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THE SYNTHESIS OF 4,5-BENZOHOMOTROPONE

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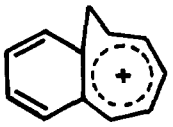
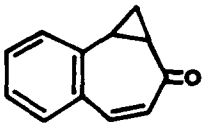
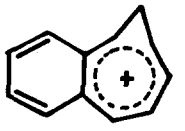
In the aspect of homoaromaticity, homotropone and homotropylium cation have attracted interests of chemists and several kinds of homotropones[1], homotropylium cations[2] and their benzo- and dibenzo-analogues[3] have been reported. Merk and Pettit[4] have obtained benzohomotropylium cation (I) from benzocyclooctatetraene, but benzohomotropone (II) and benzohomotropylium cation (type III) have not been prepared. Recently we reported[5] the synthesis of 2,3-homotropone by the reaction of tropone with stable sulfonium ylides and obtained many kinds of 8-substituted-2,3-homotropones. In the extension of the homotropone synthesis to cover the benzo-derivatives, we tried to prepare 4,5-benzo-2,3-homotropone by the reaction of 4,5-benzotropone with phenacylidene dimethylsulfurane, but only the starting material was recovered unchanged. Then we focussed our attention to the reaction of dimethyloxosulfonium methylide with 4,5-benzotropone and succeeded in obtaining 4,5-benzo-2,3-homotropone and 2,7-diethoxycarbonyl-4,5-benzo-2,3:6,7-bishomotropone.



I



II



III

Into a solution of 4,5-benzotropone (IVa, 1.3 g) in tetrahydrofurane (10 ml), was added dropwise a solution of dimethyloxosulfonium methylide in tetrahydrofurane[6] (0.21 N, 48 ml) at 0°C. The reaction mixture was allowed to stand overnight at room temperature and then evaporated to give a residual syrup which partially crystallized. Purification on dry silicagel column

gave 4,5-benzo-2,3-homotropone (2,3-benzobicyclo[5,1,0]oct-4-en-6-one). IIa: mp 79-81°C; $C_{12}H_{10}O$; IR $\nu_{c=o}$ (nujol) 1640 cm^{-1}; UV λ_{max}(ethanol) 230 (log ε = 4.11)nm, 290 (3.98); MS m/e 170(M+), 142, 141 (base), 128, 115, 89, 73. Analogous reaction of 2,7-dimethyl-4,5-benzotropone (IVb) with dimethyloxosulfonium methylide gave 2,7-dimethyl-4,5-benzo-2,3-homotropone (IIb, mp 70-70.5°C, in 95% yield). The NMR spectral data of IIa and IIb in $CDCl_3$ and in D_2SO_4 are shown in the TABLE.

Comparing to the chemical shifts of the benzohomotropones (IIa and IIb) in $CDCl_3$, almost all protons shift downfield in D_2SO_4 but only one of the geminal cyclopropane protons (8-endo proton) shifts upfield. Considering the NMR spectral data of 2,3-homotropone[1], it should be presumed that IIa and IIb are converted to hydroxyhomotropylium ions (V) in sulfuric acid.

Lithium aluminumhydride reduction of IIa and IIb gave hydroxy compounds (VIa, mp 110-111°C) and VIb (mp 53-54°C), respectively, in good yield.* The conversions of VIa and VIb to benzohomotropylium cations (III) were expected in sulfuric acids, but we could not detect the benzohomotropylium cation in such conditions since these compounds decomposed in the acid at room temperature.

An attempt to obtain 4,5-benzo-2,3:6,7-bishomotropones by further homologation of IIa and IIb with dimethyloxosulfonium methylide under analogous reaction conditions was not successful. But when 2,7-diethoxycarbonyl-4,5-benzotropone (IVc) was allowed to react with dimethyloxosulfonium methylide in tetrahydrofurane, 2,7-diethoxycarbonyl-4,5-benzo-2,3:6,7-bishomotropone (diethyl 2,3-benzotricyclo[6,1,0,$0^{4,6}$]nonan-7-one-6,8-dicarboxylate, VII) was obtained in 50% yield. VII: mp 107-108°C; $C_{19}H_{20}O_5$; IR $\nu_{c=o}$(nujol) 1725, 1705 cm^{-1}; MS m/e 328(M^+), 300, 282, 255, 236, 209, 201, 181, 155, 141, 129, 115. NMR (100 MHz, δppm in $CDCl_3$) 1.32 (6H, t, J=7 Hz, $2CH_3$), 1.79 (2H, d of

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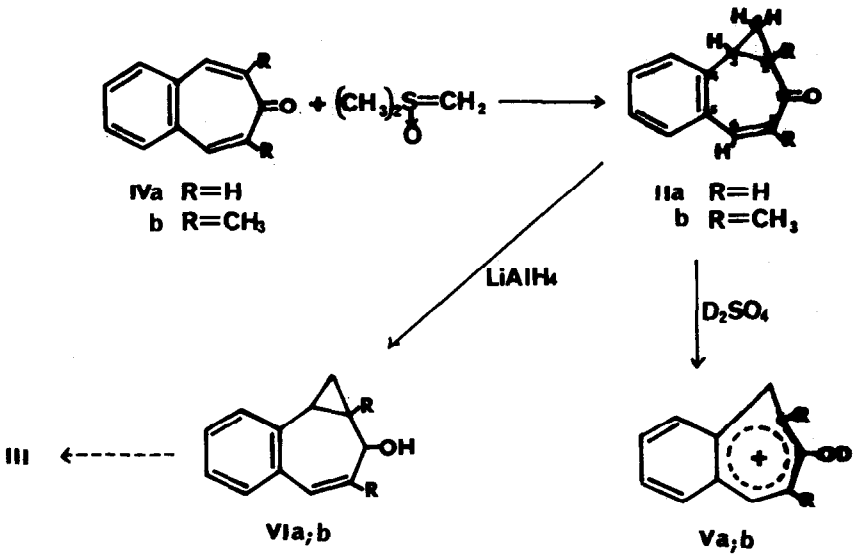
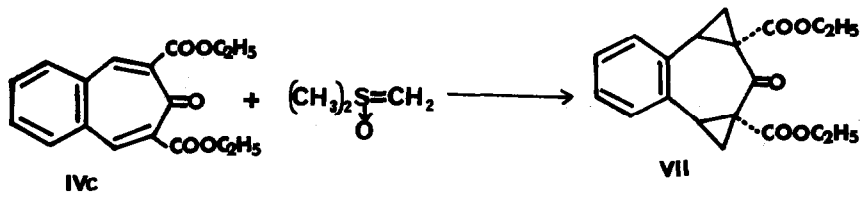
* For each of these hydroxy compounds, the presence of two stereoisomers should be possible but only one isomer was obtained. Considering the reaction mechanism and the NMR, the orientation of the hydroxy group would be syn to cyclopropane but the decisive conclusion should await for further study.



The NMR spectral data of IIa and IIb (100 MHz)

	Proton assignment	Chemical shift (δ) in $CDCl_3$ (1)	Chemical shift (δ) in D_2SO_4 (2)	Δ (1)-(2)	multiplicity	Coupling constant in $CDCl_3$
IIa	8-endo H	1.76	0.60	+1.16	td	$J_{6,7}$= 13.5
	8-exo H	1.88	2.6-3.1*	-0.7~-1.2	ddd	$J_{3,8\text{-exo}}$
	2-H	2.55	2.6-3.1*	-0.05~-0.5	dd	= $J_{2,8\text{-exo}}$=8.0
	3-H	2.55	3.44	-0.89	dd	$J_{2,8\text{-endo}}$
	6-H	6.79	7.53	-0.74	d	=$J_{3,8\text{-endo}}$=6.0
	7-H	5.96	6.21	-0.25	d	$J_{8\text{-exo},8\text{-endo}}$
	aromatic H	7.2-7.5	7.1-7.3			= 4.4
IIb	8-endo H	1.53	0.61	+0/92	dd	$J_{6,7\text{-}CH_3}$=1.5
	8-exo H	1.90	2.90	-1.00	dd	$J_{3,8\text{-exo}}$=7.3
	3-H	2.44	3.73	-1.39	dd	
	6-H	6.63	7.48	-0.85	d	$J_{3,8\text{-endo}}$=9.0
	2-CH_3	1.39	1.33	+0.06	s	$J_{8\text{-exo},8\text{-endo}}$
	7-CH_3	2.02	1.93	+0.09	d	=4.5
	aromatic H	7.1-7.4	7.1-7.3			

*The center of these multiplets are ca2.75 and ca2.95.



IVc VII

d, J=5.0 and 9.5, end-8 and endo-9), 1.99(2H, d of d, J=5.0 and 7.2, exo-8 and exo-9), 3.01(2H, d of d, J=9.5 and 7.2, 3-H and 6-H), 4.23 (2H, d of q), 4.32 (2H, d of q), 7.1-7.4 (4H, aromatic H). The NMR spectrum shows that the two cyclopropanes are completely equivalent but the methylene protons of ethoxy group are nonequivalent and the latters are shown as ABX_3 system[7] (J_{AB}=11 Hz, $J_{AX}=J_{BX}$=7). Examination of the Dreiding model of VII shows that if the two cyclopropane rings are in anti, they are nonequivalent, while if they are in syn, they are equivalent. Base catalized hydrolysis of VII followed by treatment with acetic anhydride gave an acid anhydride. These data suggested that the two cyclopropane rings of VII are syn. The definite configuration will be revealed by X-ray analysis.

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