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SYNTHESIS OF 2,4-DIMETHYLHEPTALENE-3,8-DIONE

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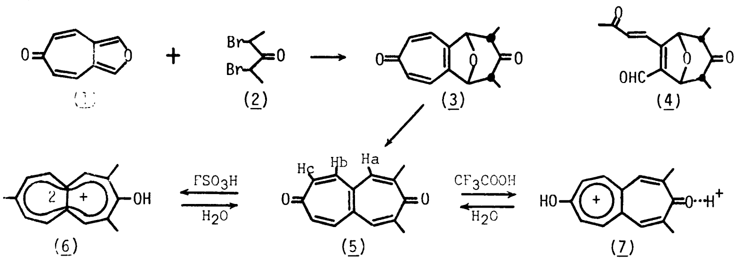
Title compound (5) has been synthesized starting from [4,5-c]furotropone, and its physical properties were discussed in connection with heptalenium cations.

Recently, we have reported the synthesis of methoxy derivatives of heptalene-3,6- and -3,8-diones, and the formation of dihydroxyheptalenium dications in a strong acidic medium.[1] However, their ^{1}H-NMR spectra in $CDCl_3$ or in FSO_3H showed complex patterns and we could not assign all signals.

In this paper, 2,4-dimethylheptalene-3,8-dione having a symmetrical plane was synthesized and its spectroscopic data were discussed in connection with heptalenium cations.

Reaction of [4,5-c]furotropone (1)[2] with 2,4-dibromo-3-pentanone (2) in the presence of copper and KI[3] in anhydrous CH_3CN at 60°C afforded an adduct (3) in 30% yield, pale yellow sticks, mp 153~155°C.[4] When the reaction was carried out in hydrous CH_3CN, an adduct (4) formally formed by hydrolysis of (3) was isolated in 8% yield, pale yellow sticks, mp 151~153°C.[4]

The reaction of (1) and 1,3-dibromo-2-propanone or 1,1,3,3-tetrabromo-2-propanone in the presence of Cu-KI or $Fe_2(CO)_9$[5] gave neither cycloheptatropone skeleton nor any other clear products.



The treatment of (3) with FSO_3H at room temperature followed with $NaHCO_3$ afforded 2,4-dimethylheptalene-3,8-dione (5) in 90% yield, pale yellow microneedles, mp 230~231°C, M^+ 212, IR (KBr) 1642, 1600 cm^{-1}. The compound (5) was also obtained by the treatment of (3) with BBr_3 at -50°C in 17% yield. Electronic and ^{1}H-NMR spectra of (5) in neutral and acidic media are shown in Table 1.
The electronic spectrum of (5) in conc H_2SO_4 (or in FSO_3H) shows a fine structure and slight batho-

Table 1. Electronic and NMR Spectra of (5)

Electronic Spectra; nm (log ε)			^{1}H-NMR Spectra; ppm, J in Hz		
in MeOH*	in conc H_2SO_4	in CF_3COOH	in DMSO-d_6	in FSO_3H**	in CF_3COOD
267 (4.74) 276 (4.89) 295 (4.14) 350 (3.93)sh 368 (4.01) 385 (3.94)sh 407 (3.51)sh	282 (4.66) 296 (4.89) 310 (4.44) 333 (3.65) 351 (3.87) 360 (3.78) 380 (3.98) 402 (4.02)	272 (4.82) 306 (4.54) 376 (4.13) 395 (4.10)sh	2.27 (s, CH_3) 6.78 (d, J=12, Hc) 7.49 (d, J=12, Hb) 7.73 (s, Ha)	3.18 (s, CH_3) 8.35 (d, J=12, Hc) 9.30 (d, J=12, Hb) 9.49 (s, Ha)	2.69 (s, CH_3) 7.93 (d, J=12, Hc) 8.17 (s, Ha) 8.55 (d, J=12, Hb)

* The same spectrum was obtained in CH_2Cl_2. ** The same spectrum was obtained in conc D_2SO_4.

chromic shifts compared with that in MeOH. The ^{1}H-NMR signals of (5) in FSO_3H (or in D_2SO_4) largely shift to downfield compared with those in DMSO-d_6. If the downfield shifts are due to two extra positive charges introduced by protonations, these shifts may be proportional to the change of the mean π-charge density per carbon atom and are evaluated as $\Delta\delta$ = 1.77 ppm for ring protons.[1,6] The mean value of the differences between the chemical shifts of ring protons in DMSO-d_6 and in FSO_3H is 1.75 ppm. Therefore, the dione (5) must exist as the corresponding dihydroxyheptalenium dication (6) in FSO_3H or in conc H_2SO_4.

The electronic spectrum in CF_3COOH is similar to that in MeOH, although slight bathochromic shifts and increase extinction coefficients of the maxima at around 300 and 370 nm are observed. The NMR in CF_3COOD shows that Hb and Hc signals shift to downfield in the value of 1.06 and 1.15 ppm, respectively, compared with those in DMSO-d_6, however, Ha and methyl signals shift only 0.44 and 0.42 ppm, respectively. It is assumed that these data indicate the dione (5) exists as a monocation such as (7) in CF_3COOH.

References and Notes

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4) Only one stereoisomer was isolated, and the stereochemistry was assigned from the couplig constants of the NMR. (3); M^+ 230, IR (KBr) 1704, 1623, 1565 cm^{-1}, λ max (MeOH) 233 nm (log ε 4.30), 314 (3.98)sh, 373 (4.00), NMR ($CDCl_3$) δ 1.05 ppm (d, J=7, $2CH_3$), 3.07 (d,q, J=5, 7, 2H), 5.06 (d, J=5, 2H), 6.92 (s, 4H). (4); M^+ 248, IR (KBr) 2880, 1710, 1694, 1661 cm^{-1}, λ max (MeOH) 217 (3.82), 292 (4.32), NMR ($CDCl_3$) δ 0.96 (d, J=6, CH_3), 1.03 (d, J=6, CH_3), 2.37 (s, CH_3), 3.08 (d,t, J=5, 6, 2H), 5.22 (d, J=5, 1H), 5.27 (d, J=5, 1H), 6.31 (d, J=16, 1H), 7.75 (d, J=16, 1H), 10.16 (s, CHO).

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