CHEMISTRY LETTERS, pp. 487-490, 1975. Published by the Chemical Society of Japan

ON THE PROPERTY OF DIBENZO[d,j]-6,8-BISDEHYDRO[13]ANNULENONE

Jūro OJIMA, Yōji YOKOYAMA, and Tai YOKOYAMA

Faculty of Literature and Science, Toyama University
Gofuku, Toyama 930

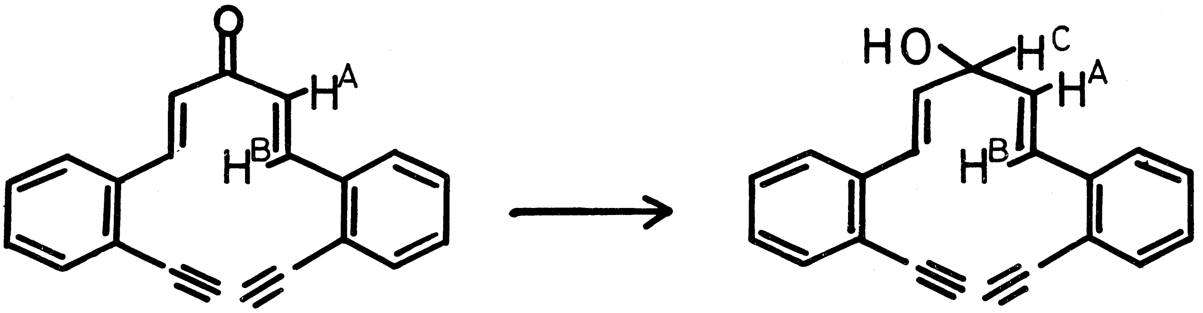
An annelated[13]annulenone (3) and its precursor (1) were converted into the corresponding alcohols (4) and (2), respectively. Comparison of the NMR spectrum of the alcohol (2) with that of (4) suggested that (3) is weakly paratropic.

In a previous paper, we have reported a synthesis of dibenzo[d,j]-6,8-bisdehydro[13]annulenone (3), and showed that two benzene rings fused on the inner thirteen membered ring system reduce, but do not completely suppress, the paramagnetic ring current.1) This conclusion was derived by comparing the chemical shifts of H^A and H^B protons of (3) with those of the acyclic ketone (1) which is an atropic molecule.

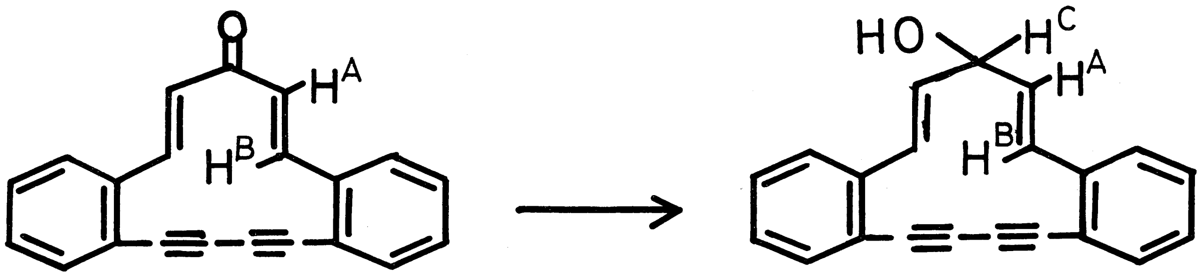
However, quite recently, Prof. Sondheimer has cast a doubt on our idea that (3) is weakly paratropic and suggested us to see the chemical shift differences between the open alcohol (2) and the closed alcohol (4) from the following point of view.2) The chemical shift differences between a molecule to be tested and the corresponding atropic model have been usually used as a criterion to decide whether a molecule has a ring current or not. In this judgement, even though a molecule to be compared with an atropic molecule might be also atropic, it is assumed that the chemical shift differences in them would be exactly zero. Accordingly, strictly speaking, the validity of this assumption must be examined, if possible, by seeing these differences in the corresponding atropic molecules when these differences are so small as observed in our study. Along this line we attempted the following.

Reduction of the acyclic ketone (1) in ether with ethanolic $NaBH_4$ for 20 hours at room temperature, followed by chromatography on alumina, gave 20% yield of the alcohol (2) as a pale yellow oil. Mass: m/e 284 (M^+, 10%), 129 (base); IR (neat): 3300(-OH), 3250(-C≡CH), 2100(-C≡C-), 1700, 1640, 1595($>C=C<$), 905 cm^{-1} ($^{H}{>}C=C{<}_{H}$); UV (EtOH): $\lambda_{max}(\varepsilon)$ 226 sh nm(12,100), 233(15,000), 239(12,800), 249 (8,550), 264(8,430), 276(6,350); NMR: see Table 1.

Reduction of the ketone (3) in ether with ethanolic $NaBH_4$ for 2 hours at room temperature, followed by chromatography on alumina, gave 91% yield of the alcohol (4) as colorless needles, which decomposed at 150°C[3)] on attempted melting point determination. Mass: m/e 282 (M^+, 25%), 253 (base); IR (KBr): 3350, 3250(-OH), 2150 (-C≡C-), 1640($>C=C<$), 975, 965 cm^{-1}($^{H}{>}C=C{<}_{H}$); UV (EtOH): $\lambda_{max}(\varepsilon)$ 257 nm(20,700), 268(20,000), 297(13,200), 322(16,500), 343(17,500), 386 sh(3,310); NMR: see Table 1.



(1) (2)



(3) (4)

Table 1. ^{1}H-NMR parameters of (1)—(4) in $CDCl_3$ at 60 MHz

(τ-values, internal standard TMS, J in Hz)

	(1)	(2)	(3)	(4)	Δ(3)-(1)[a]	Δ(4)-(2)[a]
H^A	2.84	3.87	3.24	4.10	+0.40	+0.23
	d, 16	dd, 16 6	d, 16	dd, 16 6		
H^B	1.82	3.07	1.53	3.27	-0.29	+0.20
	d, 16	d, 16	d, 16	d, 16		
H^C		5.65		4.91		
		t, 6		t, 6		
-OH		7.13		8.10		
		broad s		broad s		
-C≡CH	6.54	6.80				
	s	s				
aromatic protons	2.22—2.76	2.6—2.90	2.5—2.8	2.50—2.87		

a) This shows the chemical shift differences.

Now, we can see the chemical shift differences in compounds (2) and (4) which are definitely atropic.

As shown in Table 1, the chemical shift differences of H^A proton between (2) and (4) (+0.23) is smaller than that of H^A between (1) and (3) (+0.40). Whereas, as for H^B proton the reverse is observed (+0.20, -0.29).

This result seems to suggest that the compound (3) is weakly paratropic although the differences in chemical shift of both H^A and H^B proton signals are small.

The authors wish to thank Prof. F. Sondheimer in University College London for useful suggestions and sending us unpublished result.

This research was financially supported by the grants from the Minstry of Education.

References and Notes

1) J. Ojima, Y. Yokoyama, and T. Yokoyama, Chem. Lett., 1261 (1974).

2) F. Sondheimer, private communication.

3) This temperature is not corrected.

(Received February 15, 1975)