-isomer which is confirmed by single crystal X-ray analysis of 8. The crystal structure (Figure 1) clearly indicated that the six membered ring exists in a perfect chair conformation and the two substituents (Br and CH₃) at the junction carbons (3a and 7a) are cis to each other.

**Experimental Section**

Melting points were determined in open capillary tubes and are uncorrected. IR spectra were recorded on a Shimadzu 8101-A FTIR spectrophotometer; $^1$H and $^{13}$C NMR spectra were recorded on a Bruker WT 300 MHz FT NMR spectrophotometer in CDCl₃ with TMS as an internal standard and chemical shifts are recorded in $\delta$ values. All yields refer to pure isolated products.

**3-Hydroxy-4,4,7a-trimethyl-5,6,7,7a-tetrahydro-1-benzofuran-2(4H)-one 3.** A solution of potassium permanganate (10.0 g, 63.3 mmoles) in water (150 mL) was added dropwise, in 4.5 hr, to a stirred solution of $\beta$-ionone (5.0 g, 26 mmoles) in acetone (55 mL) and water (15 mL) at 0-5°C, and was not allowed to exceed 6°C during the addition. The mixture was kept overnight at room temperature. To the reaction mass was added sodium acetate (1.25 g) and then treated with SO₂ gas (prepared by the action of dil HCl on Na₂SO₃) until a clear pale yellow solution was obtained. It was then saturated with NaCl and extracted with ether ($4 \times 25$ mL). The combined ether extracts were treated with saturated NaHCO₃ solution ($4 \times 25$ mL). Acidification of the alkaline phase followed by ether extraction afforded yellow oil (1.87 g), which was subjected to steam distillation. The steam volatile fraction was discarded and the residue remaining in the flask on cooling gave a waxy solid (0.509 g, 10%). Recrystallization from hot water, afforded colourless cubic plates of 3 having m.p. 121°C (Lit. ref. 3 122°C), which was further purified by sublimation under reduced pressure, however the m.p. did not change. IR (KB̅r): 3340 (OH), 2925, 1735, 1455, 1465, 1400, 1390, 1330, 1310, 1270, 1240, 1210, 1110, 1035, 900, 780, 650 cm⁻¹; UV (ethanol): 238 nm [Lit$^3$ UV (ethanol): 238 nm]; $^1$H NMR (300 MHz, CDCl₃): $\delta$ 1.19 (s, 3H, C₄-CH₃), 1.45 (s, 3H, C₄-CH₃), 1.53 (s, 3H, C₇a-CH₃), 1.5-2.21 (m, 6H, C₅, C₆ and C₇-H); $^{13}$C NMR (75 MHz, CDCl₃): $\delta$ 19.9 (C-6), 25.2 (C-8), 25.7 (C₄-CH₃), 29.7 (C₇a-CH₃), 35.8 (C₄-CH₃), 41.6 (C-7), 85.1 (C-7a), 133.9 (C-3), 141.3 (C-3a), 170.1 (C-2); CIMS: $m/z$, (relative intensity) 219 (M$^+$ + Na, 100), 197 (M$^+$ + 1, 55), 179 (29), 151 (36), 139 (17), 123 (37), 121 (29), 109 (23), 95 (26), 93 (13), 69 (17%).

**3a-Bromo-4,4,7a-trimethylhexahydro-1-benzofuran-2,3-dione 8.** Potassium bromate (0.085 g, 0.5 mmoles) was added to a solution of 3 (0.07 g, 0.36 mmoles) in acetic acid (2 mL). To this mixture was added with stirring 48% HBr (0.3 mL) and then stirred at room temperature for 10 min. Water (10 mL) was added to the reaction mixture and a pale yellow solid separated out, was filtered, washed with dilute NaHSO₃ (3 × 2 mL), water (3 × 2 mL) and dried to give 8 (0.09 g, 92%). Recrystallization from petroleum ether containing traces of benzene, gave pale yellow crystalline solid, which melted with decomposition at 214°C (Lit. ref.3 166-73°C, from ether and petroleum ether). IR (KB̅r): 2940, 1790, 1775, 1455, 1385, 1310, 1270, 1245, 1160, 1145, 1060, 1035, 900, 875, 805, 705, 690 cm⁻¹; $^1$H NMR
(300 MHz, CDCl₃): δ 1.29 (s, 3H, C₄-CH₃), 1.46 (s, 3H, C₄-CH₃), 1.53-1.75 (m, 4H, C₅ and C₆ Hs), 1.79 (s, 3H, C₇a-CH₃), 2.48 (m, 1H, H-7b), 2.52 (m, 1H, H-7a); ¹³C NMR (75 MHz, CDCl₃): δ 18.6 (C-6), 23.8 (C-8), 26.3 (C₆=CH₂), 27.1 (C₅=CH₂), 36.8 (C-7), 38.9 (C-4), 42.1 (C-5), 80.0 (C-7a), 85.4 (C-3a), 159.8 (C-2), 183.0 (C-3); EIMS: m/z, (relative intensity) 274.2, 276.2 (M +), 204.2, 202.2 (36), 187.1, 189.1 (87), 167.2, 152.2, 151.2 (72), 123.2 (100), 107.2 (79), 93.1 (27), 81.1 (54), 79.1 (27), 55.1 (23), 53.1 (26), 43.1 (55%).

Crystallographic data

Single crystals of the bromolactone 8 were obtained from petroleum ether containing traces of benzene. X-ray intensity data for 8 were collected on a Bruker SMART APEX CCD diffractometer with graphite monochromatized (Mo Kα = 0.71073 Å) radiation at room temperature (293 ± 2 K). All the data were corrected for Lorentzian polarization and absorption effects using Bruker’s SAINT and SADABS programs. SHELXS-97 and SHELXL-97 programs were used for crystal structure solution and full-matrix least-squares refinement on F². Hydrogen atoms were positioned and refined using the riding model. The perspective view of the molecule is shown in Figure 1. Crystal data: C₁₁H₁₅BrO₃, M = 275.14, crystal system monoclinic, space group P2₁/c, crystal size 0.83 × 0.82 × 0.34 mm³, a = 7.6212(14)Å, b = 11.5812(2)Å, c = 13.2073(3)Å, β = 93.974(1)°, T = 297(2)K, V = 1162.8(4)Å³, μ = 3.520 mm⁻¹, Dealc = 1.572 g cm⁻³, Z = 4, F(000) = 560, reflections collected = 5011, unique reflections = 1964, refined parameters = 139, observed reflections = 1487, R = 0.0611, W(R) = 0.1731, Goodness of fit = 1.039, Absorption correction multi-scan, Index ranges = −7 ≤ h ≤ 9, −13 ≤ k ≤ 13, −15 ≤ l ≤ 15, T_min = 0.1582, T_max = 0.3764, Δρ_max, Δρ_min = 1.209, -0.673 e Å⁻³.

Supplementary material

Crystallographic data (excluding structure factors) for the structure of compound 8 reported in this paper has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 614663. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: 144 1223 336033 or email: deposit@ccdc.cam.ac.uk]

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References

1 Tiemann, Ber, 31, 1898, 857.
6 Sheldrick G M, SHELXS-97 and SHELXL-97 programs for crystal structure solution and refinement, University of Göttingen, Germany, 1997.