Phenol–Keto Tautomerism in Tricyclic [10]Annulenes; Preparation and Properties of 7b-Methyl-2a,7b-Dihydrocyclopent[cd]inden-2-(2H)-one

Raymond McCague, Christopher J. Moody, and Charles W. Rees
Department of Chemistry, Imperial College of Science & Technology, London SW7 2AY, U.K.

The 2-'phenol' in the tricyclic [10]annulene series appears to exist entirely in the keto form (4); the 'phenolate' anion is readily formed, and can be methylated on oxygen, or on carbon to give isomer (9) exclusively.

One consequence of the delocalisation energy of the benzene ring is that phenols, unlike simple enols, are much more stable in the enol (1) than the keto form (2). Although the relationship of phenols to enols is reflected in the fact that both can be alkylated on oxygen or carbon, it is only recently in the work of Ripoll and co-workers that the keto tautomer of phenol has been observed directly by spectroscopic methods at low temperature.[1]
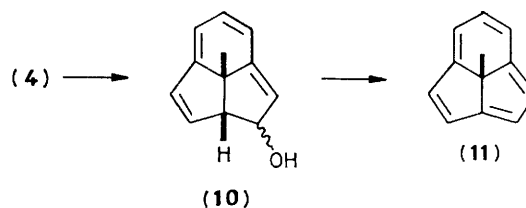
We have described the synthesis and properties of the 10π

aromatic system, 7b-methyl-7bH-cyclopent[cd]indene.[2,3] We now report the synthesis and properties of the 2-hydroxy derivative (3) and demonstrate that, unlike phenol, the tautomeric equilibrium lies far on the side of the keto form (4).

The tricyclic ketone (5)[3] was readily converted into the tetraenone (4) by trimethylsilylation on oxygen, elimination of methanol (to give 7), and desilylation. This sequence of reactions was effected in high yield in a one-pot operation, by

treatment of (5) with excess of chlorotrimethylsilane and sodium iodide in refluxing acetonitrile in the presence of triethylamine,[4] followed by addition of water at 0 °C to give (4) (81%) as an orange-red oil, λ_{max} (EtOH) 252 (log ϵ 4.34), 335 sh (3.11), and 446 nm (3.03). There are no signals upfield of tetramethylsilane (TMS) in the n.m.r. spectrum, the central methyl group resonating at δ (CDCl$_3$) 1.41, and the i.r. spectrum shows a carbonyl stretch at 1692 cm^{-1}. These data are completely consistent with the ketone structure (4), and there is no spectral evidence for the presence of any significant amount of the enol tautomer (3). It is interesting to note that the 2-hydroxyannulene (3) ketonises to the tetraenone (4) with the hydrogen on C-2a, rather than to the more strained isomer with the hydrogen on C-1.

The ketone (4) forms a mauve 2,4-dinitrophenylhydrazone, m.p. 180—182 °C, and is slightly soluble in water. No deuterium exchange was observed on shaking a carbon tetrachloride solution of (4) with deuterium oxide, or in the presence of acid even at reflux. However, complete exchange of H-2a was observed in the presence of a catalytic amount of tetra-n-butylammonium hydroxide after 2 h at 40 °C. Deuterium exchange was also complete after 1 h at 60 °C in Me$_2$SO containing a trace of the same catalyst; the resulting solution

(1)   (2)

(3)   (4)

(5)   (4)   (6)

(9)   (8)   (7)

Scheme 1. *Reagents:* i, Me$_3$SiCl, NaI, Et$_3$N, MeCN, 80 °C; ii, H$_2$O, 0 °C; iii, base (see text); iv, NaOAc, AcOH–H$_2$O, −78 °C; v, Me$_3$SiCl, NaI, Et$_3$N, MeCN, 20 °C; vi, KF, AcOH, H$_2$O, CH$_2$Cl$_2$, PhMe$_3$N$^+$Cl$^-$, 40 °C; vii, MeLi, DME; viii, KH, 18-crown-6, DME; ix, MeOSO$_2$F; x, NaH, THF, LiBr, 20 °C; xi, MeI, 40 °C.
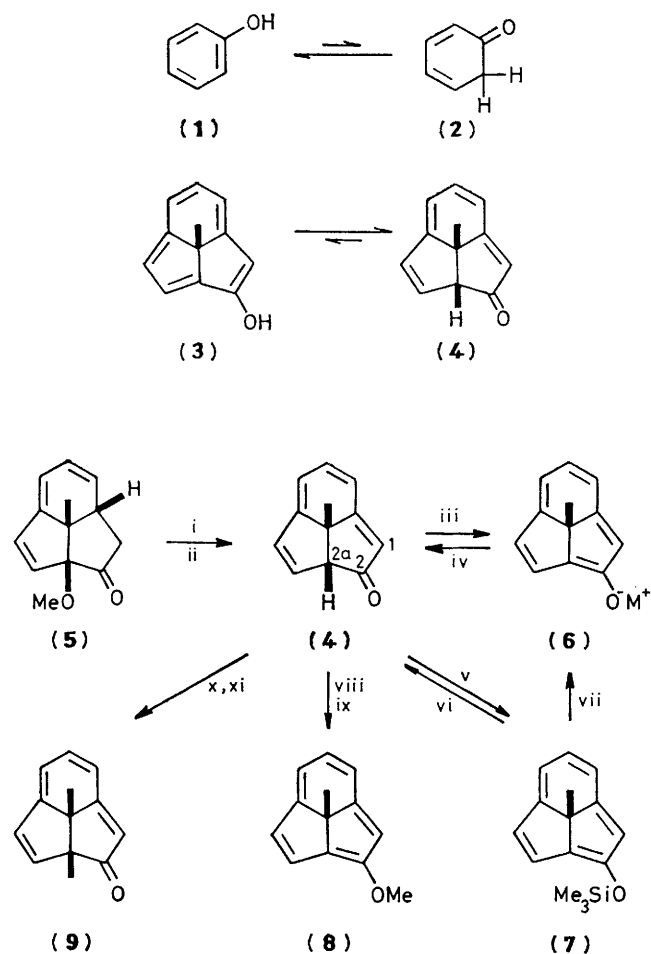

(4) ⟶ (10) ⟶ (11)

showed no n.m.r. signals upfield of TMS, or in the aromatic region. Since deuterium exchange had taken place, the keto–enol equilibrium must have been established, if initial protonation is on oxygen as we assume. Thus, the equilibrium mixture contains no detectable amount (<1%) of the annulenol (3). Under all conditions only monodeuteriation was observed and this was exclusively at the 2a-position. Treatment of (4) with sodium hydride in tetrahydrofuran led to rapid evolution of hydrogen and formation of a deep yellow solution of the sodium salt (6, M = Na).

The ketone (4) is a useful precursor to the 2-oxygenated [10]annulenes (6), (7), and (8), and the parent (11). It reacts rapidly at room temperature with the chlorotrimethylsilane–sodium iodide combination[4] to give the trimethylsilyl ether (7) (74%). The [10]annulene (7) is a yellow oil which shows the expected n.m.r. signal upfield of TMS at δ (CDCl$_3$) −1.51 for the central methyl group. Desilylation of (7) with fluoride ion returned the ketone (4) exclusively. The trimethylsilyl ether (7) is also a convenient source of the lithium enolate (6, M = Li). Thus, treatment of (7) with one equivalent of methyl-lithium in 1,2-dimethoxyethane (DME) at 0 °C gave a deep yellow solution of the lithium salt (6, M = Li). This solution shows a signal upfield of TMS at δ (DME) −1.45 for the central methyl group [*cf.* δ −1.62 for (7) in the same solvent] indicating that the anion can support a diamagnetic ring current and is, therefore, an aromatic 'phenolate'. Quenching of the solution with a neutral buffer or aqueous acetic acid at −78 °C gave a red solution which on immediate examination by n.m.r. spectroscopy showed no signals upfield of TMS.

Methylation occurred on both oxygen and carbon. Treatment of (4) with potassium hydride and 18-crown-6 in DME followed by methyl fluorosulphonate gave the 2-methoxy-annulene (8) (70%) as a yellow oil; the O-methyl structure was established by the n.m.r. signal at δ (CDCl$_3$) −1.51, for the central methyl group, and the absence of any carbonyl i.r. absorption. Treatment of the lithium enolate (6, M = Li) (generated from the sodium enolate and lithium bromide) in tetrahydrofuran with iodomethane at 40 °C gave the C-2a-methyl ketone (9) (59%) as an orange-red oil, ν_{max} 1694 cm^{-1}, δ (CDCl$_3$) 1.18 (2a-Me) and 1.47 (7b-Me), together with the ether (8) (19%).

Reduction of the ketone (4) with di-isobutylaluminium hydride in hexane at 0 °C gave a separable mixture of epimeric alcohols (10). The alcohols are rapidly dehydrated to the unsubstituted [10]annulene (11) [77% overall from (4)] by treatment with toluene-4-sulphonic acid in dichloromethane at room temperature.

We have thus demonstrated keto–enol tautomerism in the tricyclic [10]annulene series, but in common with all other approaches to annulenols,[5–7] we have not isolated the enol form; in attempts to prepare 1,6-methano[10]annulen-2-ol[5] and a bisdidehydro[14]annulenol[7] the enol forms were detected spectroscopically but not isolated. The much greater stability of the ketone (4), which is less planar and hence less strained than the annulenol (3), shows that the aromatic delocalisation energy of the 10π system in (3) is not sufficient to compensate for the greater strain energy in the annulenol.

References

1 M.-C. Lasne, J.-L. Ripoll, and J.-M. Denis, *Tetrahedron Lett.*, 1980, **21**, 463.
2 T. L. Gilchrist, D. Tuddenham, R. McCague, C. J. Moody, and C. W. Rees, *J. Chem. Soc., Chem. Commun.*, 1981, 657.
3 R. McCague, C. J. Moody, and C. W. Rees, *J. Chem. Soc., Chem. Commun.*, 1982, 497.
4 P. Cazeau, F. Moulines, O. Laporte, and F. Duboudin, *J. Organomet. Chem.*, 1980, **201**, C9.
5 E. Vogel, W. Schröck, and W. A. Böll, *Angew. Chem., Int. Edn. Engl.*, 1966, **5**, 732.
6 S. Masamune, D. W. Brooks, K. Morio, and R. L. Sobczak, *J. Am. Chem. Soc.*, 1976, **98**, 8277.
7 Y. Onishi, T. Satake, M. Iyoda, and M. Nakagawa, *Tetrahedron Lett.*, 1979, 3169.