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[2]PARACYCLO[2](3,7)TROPOLONOPHANE

SYNTHESIS, PHYSICAL PROPERTIES AND CHEMICAL BEHAVIOR

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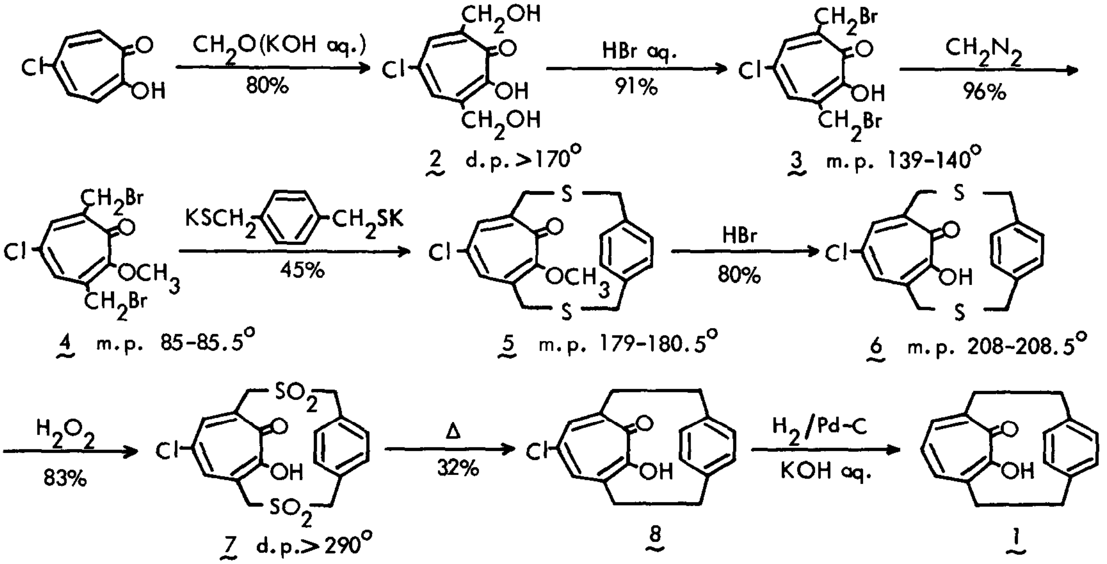
[2.2]Phanes incorporating nonbenzenoid aromatic rings, such as azulene and tropylium ion have recently been synthesized[1] with interest connected to charge-transfer (CT) interaction and amplified strain effect inherent in the molecules. Tropolone is unique in many ways among nonbenzenoid ring systems and property change caused by its incorporation in a phane system is worth an investigation. Noteworthy is the possible existence of deconjugated keto form, as has been observed in a few crowded tropolones[2].

Synthesis Starting from 5-chlorotropolone[3], synthesis was achieved by the reaction sequence shown in Chart. Yield of the reactions and the melting point of the intermediates are also shown[4]. The PMR spectrum of dithia[3.3]tropolonophane 6 exhibits benzene proton signals at 6.83 and 6.98 ppm, disclosing the rigidity of the molecule at room temperature. Although irradiation of 5 and 6, as well as pyrolysis of the sulfone corresponding to 5 failed to induce desulfurization, pyrolysis (480°, 2 Torr. Argon) of 7 afforded chlorotropolone 8, yellow granules, m.p. 192-193°, along with 5-chloro-3,7-dimethyltropolone



2 d.p. >170°

3 m.p. 139-140°

4 m.p. 85-85.5°

5 m.p. 179-180.5°

6 m.p. 208-208.5°

7 d.p. > 290°

8

1

(Y. 5%). On catalytic reduction (Pd-C) in alkaline media, the normal procedure for dehalohydrogenation of halotropolones5), **8** gave mainly over hydrogenation product and, even in the presence of deactivator (quinoline), the yield of **1** was 49%6).

X-ray analysis The crystals of **1** belong to orthorhombic system with four molecules in a unit cell of dimensions a=9.501(2), b=15.586(4), c=8.539(2)Å. The space group is Pmnb. The structure was solved by the direct method using 794 unique reflections collected by CuKα radiation and refined by block-diagonal least squares calculations. The final R value is 5.4%. Since the molecule is situated on the crystallographic mirror plane, one half of the molecule is independent. Bond lengths and angles thus obtained are shown in Fig. 1, together with the corresponding averaged value of tropolone7). Apart from the longer C_1-C_2 bond in **1**, the parameters for these two compounds are in good agreement verifying that **1** has tropolone structure and not the keto form. The major distortion of the molecule is shown in side view (Fig. 2) together with interplanar atomic distances and bending angles of two aromatic rings. Tropolone ring bents much more than benzene. Contrary to tropolone itself, **1** has monomeric structure without intermolecular hydrogen bonding in crystalline state.

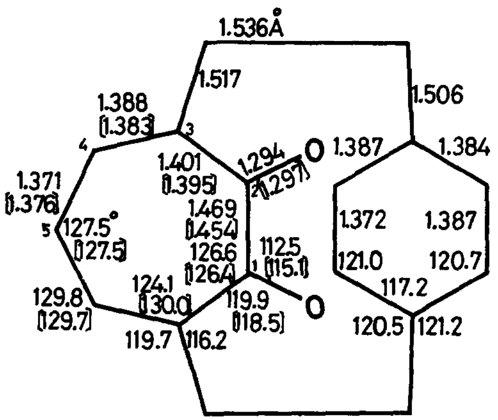


Fig. 1 Bond lengths and angles in **1**
[ ] averaged values for tropolone

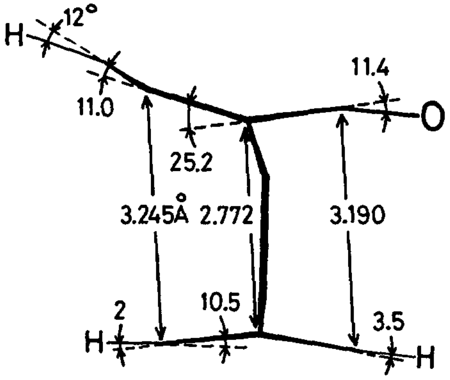


Fig. 2 Side view of the molecule of **1** with the bending angles and interplanar atomic distances

Physical properties **1** is pale yellow plates of m.p. 186.5-188°, and shows $FeCl_3$ color reaction typical of tropolones. Spectroscopic data of **1**, **8** and 3,7-dimethyltropolone **9** listed in Table, especially the presence of OH band in IR and AB_2 pattern in PMR spectra, support the tropolone structure both for **1** and **8**. Electronic spectra of **1** and **8** (Fig. 3a,b) show broadened and red-shifted absorption characteristic for [2.2]phanes compared with **9**8). However, no clear additional band was recognized. In acidic media (Fig. 3c), on the other hand, absorption extends to long wave length as a shoulder compared with **9**. This is probably due to the strong CT interaction similar to the case of [2]paracyclo[2](1,4)tropyliophane1b).

Chemical reactions **8** was converted smoothly with diazomethane to its methylether (m.p. 131.5-132.5°, Y. 95%) which, with methylamine, afforded methylaminotropone derivative (m.p. 198-198.5°(dec.), Y.~100%).

Table Spectral data of 1, 8 and 9

	1	8	9
MS (m/e)	252 (M^+, b.p.)	286, 288 (3: 1, M^+, b.p.)	
IR (ν^{KBr})	3050 (br.), 2920, 2850, 1598, 1537, 1442, 1358, 1045, 737 cm^{-1}	3050 (br.), 2920, 2850, 1598, 1535, 1432, 1360, 739 cm^{-1}	3170, 2910, 1598, 1544, 1477, 1343, 1228, 794 cm^{-1}
ES (λ_{max}^{MeOH} log ε)	228 (4.14), 248 (4.05) 265 (4.03 sh), 364 (3.74) 400 nm (3.14 sh)	228 (4.18), 248 (4.07) 261 (4.07), 370 (3.84) 414 nm (3.22 sh)	244 (4.50), 251 (4.43 sh) 305 (3.65 sh), 320 (3.72) 334 (3.68 sh), 357 (3.71) 369 (3.76), 398 nm (2.85 sh)
NMR (δ_{CDCl_3})	6.84 (2H, $A\underline{B}_2$) 6.49 (1H, $\underline{A}B_2$) 6.70 (2H, m) 6.07 (2H, m) 3.85-2.2 (8H, complex)	6.94 (2H, s) 6.68 (2H, m) 6.22 (2H, m) 3.85-2.25 (8H, complex)	7.36 (2H, $A\underline{B}_2$) 6.86 (1H, $\underline{A}B_2$) 2.46 (6H, s)

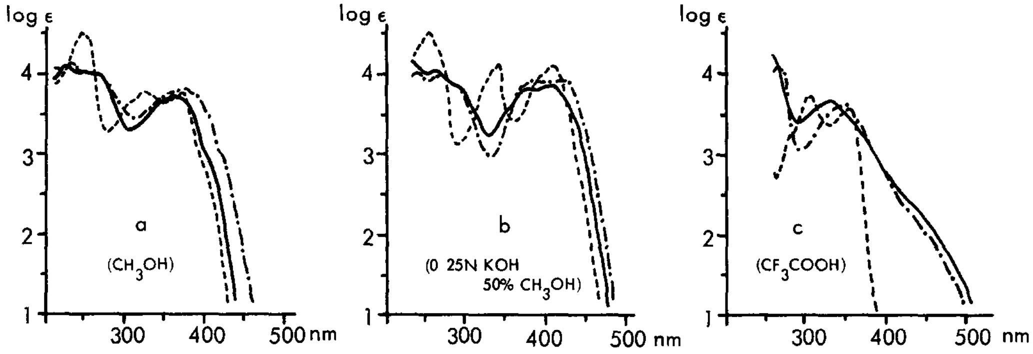
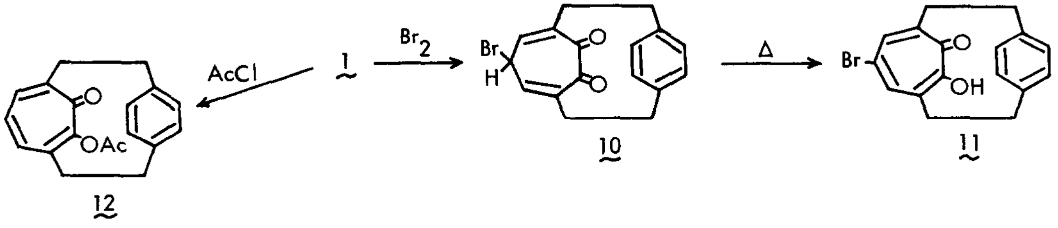
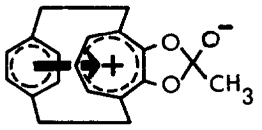


Fig. 3 Electronic spectra of 1 (———), 8 (—·—·-) and 9 (-----)

These are the reactions normal for troponoids[9]. Bromination (1 eq. Br_2) of 1, however, afforded yellow microcrystals 10 in quantitative yield[10]. The keto form in 10 was verified from its spectra: IR spectrum shows a strong band at 1664 cm^{-1} and no band characteristic to tropolones. PMR signals due to seven-membered ring appear at 4.59 (1H, t) and 6.33 ppm (2H, d) which couple each other with J=8.5 Hz. On heating in t-BuOH, 10 was converted to the bromotropolone derivative 11 (m.p. 202-203°, Y. 55%) and 1 (Y. 5%)[9]. 10 is the first keto form with cyclohepta-1,5-dien-3,4-dione structure[2].





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Another reaction studied is acetotropy[11]. Acetate 12, m.p. 156-157°, obtained by the reaction of acetylchloride on 1 (Y. 55%), exhibits in its PMR spectrum at room temperature two-proton signals due to the benzene ring at δ: 6.84 and 6.28 ppm as narrow multiplets, showing rapid acetotropy. The process is frozen at -120°, changing the former signal to the AB type ($\Delta\nu$= 15.3 Hz, J=7.5 Hz). From coalescence temperature (-100°), $\Delta G^{\ddagger}$ was calculated to be ca. 8.7 kcal/mol at -100°, which is considerably lower than that of tropolone acetate ($\Delta G^{\ddagger} \approx 10.8$ kcal/mol)[11]. This is probably the reflection of the CT interaction stabilizing the transition state 13.

Thus, tropolone system in 1 and 8 shows somewhat modified behavior from tropolones in general. Such unusual reactions as ease of hydrogenation and the formation of 10 appears to be associated with the strain in tropolone moiety incorporated in a phane system. Strong CT interaction occurs when the seven-membered ring is positively charged, as shown in acidic electronic spectrum and in acetotropy.

References and Notes

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2) Cyclohepta-1,3-diene-4,5-dione system. See M. Yasunami, K. Takase and T. Nozoe, Tetrahedron Letters, 4327 (1970).

3) T. Nozoe, S. Seto, S. Ebine and S. Itô, J. Amer. Chem. Soc., 73, 1895 (1951).

4) All the compounds described in this paper gave correct elemental analyses and properly characterized by ES, IR, PMR and mass spectra.

5) T. Nozoe, T. Mukai, M. Kunori, T. Muroi and K. Matsui, Sci. Repts. Tohoku Univ., Ser. I, 35, 242 (1952).

6) Even in this case, dihydro (colorless scales; m.p. 187-189.5°, Y. 4%) and tetrahydro (colorless granules; m.p. 177-178°, Y. 10%) compounds of 1 were obtained.

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10) 10 changes its crystalline form at 100-110° and then melts at 198-200°. Since the melting point corresponds to that of 11, the enolization (1,5-hydrogen shift) may have taken place at ~100°.

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