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SYNTHESIS AND PROPERTIES OF 8H-CYCLOHEPTA[d]TROPOLONE

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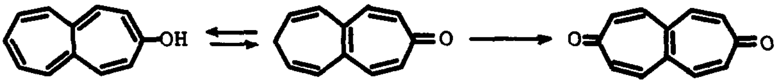
Cycloheptatropone (A) is of interest because it is an isomer of hydroxyheptalene (B) and promising precursor for heptalenedione (C) which can be expected as stable non-benzenoid aromatic compounds by a contribution of dipolar 10π heptalenium dication.



(B) (A) (C)

In the present paper, the synthesis of 8H-cyclohepta[d]tropolone has been accomplished and its several properties have been studied.

Cycloaddition of 1,6-dihydroazulene[1] (1) with chloroketene and dichloroketene in n-hexane at room temperature afforded (2 + 2) cycloadducts (2) and (3) in 22% and 84% yields, respectively; (2) $\nu_{C=O}$ 1790 cm^{-1}, (3) $\nu_{C=O}$ 1809 cm^{-1}. Hydrolysis[2] of the adduct (2) with triethylammonium acetate did not give any clear products, however, treatment of the adduct (3) with the same reagent in acetone-water resulted in the formation of 8H-cyclohepta[d]tropolone (4) in 90% yield; 4, yellow prisms, mp 140~141°C; ir (KBr) 3230, 1603, 1550 and 760 cm^{-1}; uv λ_{max}^{MeOH} nm (log ε) 245^{sh}(4.30), 250 (4.35), 289 (4.43), 348 (3.96), 392^{sh}(3.68); nmr ($CDCl_3$) δ 8.1 ppm (br s, OH), 7.52 (d, J=12 Hz, H-5), 7.34 (s, H-1), 7.20 (d, J=12 Hz, H-4), 6.55 (d, J=10 Hz, H-6 and H-10), 6.06 (d,t, J=10 and 7Hz, H-7 or H-9), 5.95 (d,t, J=10 and 7 Hz, H-9 or H-7), 2.37 (t, J= 7 Hz, H-8,8); MS M^+ m/e 186. The contribution of isomeric dihydroxyheptalene (4a) was completely eliminated from the above data.

The reaction of the adduct (3) with triphenylmethyl tetrafluoroborate afforded an oily tropylium tetrafluoroborate (5), however, the treatment of the cation with aqueous solution of sodium hydrogen carbonate did not give an expected tropone (6),3) and any clear products could not be obtained.

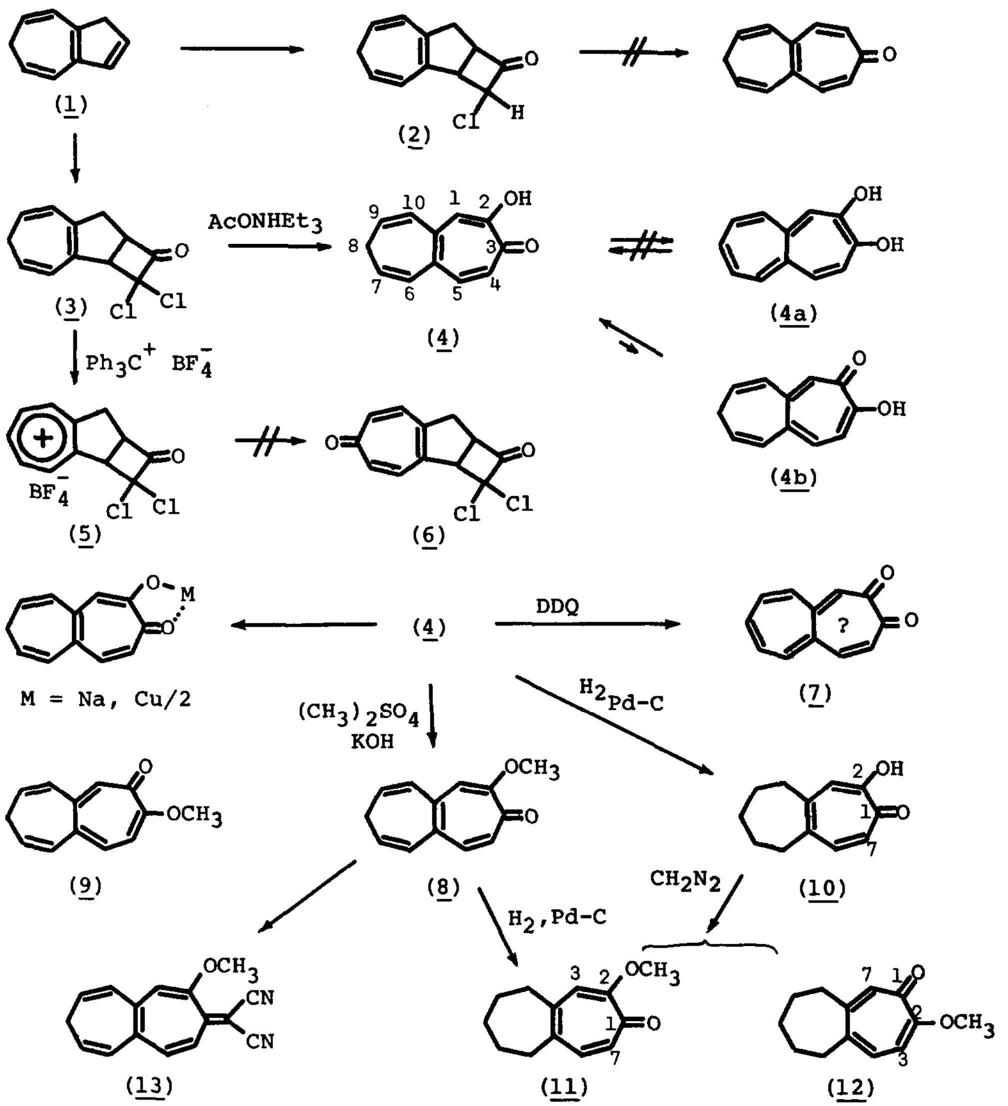
The pKa value of the tropolone (4) was determined as 7.0 by spectroscopic method, and 4 gave a sodium salt and a copper chelate complex similar to tropolone itself.

When the tropolone (4) was treated with DDQ in methylene chloride, color of the solution changed to bright red (new maxima at 436 and 500 nm appeared) which could be arised by the formation of heptalene-2,3-dione (7), however, the color changed to brown in short time and no clear products could be obtained.

The tropolone (4) did not react with diazomethane in ether even in the presence of BF$_3$, however, 4 reacted with dimethyl sulfate in potassium hydroxide solution to give a methyl ether (8) in 49% yield, which could not be hydrolyzed with dilute acid differ from tropolone methyl ether. In the reaction, an isomeric ether (9) could not be obtained. (8); Yellow needles, mp 103~104°C; ir (KBr) 3030, 1633, 1610, 1592, 1570 and 698 cm^{-1}; uv λ_{max}^{MeOH} nm (log ε) 233^{sh}(4.12), 250 (4.39), 290 (4.41), 348 (4.01), 382^{sh}(3.78); nmr (CDCl$_3$) δ 7.29 ppm (d, J=13 Hz, H-5), 7,01 (d, J=13 Hz, H-4), 6.77 (s, H-1), 6.53 (d, J=10 Hz, H-6 or H-10), 6.48 (d, J=10 Hz, H-10 or H-6), 5.98 (d,t, J= 10 and 7 Hz, H-7 or H-9), 5.90 (d,t, J=10 and 7 Hz, H-9 or H-7), 3.99 (s, OCH$_3$), 2.36 (t, J=7 Hz, H-8,8); MS, M$^+$ m/e 200.

The reactivity of 4 to methylation reactions is very similar to that of 4,5-benzotropolone.4) From the methylation experiments, it is assumed that the tautomerism between 4 and 4b must lies so far to 4, and this must be attributed to the difference of the stabitities of the two tautomeric forms; 4 which has normally conjugated cycloheptatriene moiety may be more stable than 4b which has a cross conjugated system.

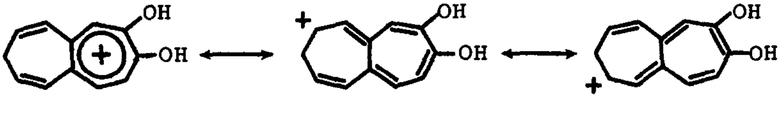
Catalytic hydrogenation of 4 in the presence of Pd-C afforded 4,5-pentamethylenetropolone (10) in 73% yield, which was easily methylated with diazomethane to give two kinds of ethers, 2-methoxy-4,5-pentamethylenetropone (11) and 2-methoxy-5,6-pentamethylenetropone (12) in 43% yield in the ratio of



6 : 5. On the other hand, catalytic hydrogenation of methyl ether (8) gave tetrahydro ether (11). (10); Pale yellow crystals, mp 145~146°C; nmr ($CDCl_3$) δ 7.37 (s, H-3), 7.23 (d, J=11.2 Hz, H-6), 7.06 (d, J=11.2 Hz, H-7), 2.85 (m, 4H), 1.75 (m, 6H). (11); Colorless micro needles, mp 89~90°C; nmr ($CDCl_3$) δ 7.16 (d, J=12 Hz, H-6), 6.98 (d, J=12 Hz, H-7), 6.68 (s, H-3), 3.93 (s, OCH_3), 2.8 (m, 4H), 1.75 (m, 6H). (12); Colorless micro needles, mp 92~94°C; nmr ($CDCl_3$) δ 7.18 (s, H-7), 6.87 (d, J=11 Hz, H-4), 6.50 (d, J=11 Hz, H-3), 3.89 (s, OCH_3), 2.75 (m, 4H), 1.7 (m, 6H).

Reaction of 8 with malononitrile in acetic anhydride afforded dicyanoheptafulvene derivative (13) as reddish needles in 73% yield, mp 221~222°C.

All signals in nmr spectrum of 4 in CF_3COOH shifted to lower field than those in $CDCl_3$ by the formation of tropylium ion (14), the differences in the chemical shifts are 0.9~1.1 ppm for the tropolone ring protons and 0.26~0.55 ppm for the protons of tropilidene moiety. It is observed that the shifts of H-7 and H-9 (0.55) are larger than those of H-6 and H-10 (0.41) and that the shifts of H-8 is also large (0.26) even the protons are far from the tropolone ring.[5] These facts may be explained by the contribution of cations (14b,c).



(14a) (14b) (14c)

Uv spectra of 4 and 10 in alkaline medium shifted to longer wave length than the corresponding spectra in hexane or MeOH by the formation of tropolonate anions. Uv spectra of 4 and 8 in various solvents (MeOH, hexane and conc. H_2SO_4) show three main maxima at around 250, 290 and 350 nm with a shoulder at around 370 nm, whereas the spectra of tetrahydro derivatives (10, 11 and 12) show two maxima at around 250 and 350 nm with a shoulder at around 360 nm.

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5) It is observed that the differences of chemical shifts of 4,5-benzotropone in $CDCl_3$ and CF_3COOH are 0.7 ppm for tropone ring and 0.4 for benzene ring.