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HEPTALENE-1,8-DIONE AND HEPTALENE-3,8-DIONE DERIVATIVES

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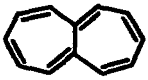
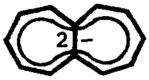
Heptalene (A) is a typical non-aromatic cyclic unsaturated compound having 12π electrons and was synthesized as extremely unstable compound,[1,2] and its fine structure was also studied by nmr spectroscopy.[2] Furthermore, dianion of heptalene (B) having 14π electrons was also synthesized by reduction of heptalene with lithium, and the compound was found to be aromatic with π-bond delocalized planar geometry.[3] However, the chemistry of heptalenium dication (C) having 10π electrons which may be aromatic was not studied yet.


(A)



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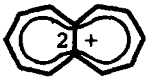
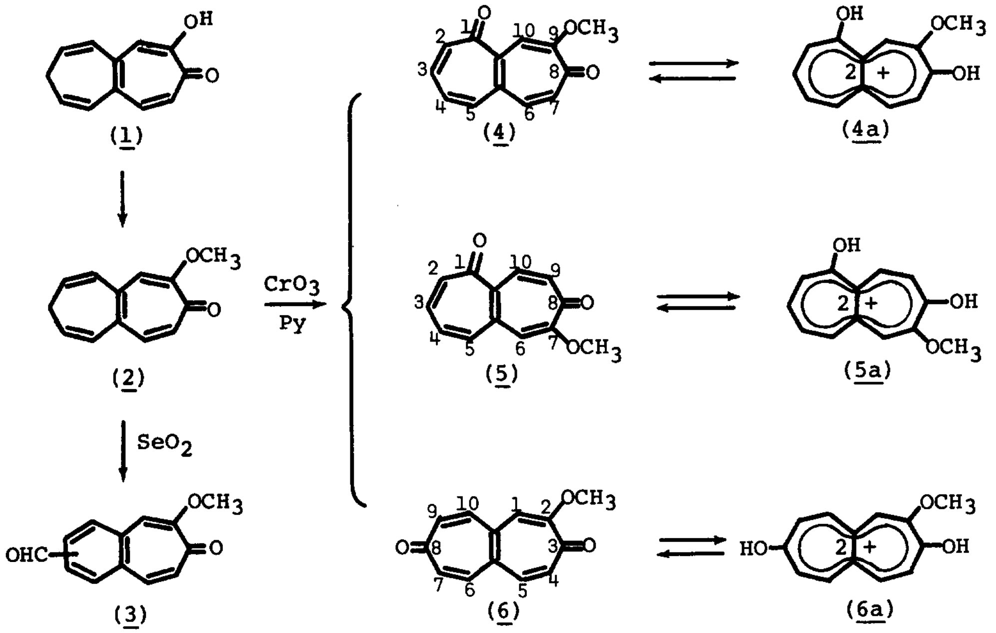


(C)

In the present paper, methoxy derivatives of heptalene-1,8-dione and heptalene-3,8-dione were synthesized and their properties were studied in connection with heptalenium dications.

We have reported in the preceding paper that we have obtained 8H-cyclohepta[d]tropolone (1) and its methyl ether (2) and that an attempted oxidation of 1 to heptalene-2,3-dione was unsuccessful.[4]

Although the oxidation of 2 with SeO$_2$ afforded a mixture of formylbenzotropones (3) in poor yield,[5] the oxidation of 2 with CrO$_3$-pyridine complex in pyridine yielded three products, (4), (5) and (6) in the yields of 49.5, 27 and 11%, respectively. These compounds show the same molecular ion peaks in their mass spectra at m/e 214 (base peak; m/e 115) which correspond to desired diones, and the structures of these products were determined to be 9-methoxy-



heptalene-1,8-dione, 7-methoxyheptalene-1,8-dione and 2-methoxyheptalene-3,8-dione, respectively, mainly by their nmr spectra.

Physical properties of these compounds were shown in Table 1.

IR spectra of 4 and 5 show the complicated absorption bands between 1550~1640 cm^{-1}, however, the spectrum of 6 shows simple two bands and its simplicity may due to the symmetrical structure of 6.

The solutions of these compounds in strong acids such as conc. H_2SO_4 or FSO_3H are reddish and the UV spectra revealed considerable bathochromic shifts (30~50 nm) compared to those in MeOH. NMR signals of these compounds in the acidic solution shifted to downfield as shown in Table 1.

Both the ring protons and methoxy protons of 2-methoxytropone in FSO_3H resonate 0.5 ppm downfield than those in $CDCl_3$.

If the downfield shifts of the compounds (4, 5 and 6) are due to the two extra positive charges introduced, these shifts may proportional to the change of the mean π-charge density per carbon atom and are evaluated as

$$\Delta\delta = 10.6 \times \frac{2}{12} = 1.77 \text{ ppm} \quad ^{6)}$$

Table 1. Physical properties of compounds (4), (5) and (6).

	4	5	6
mp (°C)	171~172	147~148	202~203
Color	yellow needles	yellow needles	yellow cryst.
IR (KBr) cm^{-1}	1618, 1595 1583, 1550	1625, 1580 1550	1615, 1596
λ_{max}^{MeOH} nm (log ε)	258 (4.39) 283 (4.10) 315^{sh} (3.85) 375 (4.03) 412^{sh} (3.73)	251 (4.14) 258^{sh} (4.08) 300 (4.21) 350^{sh} (3.66)	273 (4.31) 366^{sh} (3.63) 375 (3.64) 395^{sh} (3.50) 420^{sh} (3.19)
$\lambda_{max}^{conc.\ H_2SO_4}$ nm (log ε)	247 (4.35) 296 (4.23) 324 (4.40) 358 (3.67) 400 (4.39) 430^{sh} (3.63) 456 (3.72)	255 (4.27) 283 (4.31) 333 (4.62) 402 (3.72) 422^{sh} (3.58)	292 (4.61) 300 (4.61) 318 (4.52) 384 (3.94) 435 (3.93)
H-nmr δ ppm in $CDCl_3$	4.07 (s, OCH_3) 6.7~7.3 (m, 6H) 7.48 (d, J=13 Hz, H-6) 7.82 (s, H-10)	4.01 (s, OCH_3) 6.85 (s, H-6) 6.9~7.1 (m, 4H) 7.16 (d, J=13 Hz, H-7) 7.98 (d, J=13 Hz, H-6)	4.00 (s, OCH_3) 6.7~7.1 (m, 4H) 7.1~7.5 (m, 3H)
H-nmr δ ppm in FSO_3H	4.65 (s, OCH_3) 8.4~8.9 (m, 3H) 8.9~9.3 (m, 2H) 9.4~9.7 (2H)	4.67 (s, OCH_3) 8.2~8.7 (m, 3H) 8.7~9.2 (m, 4H)	4.67 (s, OCH_3) 8.0~8.5 (m, 3H) 8.5~8.9 (m, 2H) 9.0~9.5 (m, 2H)
Δδ ppm*	1.80	1.76	1.60

* The differences in chemical shifts of the center of gravity of the ring protons between observed values in $CDCl_3$ and in FSO_3H.

The observed Δδ values are in accord with the evaluated value.

These observations suggest that the compounds must exist as the corresponding dihydroxyheptalenium dications (4a, 5a and 6a) in the strong acidic media.

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