

UNUSUAL PRODUCTS OF OXIDATION WITH Cr(VI) OF METHYL
5-METHYL-7-METHOXY-8-ISOPROPYL-3,4-DIHYDRO-2-NAPHTHOATE

V.Viswanatha and G.S.Krishna Rao

Department of Organic Chemistry, Indian Institute of Science,
Bangalore 560012, India

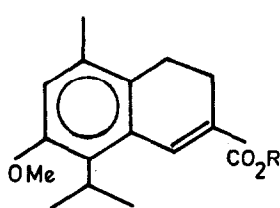
(Received in UK 3 September 1973; accepted for publication 21 September 1973)

We reported from these laboratories in 1970 on the chromic acid oxidation of cyclobutanones to γ -lactones¹. Now we describe two more instances of a novel course of oxidation by Cr(VI) in connection with the oxidation of methyl 5-methyl-7-methoxy-8-isopropyl-3,4-dihydro-2-naphthoate (1c), from which it was intended to obtain the α -naphthol (2a) or the β -naphthol (2b), or a mixture of both, required for the synthesis of a natural product.

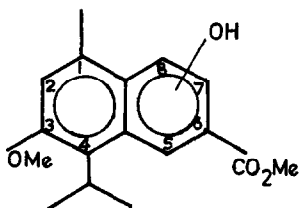
The title compound was prepared from 5-methyl-7-methoxy-8-isopropyl-tetralone² (3) by ethoxycarbonylation to the corresponding β -keto ester, sodium borohydride reduction and formic acid dehydration of the resulting β -hydroxy ester to 1a. This was hydrolysed to the acid 1b³, m.p.217-218° (benzene); δ^4 (CDCl₃) 1.36 (6H, d, J 7 Hz, -CHMe₂), 2.28 (3H, s, Ar-Me), 2.42 to 2.86 (4H, m, -CH₂-CH₂-), 3.58 (1H, septet, J 7 Hz, -CHMe₂), 3.8 (3H, s, -OMe), 7.71 (1H, s, Ar-H), 8.14 (1H, s, CH=C-CO₂H) and 10.05 (1H, s, -CO₂H). Its methyl ester 1c³ had m.p.54.5-55.5° (light petroleum).

t-Butyl chromate⁵ oxidation of 1c gave a neutral product (yellow needles) in low yield, m.p.122-122.5° (light petroleum). In its IR spectrum the presence of ester and quinone was indicated (1745, 1674 and 1641 cm⁻¹)⁶.

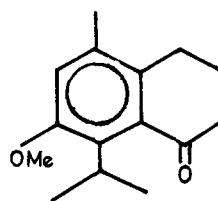
It absorbed in the UV at 229 ($\log \epsilon$ 4.41), 258 (4.32), 325 (sh)(3.52) and 370 nm (sh)(3.32). Its molecular weight, m/e 258 (M^+), and elemental analysis indicated a molecular formula $C_{15}H_{14}O_4$. The PMR spectrum⁴ ($CDCl_3$) showed the presence of an isopropyl group (1.23, 6H, d, J 7 Hz), a methine proton (3.29, 1H, septet, J 7 Hz), an ester methyl (4.01, 3H, s) and four low field protons [6.85, 1H, d, J 1 Hz (H_1 or H_4); 8.11, 1H, d, J 8 Hz and 8.34, 1H, dd, J 2 Hz and 8 Hz (H_7 and H_8); 8.76, 1H, d, J 2 Hz (H_4 or H_1)]. Most revealing in the PMR spectrum is the absence of the aromatic methyl and the ester methyl of 1c. The analytical and spectral values are consistent with a 2,6-naphthaquinone structure such as 4 for the product. Though oxidative desalkylation by nitric⁷ and chromic⁸ acids have been reported, our present finding appears to be the first instance where *t*-butyl chromate reacted similarly, while additionally removing an aromatic methyl, lost apparently by oxidation to carboxyl followed by decarboxylation.



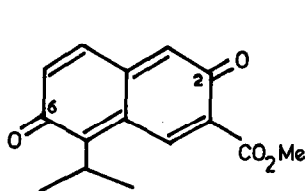
1 a, R=Et
b, R=H
c, R=Me



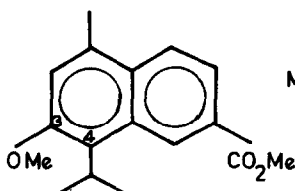
2 a, 8-OH
b, 7-OH



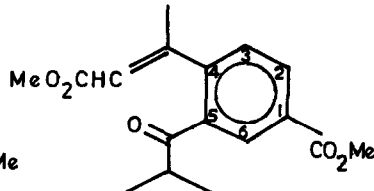
3



4



5



6

Pyridine-chromium trioxide⁹ oxidation of 1c afforded a mixture of two neutral products, separated by silica gel column chromatography. Elution with hexane-benzene (2:1) gave the naphthoic ester³ (5), m.p.96-97° (light petroleum); δ^4 (CCl₄) 1.45 (6H, d, J 7 Hz, -CHMe₂), 2.62 (3H, s, Ar-Me), 3.89 and 3.91 (3H, 3H, each s, -OMe and -CO₂Me), 3.91 (1H, m, merged, -CHMe₂), 7.1 (1H, s, H₂), 7.84 (2H, bs, H₇ and H₈, split into AB quartet with a dd pattern J 1.5 Hz (H₇,H₅) and J 8 Hz (H₇,H₈) in 2:3 CCl₄ + C₆D₆) and 8.84 (1H, bs, H₅). Elution with benzene gave an oil which solidified on sublimation (115-125°/2 mm), m.p.87-89° (aqueous methanol). In the IR it showed unsaturated ester and ketone (1725 and 1695 cm⁻¹) and absorbed in the UV at 222 nm (log ϵ 4.58). The molecular weight, m/e 304 (M⁺), and elemental analysis indicated a molecular formula, C₁₇H₂₀O₅. The PMR spectrum⁴ (CCl₄) showed the presence of an isopropyl group (1.12; 6H; d, J 7 Hz), a vinyl methyl (2.19, 3H, d, J 1.5 Hz), two ester methyl groups (3.4, 3H, s and 3.9, 3H, s), a methine proton (3.48, 1H, septet, J 7 Hz), a vinylic proton (5.73, 1H, q, J 1.5 Hz) and three aromatic protons (7.06, H₃, d, J 8 Hz; 8.04, H₂, dd, J 1.5 Hz and 8 Hz; 8.29, H₆, d, J 1.5 Hz). These data support the structure 6 for the more polar neutral product, the formation of which is explained by the oxidative cleavage of the C₃-C₄ bond of 5.

Acknowledgements. One of us (V.V.) is indebted to the C.S.I.R., New Delhi for Junior Research Fellowship. The authors thank Dr.K.Subrahmania Ayyar and Dr.S.R.Ramadas for the mass spectra and Dr.G.S.R.Subba Rao and Prof.D.K.Banerjee for helpful discussions.

References

1. L.R.Subramanian and G.S.Krishna Rao, J.Indian Instt.Sci., 52, 112 (1970).
2. P.B.Talukdar, J.Org.Chem., 21, 506 (1956).
3. The compounds gave correct elemental analyses.
4. The PMR data (Varian HA-100D) are in ppm downfield with respect to TMS.
5. D.L.Roberts, R.A.Heckman, B.P.Hege and S.A.Bellin, J.Org.Chem., 33, 3566 (1968); L.F.Fieser and M.Fieser, "Reagents for Organic Synthesis", John Wiley and Sons, Inc., 1967, p.86.
6. We are unable to explain the anomalous absorption of the ester carbonyl which is on the high side.
7. G.S.Krishna Rao, K.Visweswara Rao and T.R.Seshadri, Proc.Indian Acad.Sci., 27A, 245 (1948); 28A, 103 (1948).
8. J.Correa and J.Romo, Tetrahedron, 22, 685 (1966).
9. W.G.Dauben, M.Lorber and D.S.Fullerton, J.Org.Chem., 34, 3587 (1969); R.Ratcliffe and R.Rodehorst, Ibid., 35, 4000 (1970).