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SYNTHESIS AND PROPERTIES OF 2-HYDROXY-2,4,6-CYCLOOCTA-TRIENONE (1,7-π-HOMOTROPOLONE)

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Homoaromaticity has received considerable attentions as represented by fairly extensive investigations on homotropylium ion 1 and its derivatives.[1-3] Although, in this view, 2,3- and 4,5-σ-homotropones were synthesized, they do not show appreciable homoaromaticity.[4,5] 2,4,6-Cyclooctatrienone 2 has also been concluded not to be homoaromatic from the result of variable-temperature ^{1}H-NMR study.[1,6]

Although being formally a derivative of tropone, tropolone (2-hydroxy-tropone) has peculiar properties because of its highly mobile tautomeric system. There can be three isomeric 2-hydroxycyclooctatrienones as the candidates for π-homotropolones. It is expected that electron-releasing property of an enol and capability of an α-ketol group to form intramolecular hydrogen bond may have favorable influences on the homoconjugation and the molecular geometries of 2-hydroxycyclooctatrienones. We wish here to report the synthesis and noteworthy properties of 2-hydroxy-2,4,6-cyclooctatrienone 5 which we consider to be called 1,7-π-homotropolone, the first compound among the three possible π-homotropolones.

Oxidation of 2,6-cyclooctadienone 3[7] with SeO_2 in refluxing THF (15 hr.) gave 3,7-cyclooctadiene-1,2-dione 4 in 41% yield [yellow prisms, mp. 30-31°C]. Heating to reflux of 4 with NEt_3 (0.1 equiv.) in benzene for 6 hr. caused double bond migration and enolization to afford 2-hydroxy-2,4,6-cyclooctatrienone 5 in 65% yield [pale yellow needles, mp. 40-42°C].

The ^{1}H-NMR spectrum of 5 in CF_3COOH-conc. H_2SO_4 (1:1) shows signals at δ= 0.86(1H, dd, J=10.5, 10.0 Hz), 4.30(1H, dd, 10.0, 7.5), 5.70(1H, dt, 10.5, 7.5), and 7.1-7.9 (4H, m), indicating the formation of 1,2-dihydroxyhomotropylium ion 6. Compound 5 formed an acetate 7 as a pale yellow liquid (Py-Ac_2O, 46%). When treated with NBS (1.0 equiv.) in $CDCl_3$ in a nmr tube at room temperature, 5 easily and cleanly yielded 3-bromo-4,6-cyclooctadien-1,2-dione 8 which shows ^{1}H-NMR siganls at δ 3.32(1H, dd, J=14.4, 6.2 Hz), 3.83(1H, dd, 14.4, 8.0), 5.21 (1H, d, 4.0), and 5.6-6.8 (4H, m). On attempts to isolate (Florisil, SiO_2), however, 8 readily reenolized to afford 2-hydroxy-3-bromo-2,4,6-cyclooctatrienone 9 in 60% yield [pale yellow needles, mp. 84-85°C].

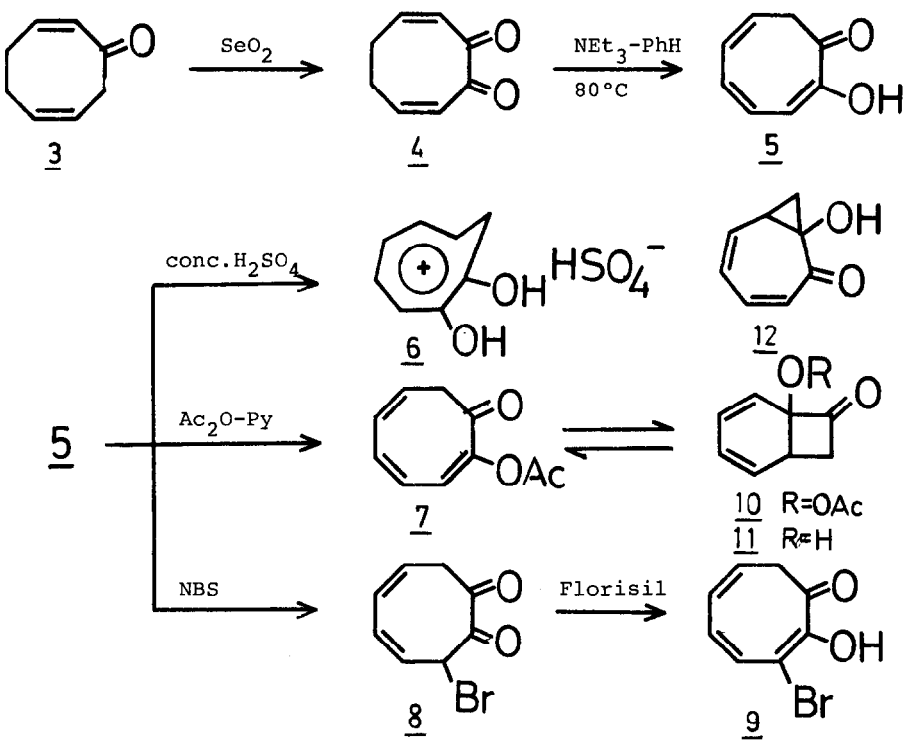


Table I. Spectral Data of 4, 5, 7, 9, and 2

Compd.	IR, ν cm^{-1}	UV, λ nm (log ε)[a]	^{1}H-NMR, δ ppm (multiplicity, J Hz)[b]
4	1688, 1650 1623	238 (3.69), 247sh (3.66) 310 (2.33), 319 (2.28) 390 (1.43)	2.56 (4H, m), 6.01 (2H, d, 13.0) 6.46 (2H, m)
5	3380, 1648 1618, 1555	239 (4.05), 298 (3.78) 341sh (3.42) (0.1N NaOH) 252 (3.86) 329sh (3.59), 361 (3.03)	2.45 (1H, br), 3.45 (1H, br), 5.56 (1H, ddd, 10.0, 8.5, 8.0), 6.3-6.7 (4H, m), 7.17 (1H, br. s, OH)
7	1792(medium) 1768(strong) 1670(strong)	219 (4.03), 236sh (3.92) 286 (3.70), 340 (3.03)	2.08 (0.6H, s), 2.23 (2.4H, s), 3.04 (1.6H, d, 8.5), 3.4-3.7 (ca 0.4H, m), 5.7-6.7 (ca 5H, m)
9	3450, 1648 1612, 1589	253 (4.11), 293 (3.70) 360 (3.68)	3.10 (2H, br), 5.66 (1H, dt, 9.0, 8.5), 6.39 (2H, m), 6.78 (1H, d, 12.0), 7.76 (1H, br. s, OH)
2	1658, 1622 1562	215 (4.17), 237 (3.92) 285 (3.71), 345 (2.97)	2.97 (2H, d), 5.77 (1H, q), 6.1-6.6 (4H, m)[c]

[a] in methanol unless otherwise indicated; [b] in $CDCl_3$ at 100 MHz at normal temperature unless noted; [c] ref. 6

The spectral data of 4, 5, 7, and 9 are summarised in the Table I compared with those of 2,4,6-cyclooctatrienone 2. The carbonyl frequencies of 5 and 9 are ca 10-20 cm^{-1} lower than those of 2 and 7. The UV spectra of 5 and 9 are

appreciably different from that of 2, particularly by showing relatively intense absorption at 341 and 360 nm, respectively. The ^{1}H-NMR spectra of 5 and 9 are especially informative on the interesting property of these compounds; while the methylene protons of 2 and 7 appear as a sharp doublet at normal temperature, those of 5 and 9 do as very broad signals to indicate that ring inversion in these compounds are considerably slow. The chemical shift of H-7 of 5 (δ5.56) is 0.21 ppm higher than that of 2 (δ 5.77), whereas those of other olefin protons are ca 0.2 ppm lower. The IR and NMR data suggest that 7 is at equilibrium with its valence isomer 10 (ca 20%). Similar equilibration (ca 5%) has been observed for 2 itself.[6,8] In contrast to these compounds, for 5, neither the presence of valence isomer 11 nor 2-hydroxy-2,3-π-homotropone 12 (another possible isomer of 5) was indicated spectroscopically.

The variable-temperature ^{1}H-NMR spectra of the methylene protons of 5 are shown in the Figure. The free energies of activation of ring inversion at the coalescence temperature ($\Delta Gc^{\ddagger}$)[9] of 5, 7, and 9 are listed in the Table II compared with those of 1 and 2. It is remarkable that the $\Delta\nu$ of 5 (70 Hz) well below Tc is considerably larger than that of 2 (ca 25 Hz[6]) and $\Delta Gc^{\ddagger}$ of the former (15.7 kcal) is ca 4 kcal larger than the latter (11.3 kcal[6]). The $\Delta\nu$ and $\Delta Gc^{\ddagger}$ of 7 is between 2 and 5, being rather near to 2.

Figure. Variable-Temperature ^{1}H-NMR Spectra of The Methylene Protons of 5

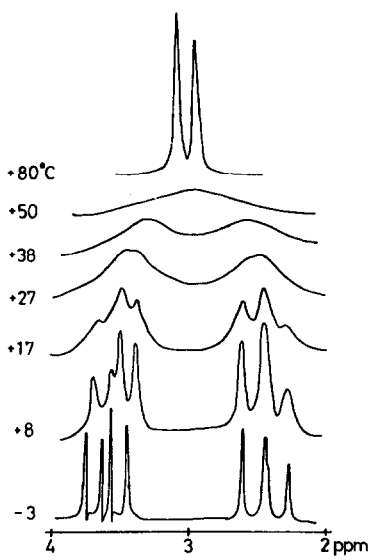


Table II. Activation Parameters for Ring Inversions (60 MHz)

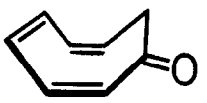
Compd.	Tc, °C	$\Delta\nu$, Hz	$\Delta Gc^{\ddagger}$, kcal/mol
1			22.3[a]
2	-44	25	11.9 (Ea)[b]
			11.3[c]
5	50[d]	70[e]	15.7[f]
7	-21[d]	46[e]	12.3[f]
9	28[d]	53[e]	14.8[f]

[a] ref. 1; [b] ref. 6; [c] calculated from the reported data in ref. 6; [d] the error is estimated to be ±3°C; [e] ±1 Hz [f] ±0.3 kcal.

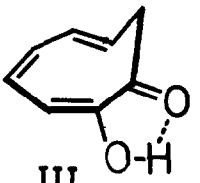
Compound 5 has pKa value of 9.0 (determined by UV method using 10% ethanolic H_3BO_3-KCl-Na_2CO_3 buffer solutions), which is less acidic than tropolone (6.7)[10] but more acidic than 1,2-cyclohexanedione (10.30).[11]

These results suggest that there are considerable differences between 2 and 5 in electron delocalization and molecular geometry. The molecular geometry of homotropylium ion 1 has been believed, though not definitely verified, to be formulated by the Winstein picture (Formula I),[1] whereas that of 2,4,6-cyclooctatrienone 2 has been considered to be a tub form (Formula II).[6] It may be expected from the physical properties that the molecuar geometry of 5 deviates from a typical tub form of cyclooctatetraene towards the Winstein picture of 1, an extreme depiction being the Formula III.

I



II



III

In conclusion, 2-hydroxy-2,4,6-cyclooctatrienones, 5 and 9, seem to have some π interactions, at least more than 2, at C-1 and C-7, and hence may be called 1,7-π-homotropolones.

X-ray crystallographic analyses of 5 and 9 will provide an important insight into the matter, and such attempts are now in progress.

REFERENCES AND NOTES

* To whom all correspondences should be addressed.

1) S. Winstein, Quart. Rev., Chem. Soc., 23, 1411 (1969), and references therein. See also: P. R. Story and B. C. Clark Jr., in "Carbonum Ions", Vol. III; Wiley, New York, N. Y., U. S. A., 1972, p 1007.

2) P. Warner, D. L. Harris, C. H. Brady, and S. Winstein, Tetrahedron Lett., 4013 (1970).

3) (a) R. Huisgen and J. Gasteiger, Tetrahedron Lett., 3661 (1972); (b) J. Gasteiger and R. Huisgen, ibid., 3665 (1972).

4) J. D. Holmes and R. Pettit, J. Amer. Chem. Soc., 85, 2531 (1963).

5) O. L. Chapman and R. A. Fugiel, J. Amer. Chem. Soc., 91, 215 (1969).

6) C. Canter, S. M. Pokras, and J. D. Roberts, J. Amer. Chem. Soc., 88, 4235 (1966).

7) T. S. Cantrell and J. S. Solomon, J. Amer. Chem. Soc., 92, 4656 (1970).

8) A. C. Cope and B. D. Tiffany, J. Amer. Chem. Soc., 73, 4158 (1951).

9) The ΔGc s were calculated from the Tc and Δν using the approximate formula $k=(\Delta\nu^2+6J^2)^{1/2}/\sqrt{2}$ and the Eyring's equation $k=RT/Nh\cdot\exp(-\Delta G^{\ddagger}/RT)$.

10) W. von E. Doering and L. H. Knox, J. Amer. Chem. Soc., 75, 297 (1953).

11) G. Schwarzenbach and H. Suter, Helv. Chim. Acta, 24, 617 (1941).