4a-METHYL-5-HYDROXY-5,6,7,8-TETRAHYDRO-2(4aH)NAPHTHALENONE.
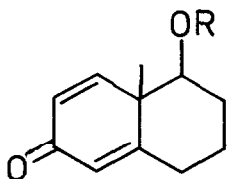
A SPONTANEOUS DIENONE-PHENOL REARRANGEMENT

K.H. BELL
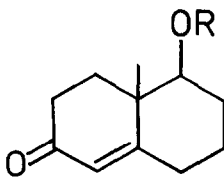
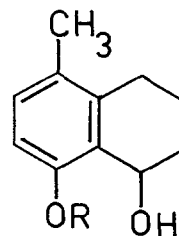CHEMISTRY DEPT., UNIVERSITY OF NEWCASTLE, SHORTLAND
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As part of a programme to examine the effect of various functional groups on the course

of the acid catalysed dienone-phenol rearrangement of bicyclic dienones, the preparation of

the hydroxy dienone I (R=H) was undertaken.

| I | II | III |

II (R=H), the obvious precursor to I (R=H), is readily available (1) by selective reduc-

tion of the corresponding diketone with sodium borohydride in ethanol at $0°$.

Attempted dehydrogenation of II (R=H) with the usual reagents (2) [selenium dioxide or

2,3-dichloro-5,6-dicyano-1,4-benzoquinone in various solvents] gave sparingly soluble resinous

products, and in some runs using stoichiometric quantities of reactants, a little unchanged

starting material, but none of the desired dienone.

However, conversion of the alcohol II (R=H) into the corresponding acetate II (R=COCH$_3$),

followed by treatment with either of the above dehydrogenating agents, gave the dienone I

(R=COCH$_3$), m.p. 84.5 (petroleum ether) in an average yield of 70%. The structure of this pro-

duct was confirmed by its i.r. spectrum [ν_{max} (CCl$_4$) 1759, 1743 (split acetate C=O), 1676

(ketone C=O), 1638, 1615 (C=C) cm^{-1}] and the n.m.r. spectrum (CDCl$_3$) in which the C4 proton

appeared as a doublet (τ 3.12, J$_{3,4}$ = 10 cps) and the C3 proton as four lines (τ 3.77,

$J_{1,3}$ = 2 cps, $J_{3,4}$ = 10 cps) with the two lines at higher field coincident with the signal from the Cl proton (τ 3.86). This vinyl absorption pattern is typical of cross conjugated dienones of this type (3).

Hydrolysis of I (R=COCH$_3$) by boiling under reflux with 1M sodium hydroxide in 50% aqueous methanol yielded a single phenolic product in 27-40% yield, together with a non-phenolic fraction. Thin layer chromatography of the alkali insoluble product showed the presence of at least four components but the i.r. spectrum could not be reconciled with the presence of any I (R=H). By diluting the reaction mixture twenty fold with methanol, the yield of the phenol was raised to 76%, suggesting it was formed by an intramolecular reaction at the expense of the intermolecularly formed non-phenolic products.

Methylation of the crude phenol in aqueous sodium hydroxide with dimethyl sulphate gave a solid methyl ether, m.p. 58-59° (aqueous methanol) analysing for $C_{12}H_{16}O_2$. The n.m.r. spectrum (CDCl$_3$) of this ether showed an AB quartet at 3.00, 3.37 τ (J = 8 cps) indicating the presence of two non-equivalent o̲r̲t̲h̲o̲ aromatic protons. Other signals were at 4.98 τ (broad, Ar-C̲H̲-OH), 6.18 τ (singlet, -OC̲H̲$_3$), 6.93 τ (slightly broadened, disappears on D$_2$O exchange, -OH̲), and 7.84 τ (singlet, Ar-C̲H̲$_3$). The i.r. spectrum (CCl$_4$) showed free hydroxyl absorption at 3610 cm^{-1} and intramolecularly bonded hydroxyl absorption, unchanged on dilution, at 3470 cm^{-1}.

On the basis of the above evidence, the methyl ether was formulated as III (R=CH$_3$) and this was confirmed by comparison with an authentic sample prepared by the following unambiguous route.

Reaction of the Grignard reagent derived from 3-bromo-4-methylanisole with succinic anhydride (4) gave 4-(2-methyl-5-methoxyphenyl)-4-oxobutyric acid, m.p. 100-101° (petroleum ether) in 58% yield. Clemmensen reduction to the corresponding aryl butyric acid, m.p. 83-4° (petroleum ether) followed by cyclization with polyphosphoric acid at 50° gave 3,4-dihydro-5-methyl-8-methoxy-1(2H)naphthalenone, m.p. 82° (petroleum ether), 2,4-dinitrophenylhydrazone, m.p. 233-235° (benzene). Reduction of the tetralone with sodium borohydride in ethanol at room temperature gave the tetralol III (R=CH$_3$), m.p. 58-59°, identical in all respects with the methyl ether obtained above.

The formation of the phenol III (R=H) can only be rationalised adequately in terms of the following mechanism

I (R=COCH_3)
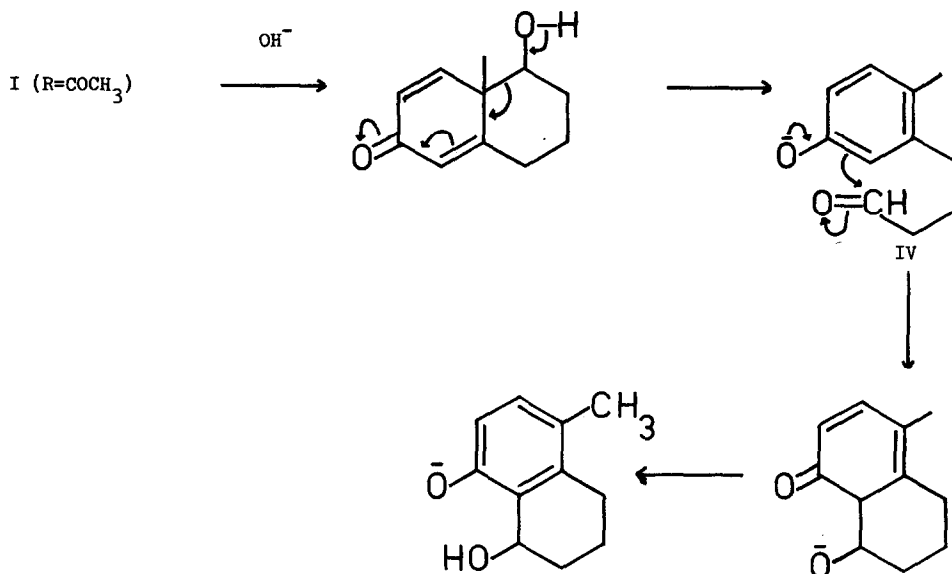
The ring B cleavage postulated above is a departure from the usual routes followed in the dienone-phenol rearrangement and has been observed previously as only a minor pathway in a few isolated cases (5).

The hydroxy dienone I (R=H) is probably incapable of separate existence and undergoes spontaneous rearrangement even under alkaline or neutral conditions. Such a phenomenon does not appear to have been reported previously. This would explain the formation of tars in the attempted dehydrogenation of II (R=H) since either III (R=H) or an intermediate such as IV would be susceptible to further attack by either of the two reagents to yield complex products (6).

The non-phenolic intermolecular products from the hydrolysis could possibly arise by Michael type additions of phenoxide ions [anion of III (R=H) or IV] to the original dienone, and these are currently under investigation.

<div align="center">ACKNOWLEDGMENT</div>

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