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Naphthalene-1,3,8-triol

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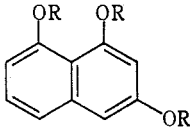
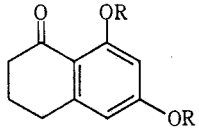
Abstract

One of the two compounds described in the literature as naphthalene-1,3,8-triol is 6,8-dihydroxy-3,4-dihydronaphthalen-1(2*H*)-one. It may be converted into naphthalene-1,3,8-triol by a bromination–dehydrobromination procedure.

We required an authentic sample of the title compound (1) for comparison with a degradation product and followed the multi-stage procedure of Stetter and Heidel,[1] which was the only reported synthesis at the time. Dehydrogenation of the appropriate decalintrione led to compounds whose melting points corresponded with those reported for the triol (1) and its triacetate (2). They were in fair agreement with more recent data for these compounds, obtained by transformations of the fungal metabolite scytalone.[2,3] However, the stability of the supposed triol[1] towards atmospheric oxidation seemed hardly consistent with this formulation. Investigation has led to the conclusion that the two structures arising from Stetter and Heidel's procedure[1] require revision to the tetralone (3) and its diacetate (4) respectively.



(1) R = H
(2) R = Ac



(3) R = H
(4) R = Ac

The u.v. absorption of the former compound was consistent with the revised formulation (λ_{max} 317 nm) and it lacked naphthalenic fine structure. Its p.m.r. spectrum contained two-proton triplets at δ 2·83 and 2·57, together with a two-proton multiplet at 2·05. The spectrum of the diacetate (4) was equally definitive and is detailed in the Experimental.

Direct aromatization of (3) to (1) could not be accomplished with palladium/charcoal. However, treatment of the diacetate (4) with *N*-bromosuccinimide followed by

[1] Stetter, H., and Heidel, H., *Chem. Ber.*, 1966, **99**, 2172.
[2] Aldridge, D. C., Davies, A. B., Jackson, M. R., and Turner, W. B., *J. Chem. Soc., Perkin Trans. 1*, 1974, 1540.
[3] Findlay, J. A., and Kwan, D., *Can. J. Chem.*, 1973, **51**, 1617.

acetylation with acetic anhydride and pyridine gave an almost quantitative yield of the triacetate (2). It showed characteristic naphthalenic fine structure and apart from the acetate signals it resonated exclusively in the aromatic region of the spectrum. Finally, its melting point agreed with that reported by Findlay and Kwan from scytalone.[3]

Treatment of (2) in methanolic alkali with careful exclusion of air gave naphthalene-1,3,8-triol (1). It was never prepared on more than a small scale as required, forming a solid which darkened readily on standing in air. Its electronic absorption retained naphthalenic fine structure. As expected, several of the ring protons were easily exchanged under neutral conditions.[4] In the mass spectrometer up to six protons were exchanged in the presence of MeOD or of acetone–deuterium oxide. Its p.m.r. spectrum in acetone[D_6] showed multiplets at δ 6·4 (3H) and 7·0 (2H). The former signals, presumably protons *ortho* to hydroxyls, disappeared on addition of D_2O. Finally, its melting point agreed with that reported from scytalone.[2]

Treatment of either (2) or (1) with methanolic alkali in the presence of air gave 2,5-dihydroxy-1,4-naphthoquinone which was identical with an authentic sample. The products of aerial decomposition of (1) in the solid phase were unidentified.

Experimental

Unless otherwise stated, electronic spectra were measured in methanol and i.r. spectra as KBr discs.

6,8-Dihydroxy-3,4-dihydronaphthalen-1(2H)-one (3)

Prepared according to the procedure assigned for naphthalene-1,3,8-triol, the *tetralone* had m.p. 208–209° (lit.[1] 205–207°) from aqueous ethanol (Found: C, 67·2; H, 5·7. $C_{10}H_{10}O_3$ requires C, 67·4; H, 5·6%). λ_{max} (log ε) 224 (4·12), 284 (4·15), 317 (3·84) nm. ν_{max} 3100, 1620 cm^{-1}. *m/e* 178, 160, 150, 122. δ [$(CD_3)_2CO$] 2·05, 2H, m; 2·57, 2H, t, *J* 9 Hz; 2·83, 2H, t *J* 9 Hz; 6·13, 1H, d, *J* 3 Hz; 6·25, 1H, m; 13·8, 1H, s.

8-Oxo-5,6,7,8-tetrahydronaphthalene-1,3-diyl Diacetate (4)

A solution of the foregoing compound (30 mg) in pyridine (2 cm^3) and acetic anhydride (3 cm^3) was heated on the water bath for 30 min. Solvents were then removed in vacuum to give the *diacetate* (2) (41 mg) from hexane, m.p. 110–111° (lit.[1] for assigned triacetate 111°) (Found: C, 64·3; H, 5·5. $C_{14}H_{14}O_5$ requires C, 64·1; H, 5·4%). λ_{max} (log ε) 217 (4·16), 255 (4·12), 290 (3·55) nm. ν_{max} 3400, 1765, 1680 cm^{-1}. *m/e* 262, 220, 178, 150. δ ($CDCl_3$) 2·25, 2H, m; 2·29, 3H, s; 2·36, 3H, s; 2·59, 2H, t, *J* 9 Hz; 2·98, 2H, t, *J* 9 Hz; 6·71, 1H, d, *J* 3 Hz; 6·96, 1H, d, *J* 3 Hz.

Naphthalene-1,3,8-triyl Triacetate (2)

A mixture of the diacetate (4) (220 mg), *N*-bromosuccinimide (150 mg) and benzoyl peroxide (25 mg) in carbon tetrachloride (25 cm^3) was boiled for 20 h. After cooling and removal of solid the solvent was removed in vacuum. To the crude residue was added acetic anhydride (4 cm^3) and pyridine (4 cm^3) and the mixture was boiled for 15 min. Solvents were then removed in vacuum and the residue partitioned between ether and water. The ether phase was washed with dilute hydrochloric acid and water, dried and concentrated. This gave the triacetate (2) (208 mg) from light petroleum, m.p. 120–121·5° (lit.[3] 120–123°) (Found: C, 63·8; H, 4·8. Calc. for $C_{16}H_{14}O_6$: C, 63·6; H, 4·6%). *m/e* 302, 260, 218, 176. U.v., i.r. and p.m.r. in agreement with lit.[3]

Naphthalene-1,3,8-triol (1)

A mixture of methanol (5 cm^3) and 10% aqueous sodium hydroxide (5 drops) was flushed with a nitrogen stream for 30 min. To this was added the triacetate (2) (5 mg) and the solution was stirred

[4] Hand, E. S., and Horowitz, R. M., *J. Am. Chem. Soc.*, 1964, **86**, 2084.

for 30 min. It was then neutralized with hydrochloric acid and the mixture evaporated to dryness at room temperature. Vacuum sublimation of the crude product gave the triol (1) (2 mg), m.p. 194–196° with darkening (lit.[2] 197–199°) (Found: *m/e* 176·0473. Calc. for $C_{10}H_8O_3$: *m/e* 176·0473). λ_{max} (log ε) 243, (3·84), 294 (3·41), 305 (3·47), 330sh (3·42), 339 (3·43) nm. I.r. in agreement with lit.[2]

Hydrolysis of the triacetate (2) (5 mg) as above but in air gave an orange solution. After 15 min it was neutralized with hydrochloric acid and worked up as before. It gave 2,5-dihydroxy-1,4-naphthoquinone (3·5 mg), m.p. 206–209° (dec.) [lit.[5] 220° (dec.)]. It was undepressed in admixture with authentic material and had identical electronic absorption and chromatographic behaviour.

Acknowledgments

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[5] Thomson, R. H., *J. Org. Chem.*, 1948, **13**, 870.