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THE STRUCTURES, STEREOCHEMISTRIES, AND CONFORMATIONS OF TWO ISOMERIC TETRABROMO-2,3-BENZOCYCLOHEPTENONES [+]

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Bromination of 2,3-benzocycloheptenone, (I), has been shown1) to afford two isomeric $C_{11}H_8OBr_4$ tetrabromo derivatives, isomer A (IIa; m. 141.5-142°) and isomer B (IIb; m. 145.5-146.5). The structures of these isomers (IIa and IIb) and their products of dehydrobromination (IIIa and IIIb)1) are discussed in this report.

The 100 Mc n.m.r. spectra (see Table 1; IIa and IIb)*1) of the two isomers A and B are very similar. Both are characterized by a strongly coupled ABCD system (aromatic hydrogens) and an ABMX system ($-C_{(6)}H_2-C_{(5)}HBr-C_{(4)}HBr-$ sequence) which, in conjunction with the Overhauser experiments recorded in Table 1 (c), suggests that both compounds have the same planar structure II. The reactions discussed in the following fully confirm this proposal.

TABLE 1

(a) Chemical Shifts (δ ppm)*1

	IIa	IIb
$H_{4\beta}$	5.38	5.47
H_5	4.69	5.04
$H_{6\alpha}$	3.84	3.57
$H_{6\beta}$	3.56	3.22
H_8	ca 7.53	ca 7.60
H_9, H_{10}	ca 7.45	ca 7.5
H_{11}	ca 7.27	ca 7.29

(b) Coupling Constants (Hz)

	IIa	IIb
$J_{4\beta,5}$	1.9	1.6
$J_{4\beta,6\alpha}$	<0.1	0.8
$J_{4\beta,6\beta}$	1.1	<0.1
$J_{4\beta,8}$	0.4	0.4
$J_{4\beta,11}$	0.4	0.4
$J_{5,6\alpha}$	10.6	4.2
$J_{5,6\beta}$	4.1	10.3
$J_{6\alpha,6\beta}$	15.5	15.5

(c) Nuclear Overhauser Effects*2

	IIa	IIb
$\{H_4\}\ H_{11}$	16%	17%
$\{H_{11}\}\ H_4$	23%	20%

Measured in degassed $CDCl_3$ solution.

[+] Part VII in a series on 3,4-Benzotropolone and Related Compounds; for Part VI, see M.Hoshino and S.Ebine, Bull.Chem.Soc.(Japan),41,2949(1968).

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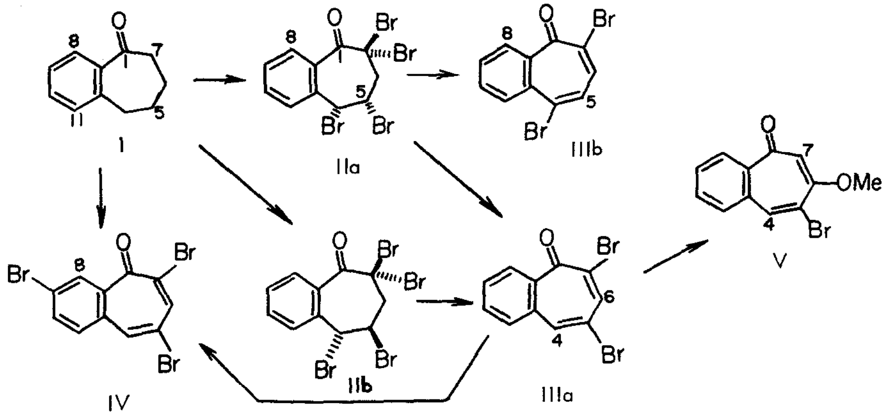


Dehydrobromination of isomer A affords both IIIa and IIIb, whereas only IIIa is obtained from IIb under similar conditions.[1)] Bromination of IIIa yields the tribromo derivative IV, which is also obtained by bromination of I under drastic conditions followed by dehydrobromination in pyridine.[1)] The structures of IIIa, IIIb, and IV are established by the n.m.r. data shown in Table 2.[1)]

TABLE 2

	(a) Chemical Shifts (δ ppm)*1							(b) Coupling Constants (Hz)			
	H_4	H_5	H_6	H_7	H_8	H_9/H_{10}	H_{11}	$J_{4,6}$	$J_{4,8}$	$J_{4,11}$	
IIIb	-	7.19	7.42	-	8.28*	ca 7.7	8.08*	-	-	-	($J_{5,6}$= 9.2)
IIIa	7.75	-	8.08	-	8.35	ca 7.7	7.55	1.7	0.5	0.5	
IV	7.71	-	8.12	-	8.51	7.80**	7.45	1.7	0.5	0.5	
V	7.89	-	-	6.42	8.43	ca 7.6	ca 7.5	-	0.5	0.5	($J_{4,7}$= ca 0.2)

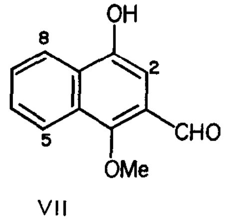
*H_8 and H_{11} assignment is ambiguous. ** H_{10} signal.

As described previously,[1)] the dibromo compounds IIIa and IIIb undergo abnormal nucleophyllic substitution at the 6-position to afford a series of 6-substituted derivatives, of which compound V is an example. The structure reported[1)] for this compound is in accord with the n.m.r. data given in Table 2.

As can be seen from Table 2, H_4 is equally coupled (0.5 Hz) to both protons H_8 and H_{11} in the 2,3-benzotropones IIIa, IV, and V, and hence these couplings cannot serve to assign the H_8 and H_{11} signals. However, in the absence of a substituent at C_4, H_8 is expected to appear at lower field than H_{11}. In IIIb, these signals cannot be unambiguously assigned, since with a 4-bromine H_{11} also shifts to lower field. The methoxyl at $C_{(6)}$

in V is coupled to H_7 (J = 0.7 Hz)[3] and, in addition, provides a relaxation pathway for H_7 as evidenced by the observation that saturation of the OMe resonance at 3.86 causes an 18% enhancement of the H_7 signal,[2,3,4] viz. $\{OMe\}\ H_7 = 18\%$.*2)

The structure of "compound VII",[1] a side-product in the methanolysis of IIIa, was also determined. The n.m.r. data shown in Table 3, particularly the N.O.E's, rigorously define the structure shown. It is noteworthy that the peri-protons, H_5 and H_8, owe little of their relaxation to the adjacent methoxyl and hydroxyl groupings. Similar behaviour has also been observed[4] in related structures such as α-naphthol and its methyl ether.



VII
(DMSO-d_6 solution)

TABLE 3

(a) Chemical Shifts (δ ppm)*1

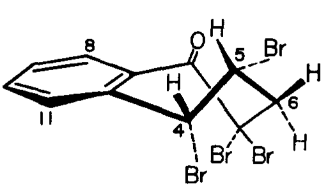
δ_5, δ_8 ca 8.2
δ_6, δ_7 ca 7.7
δ_2 7.08, δ_{OH} 10.34
δ_{CHO} 10.44, δ_{OMe} 4.03

(b) Nuclear Overhauser Effects*2.

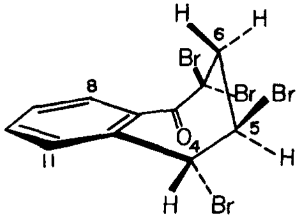
$\{OH\}\ H_2$ = ca 26%; $\{CHO\}\ H_2$ = ca 8%
$\{CHO + OH\}\ H_2$ = 34%
$\{H_2\}$ CHO = ca 8%; $\{OMe\}$ CHO = 24%
$\{OH\}\ H_8$ = nil; $\{OH\}\ H_5$ = nil

The stereochemistry of the tetrabromo isomers IIa and IIb is deduced as follows.

The magnitudes of the H_5 couplings (see Table 1) indicate that in both isomers the H_5 / H_4 dihedral angle is near 90° and the dihedral angle between H_5 and one of the H_6 protons is near 180°. This plus the stereospecific W-coupling[5] between H_4 and H_6, *suggests that IIa and IIb have the stereostructures depicted in VIa* and VIb (but not necessarily respectively). A comparison of the chemical shifts of H_5, $H_{6\alpha}$ and $H_{6\beta}$ in IIa and IIb, reveals that $H_{6\alpha}$ and $H_{6\beta}$ are at higher field in IIb than in IIa, while H_5 is at lower field in IIb than in IIa. This indicates that stereo-structure VIa should be assigned to isomer A, and VIb to isomer B, since both $H_{6\alpha}$ and $H_{6\beta}$ are more above the plane of the benzene ring in VIb than VIa, and $H_{6\alpha}$ is closer to the 4-bromine in VIa than in VIb, and H_5 is more in the plane of the benzene ring, and closer to the 4-bromine, in VIb than in VIa.

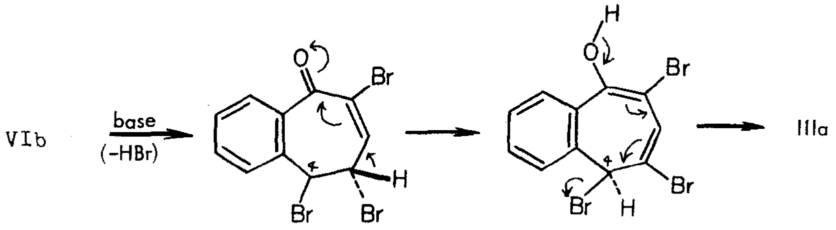


VIa [cis-Isomer IIa]



VIb [trans-Isomer IIb]

The stereostructures provide a simple explanation for the fact1) that dehydrobromination of IIa (= VIa) affords both IIIa and IIIb, whereas IIb (= VIb) affords only IIIb, since "trans-diaxial" elimination of either the 4- or 5-bromine as HBr is possible in the *cis* isomer VIa, but not in the *trans* isomer VIb. However, elimination of the 4-bromine in VIb can occur by the following mechanism.



REFERENCES AND FOOTNOTES

*1 The n.m.r. spectra were measured on an HA-100 using $CDCl_3$ solutions with TMS (δ = 0.00 ppm) as field/frequency lock, unless otherwise specified. Assignments were confirmed by multiple resonance experiments.

*2 For brevity, nuclear Overhauser effects (NOE's)2) are reported in this paper in the form "$\{OMe\}\ H_7 =$ 18%", which should be read as "saturation of the methoxyl resonance causes the H_7 signal to exhibit an 18% increase in intensity".

1) S. Ebine, M. Hoshino, and K. Takahashi, *Bull.Chem.Soc., (Japan)* **41**, 2942 (1968).

2) F.A.L. Anet, A.J.R. Bourn, *J.Am.Chem.Soc.*, **87**, 5250 (1965).

3) Methoxyl signals are commonly coupled to the adjacent proton on the same double bond, particularly in the troponoids, Cf. T. Mukai, T. Miyashi, M.C. Woods, *Tetrahedron Letters*, 433 (1967); M.C. Woods, I. Miura, A. Ogiso, M. Kurabayashi, H. Mishima, *Ibid*, 2009 (1968), and reference 4) below.

4) M.C. Woods and I. Miura, "*Abstracts 7th NMR Symposium, Nagoya, Japan (1968)*", p. 145.

5) S. Sternhell, *Rev. Pure and Applied Chem.*, **14**, 15 (1964).