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SYNTHESIS OF 2-HYDROXY-2,4,7-CYCLOOCTATRIENONE
(5,7-π-HOMOTROPOLONE)

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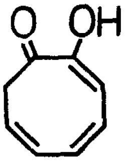
In the preceding paper, we reported the synthesis of 2-hydroxy-2,4,6-cyclooctatrienone 1 which we considered to be called 1,7-π-homotropolone.[1] As to π-homotropolone, there can be two other isomers, i.e. 2-hydroxy-2,4,7-cyclooctatrienone (5,7-π-homotropolone) 2 and 2-hydroxy-2,5,7-cyclooctatrienone (3,5-π-homotropolone) 3. We here describe the synthesis and properties of 2.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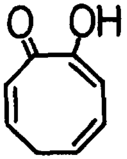
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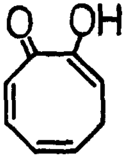
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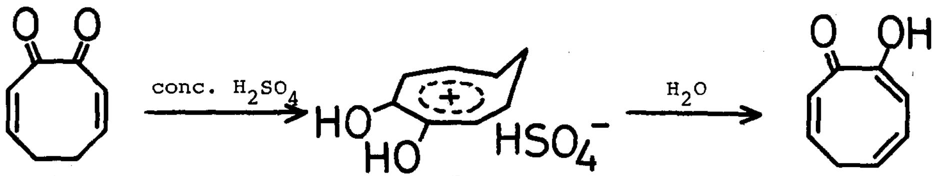
Dissolution of 3,7-cyclooctadiene-1,2-dione 4[1] in concentrated sulfuric acid exhibits ^{1}H-NMR signals at δ 0.63 (1H, dt, J=9.0, 8.5 Hz), 4.34 (1H, dt, 9.0, 8.0), 6.5-7.2 (2H, m), 7.67 (1H, dd, 8.8, 8.5), 7.77 (1H, d, 10.0), and 8.25 (1H, d, 8.8), indicating the formation of 3,4-dihydroxyhomotropylium ion 5. Pouring of the solution into ice-water gave rise to 2 as an almost colorless liquid in 62% yield.

The compound 2 is less stable than 1; on standing at room temperature at neat state, it slowly produced solids which are hardly soluble in organic solvents. Treatment of 2 with triethylamine in refluxing benzene afforded 1 in good yeild. Reaction of 2 with NBS (1.1 equiv.) in chloroform at room temperature afforded 2-hydroxy-3-bromo-2,4,7-cyclooctatrienone 6 (mp. 80.5-81.5°C) and 3,3-dibromo-4,7-cyclooctadiene-1,2-dione 7 (mp. 74.5-75.5°C) in 65% and 23% yield, respectively. The spectral data are summarised below.

2: IR (liquid): ν=3330, 1632, 1600, 1563 cm^{-1}; UV (methanol): λ=238.5 (logε 3.88), 329 nm (3.76); ^{1}H-NMR (CDCl$_3$, 60 MHz, normal temp.): δ=2.57 (2H, very br.), 5.9-6.7 (5H, m), 7.41 (1H, br. s, OH).

6: IR (KBr): ν=3240, 1630, 1600, 1550 cm^{-1}; UV (methanol): λ=222 (3.93), 254 (3.85), 327 nm (3.77); ^{1}H-NMR (CDCl$_3$, 100 MHz, normal temp.): δ=2.70 (2H, very br.), 6.00 (1H, dt, 10.7, 8.3), 6.39 (1H, d, 11.0), 6.56 (1H, d, 10.7) 6.58 (1H, dt, 11.0, 8.0), 8.22 (1H, br. s, OH).

7: IR (KBr): ν 1710, 1642, 1611 cm^{-1}; UV (methanol): λ=223 (sh, 3.86), 324 (2.20) 363 nm (sh, 1.56); ^{1}H-NMR ($CDCl_3$, 100 MHz): δ=3.01 (2H, br. dd, 8.8, 8.3), 5.77 (1H, dt, 10.5, 8.8), 6.13 (1H, dt, 10.8, 1.0), 6.40 (1H, dt, 10.5, 0.5), 7.04 ppm (1H, dt, 10.8, 8.3).



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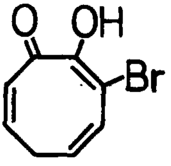

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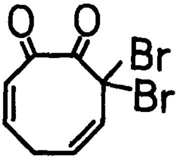

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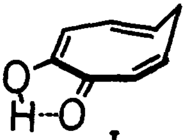

I

It is remarkable that the carbonyl absorptions of 2 and 6 appear at considerably low frequency (1632 and 1630 cm^{-1}, respectively). The ^{1}H-NMR spectra of 2 and 6 indicate that the signals of the methylene protons are almost coalescing at normal NMR temperature. The $\Delta Gc^{\ddagger}$s[2] of ring inversion of both compounds, obtained from the variable-temperature ^{1}H-NMR spectra, are listed in the Table. The values are 1.2-1.6 kcal/mol smaller than that of 1, but ca 3 kcal larger than 2,4,6-cyclooctatrienone 8.[3] The Δνs are also appreciably larger than that of 8, though smaller than 1.

Table. Activation Parameters for Ring Inversions (60 MHz)

Compd.	Tc, °C	Δν, Hz	$\Delta Gc^{\ddagger}$, kcal/mol
1	50	70	15.7[a]
2	15[b]	55[c]	14.1[d]
6	20[b]	37[c]	14.5[d]
8	-44	25	11.9 (Ea)[e] 11.3[f]

[a] ref. 1; [b] the error is estimated to be ±5°C; [c] ±1 Hz; [d] ±0.3 kcal; [e] ref. 3 [f] calculated from the reported data.

In conclusion, 2-hydroxy-2,4,7-cyclooctatrienones, 2 and 6, seem to have some homoconjugation, as 1 does, through the p-orbitals at C-5 and C-7, and hence may be called 5,7-π-homotropolone, an extreme depiction being Formula I.

REFERENCES AND NOTES

1) Y. Kitahara, M. Oda, and S. Miyakoshi, Tetrahedron Letters (preceding paper).
2) The $\Delta Gc^{\ddagger}$s were calculated from the Tc and the Δν using the approximate formula $k=(\Delta\nu^2+6J^2)^{1/2}/\sqrt{2}$ and Eyring's equation $k=RT/Nh\cdot\exp(-\Delta Gc^{\ddagger}/RT)$
3) C. Canter, S. M. Pokras, and J. D. Roberts, J. Amer. Chem. Soc., 88, 4235 (1966).