## 9-PHENYLBICYCLO[6.1.0]NONATETRAENYL ANION A NEW DIATROPIC 10 π-ELECTRON SYSTEM

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Summary: Treatment of 9-chloro-9-phenylbicyclo[6.1.0]nona-2,4,6-triene with excess bases gives, by the intermediacy of 9-phenylbicyclo[6.1.0]-1(9),2,4,6-tetraene, 9-phenylbicyclo[6.1.0]tetraenyl anion of which <sup>1</sup>H-NMR spectrum suggests some diatropic character of the molecule.

We have recently reported that the phenyl derivatives, <u>lb</u> and <u>lc</u>, of bicyclo[5.2.0]nonatetraenyl anion <u>la</u> show diatropicity, though not very strong, as a peripheral 10  $\pi$ -electron system rather than paratropicity of component antiaromatic cyclobutadiene and cycloheptatrienyl anion.<sup>1</sup> As a logical extension, we were next interested in the properties of yet unknown bicyclo[6.1.0]nonatetraenyl anion <u>2a</u> which is another anionic bicyclic 10  $\pi$ -electron system composed of two antiaromatic rings, in this case, cyclooctatetraene and cyclopropenyl anion. This paper describes the synthesis and some properties of 9-phenylbicyclo[6.1.0]nonatetraenyl anion <u>2b</u>, the first derivative of <u>2a</u>.





Photoirradiation of a solution of cyclooctatetraene and chlorophenyldiazirine<sup>2</sup> in benzene through a pyrex filter for 3 h gave a 53:47 (by <sup>1</sup>H-NMR) mixture of stereoisomeric 9-chloro-9phenylbicyclo[6.1.0]nona-2,4,6-trienes, 3a and 3b (in the order of elution from silica gel column with hexane<sup>3</sup>), in 53% yield [3a: mp 75-76°C; <sup>1</sup>H-NMR, δ(CCl<sub>4</sub>) 2.18 (2H, s), 5.9 (6H, m), 7.3 (5H, m); 3b: mp 80-81°C;  $\delta(CC1_A)$  2.50 (2H, s), 5.8 (6H, m), 7.3 (5H, m)]. Although the spectral data of 3a and 3b hardly allow to assign their stereochemistry, the syn-chloro configuration of 3a (hence the anti-chloro configuration of 3b) was suggested from its easier dehydrochlorination with bases; on treatment of ca 1:1 mixture of 3a and 3b with 1 equiv. of t-BuOK in THF at  $0^{\circ}$  for 1 h, 3a disappeared completely, whereas most of 3b remained unchanged. When the dehydrochlorination of 3a was performed in the presence of diphenylisobenzofuran, a Diels-Alder adduct 5 between 9-phenylbicyclo[6.1.0]nona-1(9),2,4,6-tetraene 4 and the furan was obtained in 50% yield [5: mp 166-167°C; <sup>1</sup>H-NMR δ(CCl<sub>A</sub>) 3.39 (1H, s), 5.40 (1H, d, J=11.7 Hz), 5.7 (4H, m), 5.95 (1H, dd, 11.7, 3.8 Hz), 6.4 (2H, m), 7.2 (15H, m), 7.7 (2H, m)]. The structure of 5 is assigned as shown chiefly from its  $^{1}$ H-NMR spectrum. The appreciably low field appearance of the juncture proton suggests its proximity to the oxygen bridge,<sup>4</sup> which is consistent with the stereochemical point of view on the transition state of the reaction. The singlet appearance of the same proton is similar to the corresponding protons in 3a, 3b, and the related compounds.<sup>5</sup>



[6.1.0]nonatetraenyl anion <u>2b</u> in THF at 23°C.

Although attempts to isolate tetraene  $\underline{4}$  have failed because of its instability, anion  $\underline{2b}$  was successfully obtained as a thermally fairly stable, deep reddish purple solution by treatment of 3a with excess lithium diisopropylamide in THF at -70 to 0°C. With the base, <u>3b</u> also produced <u>2b</u>. The  $^{
m H}$ -NMR spectrum of the solution is shown in Fig. 1. The signals can be assigned as indicated, and the parameters deduced are given above. The higher chemical shifts of H<sub>2.7</sub> and H<sub>4.5</sub> compared

to  $H_{3,6}$  coincide with the higher electron densities at  $C_{2,7}$  and  $C_{4,5}$  to  $C_{3,6}$  obtained by a SCF MO calculation<sup>6</sup> on <u>2a</u>. The average chemical shift ( $\delta_{av}$ = 5.70) of the eight-membered ring protons of 2b is ca. 1.2 ppm lower than that  $(\delta_{av}=4.48)$  of typically atropic 9-phenylmethylenecyclooctatrienyl anion  $\underline{6}'$ 



which corresponds to the ring opened species at the three-membered ring of 2b. 6 Not only decrease of the charge densities on the eight-membered ring carbons due to better delocalization but induction of some diamagnetic ring current around the 10  $\pi$ -electron periphery may be responsible for the appreciable downfield shift of 2b, which may be further supported by the considerably low field appearance of the ortho phenyl protons compared to the meta and para ones.

Quenching of anion 2b with acids or methyl iodide mainly yields an orange substance (TLC analysis); however, its high instability has so far prevented isolation and characterization. Acknowledgement: We are grateful to Dr. A. Tajiri for his kind communication of the results of the MO calculation (variable  $\beta$  SCF-CI) on <u>2a</u>.<sup>6</sup>

## **References and Notes**

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