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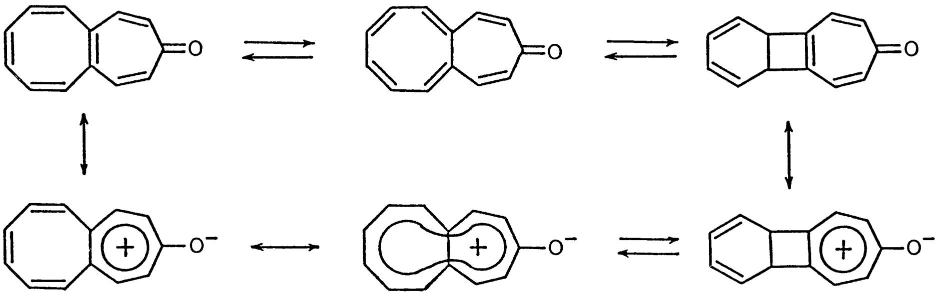
SYNTHESIS AND VALENCE BOND ISOMERIZATION OF CYCLOOCTA[d]TROPOLONE

Mitsunori ODA, Noboru MORITA, and Toyonobu ASAO*
Department of Chemistry, College of General Education,
Tohoku University, Kawauchi, Sendai 980

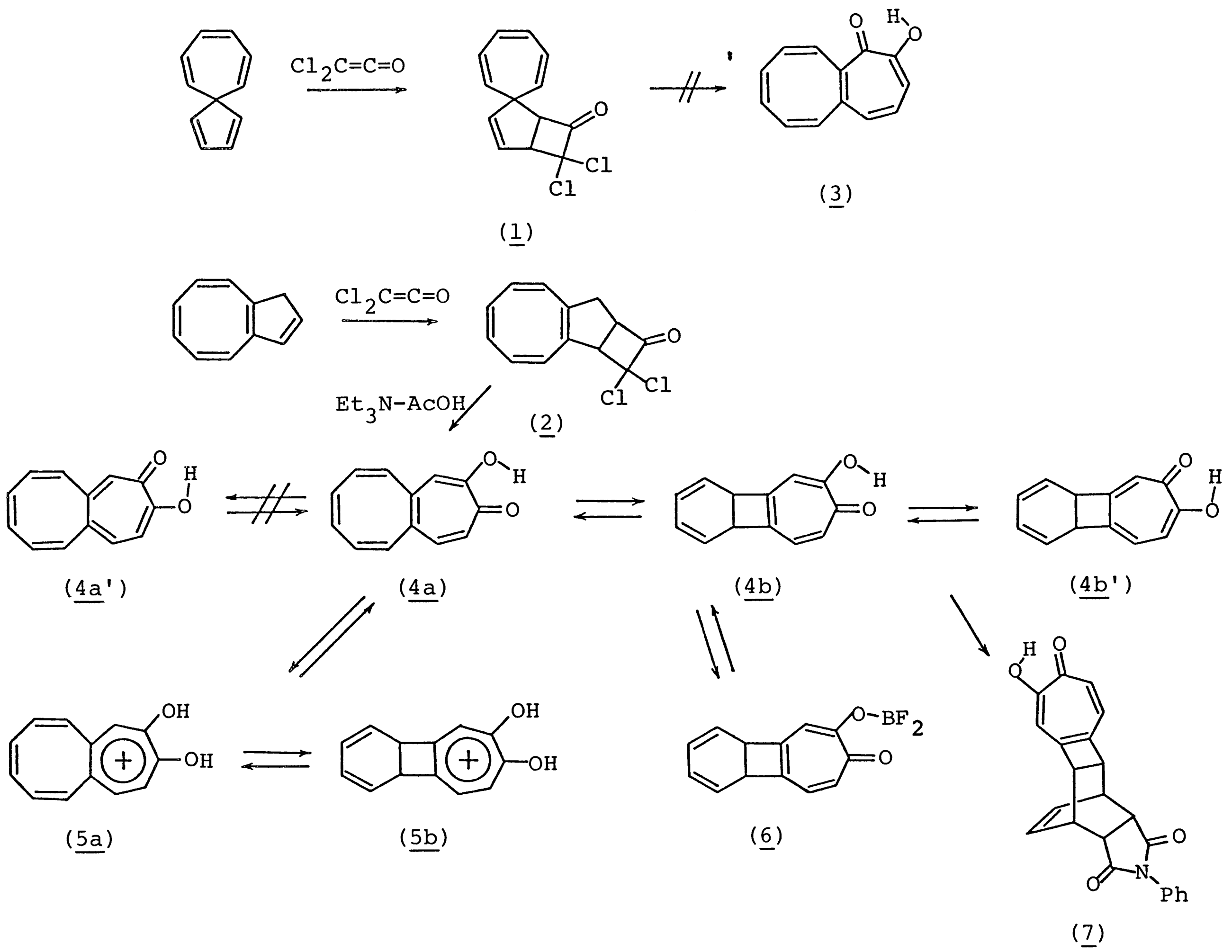
Cycloocta[d]tropolone (4) was synthesized by hydrolysis of an adduct of 1*H*-cyclopentacyclooctene and dichloroketene. The tropolone was found to exist as a mixture of valence bond isomers (4a) and (4b).

Cyclooctatropones are of interest because they can exist in several isomeric and dipolar structures as shown below though it has been reported that a cation of cyclooctatropylium ion exists only in the seven-membered ring.1)



In the present paper, we wish to describe a synthesis and valence bond isomerization of cycloocta[d]tropolone.

Cycloaddition of spiro[4.6]undeca-1,3,6,8,10-pentaene2) and 1*H*-cyclopentacyclooctene 2,3) with dichloroketene formed *in situ* from dichloroacetyl chloride and triethylamine in hexane afforded the corresponding adducts (1) and (2) in 46% and 89% yields, respectively.4) Hydrolysis5) of the adduct (1) with triethylammonium acetate in boiling aqueous acetone in an expectation of a formation of cycloocta[b]tropolone (3) did not give any clear products. However, hydrolysis of the adduct (2) by the similar condition yielded cycloocta[d]tropolone (4) as yellow leaflets in 78% yield, mp 150~152 °C, which indicated characteristic reddish colorlation in the chloroform layer with aqueous iron(III) chloride; ir (KBr), 3200, 1602, 1550, 1460 cm^{-1}; λ_{max}^{EtOH} nm (log ε), 240 (4.43), 325 (3.82), 355 (3.83), 375^{sh}(3.76), $\lambda_{max}^{0.1N\ NaOH}$ 250 (4.33), 352 (4.06), 410 (3.98).



The analysis[4)] of ^{1}H-nmr (300 MHz) of the tropolone (4) in $CDCl_3$ shown in Fig. 1 indicates that the compound exists as a mixture of cycloocta[d]tropolone (4a) and its valence bond isomer (4b) in a ratio of 1 : 1.25 at 35 °C. The ratio did not essentially change in acetone-d_6 or in methanol-d_4. However, it slightly changed to a direction of incresing of 4a by rising temperature; the ratio was almost 1 : 1 at 120 °C. ^{13}C-Nmr also supports the isomeric mixture of 4a and 4b; ^{13}C-nmr of the tropolone in $CDCl_3$ shows 25 peaks including two peaks at 39.6 and 40.6 ppm due to two sp^3 carbons of four-membered ring of 4b, and two peaks at 175.6 and 176.3 ppm due to two carbonyl carbons.

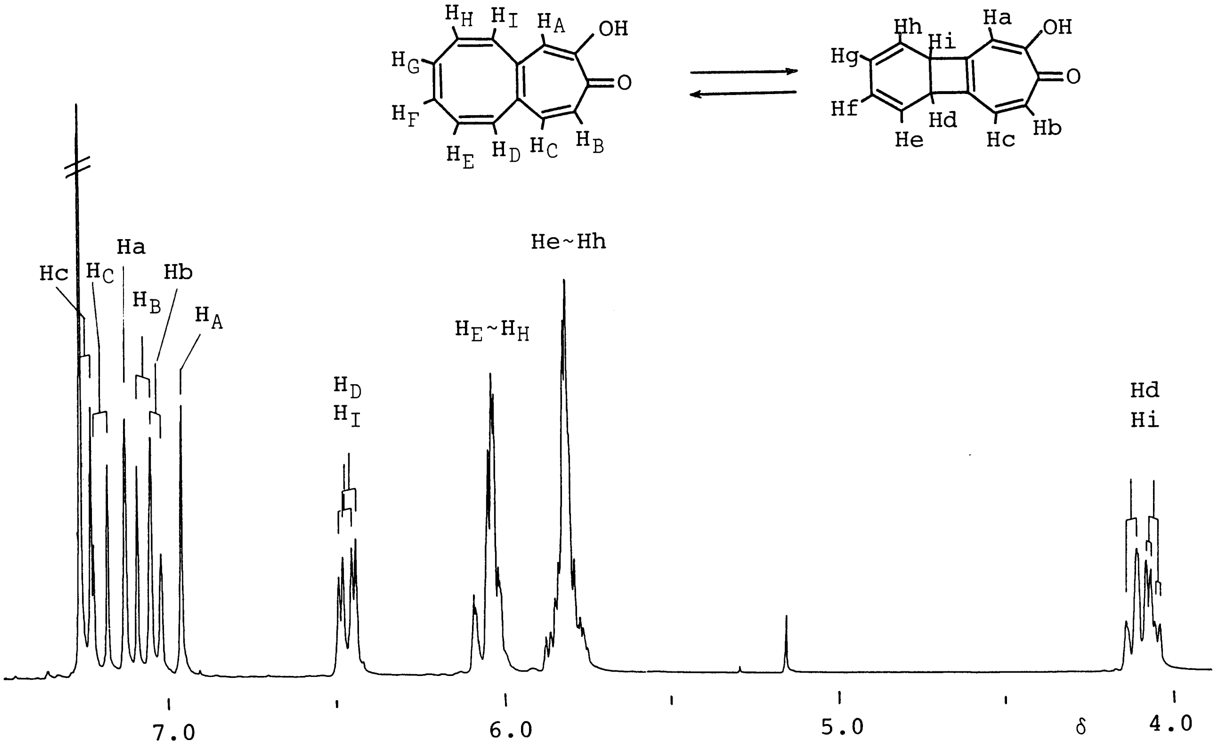


Fig. 1. ^{1}H-Nmr (300 MHz) spectrum of 4 in $CDCl_3$ at 25 °C.

The coupling constants, J_{BC} = 11.7 Hz and Jbc = 9.0 Hz, show similar value to those of tropone and tropolone, respectively, which indicate that a tautomeric form of 4a' can not be considered for 4a but a tautomeric form of 4b' can exist for 4b. The similar phenomenon was observed between cyclohepta[d]tropolone and its reduction product, 4,5-pentamethylenetropolone.[6)]

^{1}H-Nmr of 4 in CF_3COOD shows a similar pattern to that in $CDCl_3$ though tropolone ring signals shifted to downfield by 1~1.2 ppm and other signals shifted to downfield by 0.2 ppm compared to those in $CDCl_3$, which indicates the compound (4) in CF_3COOD exist as a isomeric mixture of dihydroxytropylium ions (5a) and (5b) in a ratio of ca. 1 : 1.5.

The reaction of 4 with BF_3 afforded a chelate complex (6),[4)] which has exclusively tricyclic structure as shown in scheme, but the compound easily reversed to the isomeric mixture of tropolone (4) by treatment with acid. Tropolone (4) reacted with N-phenylmaleinimide to give a Diels-Alder adduct (7) derived from 4b in quantitative yield.[4)]

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References

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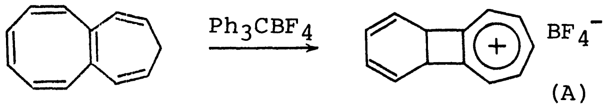

(A)

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4) Compound (1); Colorless prisms, mp 30~32 °C, ir (neat) 1800 cm^{-1}; λ_{max}^{EtOH} 261 nm (log ε 3.52); nmr ($CDCl_3$) δ 3.76 (d, J=6.5 Hz, H-12), 3.98 (d,d,d, J=6.5, 2.0, 2.0, H-9), 5.05 (d, J=9.0, H-1), 5.37 (d, J=9.0, H-6), 5.75 (d,d, J=5.4, 2.0, H-8), 6.01 (d,d, J=5.4, 2.0, H-7), 6.1~6.5 (m, H-2,5), 6.6 (m, H-3,4).
Compound (2); Colorless oil, ir (neat) 1800 cm^{-1}; λ_{max}^{EtOH} 252 (3.35), 278^{sh}(3.25); nmr ($CDCl_3$) 2.5~2.8 (m, 2H, H-3), 3.87 (d,m, J=7.6, H-1), 4.27 (d,d,d, J=7.6, 7.6, 3.5, H-2), 5.5~6.0 (m, 6H).
Compound (4); nmr ($CDCl_3$) 4.07 (d,d, J=8.0, 4.6, Hd or Hi), 4.13 (d, J=8.8, Hi or Hd), 5.75~5.9 (m, He~Hh), 6.0~6.1 (m, H_E~H_H), 6.46 (d, J=11.7, H_D or H_I), 6.47 (d, J=11.2, H_I or H_D), 6.96 (s, H_A), 7.03 (d, J=9.0, Hb), 7.07 (d, J=11.7, H_B), 7.13 (s, Ha), 7.20 (d, J=11.7, H_C), 7.25 (d, J=9.0, Hc).
Compound (6); Colorless needles, mp ca. 155 °C, nmr ($CDCl_3$) 4.3 (m, 2H), 5.87 (bs, 4H), 7.5~7.8 (m, 3H).
Compound (7); Pale yellow cryst. mp > 250 °C (d), nmr ($CDCl_3$) 3.1 (m, 2H), 3.45 (m, 2H), 3.64 (m, 2H), 5.9 (m, 2H), 6.8~7.4 (m, 8H).

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