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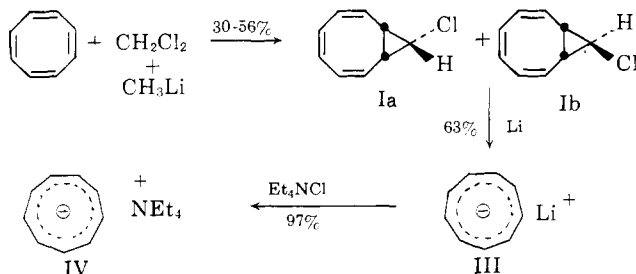
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### Cyclononatetraenide. An Aromatic 10- $\pi$ -Electron System

Sir:

One area in which both theoretical and synthetic chemists share a common interest is that of non-benzenoid aromatic compounds. The guiding principle has been the well known Hückel rule<sup>1</sup> which states that carbomonocyclic compounds having a conjugated system of  $(4n + 2)$   $\pi$  electrons should exhibit aromatic character. For the case where  $n = 2$ , there was previously only a single example where this rule had been experimentally substantiated, *i.e.*, the cyclooctatetraene dianion.<sup>2,3</sup> We now wish to report the synthesis of cyclononatetraenide,<sup>9,10</sup> a 10- $\pi$  carbocycle having  $D_{9h}$  symmetry, in two steps from cyclooctatetraene.

The reaction of cyclooctatetraene with methylene chloride and methyllithium under the general conditions described by Closs and Closs<sup>11</sup> for preparing chloro-



cyclopropanes led to a 3:1 mixture of *syn* and *anti* chlorobicyclo[6.1.0]nona-2,4,6-triene (Ia and Ib). The structural assignment of Ia and Ib in the chlorocyclopropane fraction follows from: (a)  $H^1$  n.m.r. [ $CDCl_3$  solution,  $\delta$  in p.p.m. *vs.*  $(CH_3)_4Si$ ]: multiplet centered at 6.0 (olefinic H), triplet at 3.45 ( $J = 7.6$  c.p.s., *syn*-CHCl), triplet at 2.52 ( $J = 4.3$  c.p.s., *anti*-CHCl) and an unresolved multiplet centered at 1.83 (allylic cyclopropane H); (b)  $\lambda_{max}^{isoctane}$  248  $m\mu$  ( $\epsilon$  3080); (c) the presence of tertiary cyclopropyl hydrogens<sup>12</sup>:  $\lambda_{max}^{CCl_4}$  1.67  $\mu$  ( $\epsilon$  0.79); and (d) elemental

(1) E. Hückel, *Z. Physik*, **70**, 204 (1931).

(2) (a) A. R. Ubbelohde, *Chem. Ind.* (London), 153 (1956); (b) T. J. Katz, *J. Am. Chem. Soc.*, **82**, 3784 (1960); (c) H. P. Fritz and H. Keller, *Z. Naturforsch.*, **16b**, 231 (1961).

(3) The reported<sup>4</sup> synthesis of cyclodecapentaene has been shown to be in error.<sup>5</sup> Attempts to prepare compounds having the 1,6-diazacyclodecapentaene ring system were unsuccessful,<sup>6</sup> and recent studies<sup>7</sup> of 2,3,6,7-dibenzo-1-methyl-1,4,5-triazacyclohepta-2,6-diene (and the 1-oxa and 1-thia analogs) have shown that these compounds exhibit no aromatic character attributable to the 10- $\pi$ -electron system. Recently, the synthesis of 2,3-benzo-1,4-dioxacycloocta-2,5,7-triene has been reported<sup>8</sup> and it has been concluded that the molecule is not planar.

(4) W. Reppe, O. Schichting, and H. Meister, *Ann.*, **560**, 93 (1948).

(5) (a) L. E. Craig and C. E. Larrabee, *J. Am. Chem. Soc.*, **73**, 1191 (1951); (b) A. C. Cope and S. W. Fenton, *ibid.*, **73**, 1195 (1951), and references therein; (c) D. S. Withey, *J. Chem. Soc.*, 1930 (1952).

(6) A. E. Blood and C. R. Noller, *J. Org. Chem.*, **22**, 873 (1957).

(7) N. L. Allinger and G. A. Youngdale, *J. Am. Chem. Soc.*, **84**, 1020 (1962).

(8) W. Schroth, K. Kränke, and J. Reinhardt, *Angew. Chem.*, **75**, 303 (1963).

(9) Cyclononatetraenide has also been prepared independently by T. J. Katz and P. J. Garratt, *J. Am. Chem. Soc.*, **85**, 2852 (1963).

(10) A theoretical study of the structure and electronic spectrum of cyclononatetraenide is being carried out in collaboration with Dr. H. E. Simmons and will be reported shortly.

(11) G. L. Closs and L. E. Closs, *J. Am. Chem. Soc.*, **82**, 5723 (1960).

analysis. *Anal.* Calcd. for  $C_9H_9Cl$ : C, 70.82; H, 5.94; mol. wt., 152.6. Found: C, 70.76; H, 6.14; mol. wt., 152 (mass spec.).

Upon treating the isomeric mixture Ia and Ib in tetrahydrofuran with a lithium dispersion for 2 hr. at room temperature, the multiplet at 6.0 p.p.m. in the n.m.r. disappeared and a sharp line (width at half height no greater than 0.8 c.p.s.) was observed at 6.72 p.p.m. The lithium cyclononatetraenide (III) thus formed in 63% yield (n.m.r.) was stable in an inert atmosphere. The  $C^{13}$  n.m.r. of the lithium salt III in THF consisted of a doublet at 19.0 p.p.m. ( $J = 137$  c.p.s.) to highfield from benzene.<sup>13</sup>

Metathesis of the lithium salt III with tetraethylammonium chloride produces tetraethylammonium cyclononatetraenide (IV, 97%) as a stable (inert atmosphere) white solid which was purified by recrystallization from anhydrous acetonitrile, dec. pt. 318° (*Anal.* Calcd. for  $C_{17}H_{29}N$ : C, 82.52; H, 11.81; N, 5.66. Found: C, 82.30; H, 11.55; N, 5.75);  $H^1$  n.m.r. ( $d_6$  dimethyl sulfoxide): 6.82 (aromatic H, width at half height no greater than 0.6 c.p.s.), quartet at 3.03 ( $CH_2$ ,  $J = 7$  c.p.s.), triplet of triplets at 1.05 ( $CH_3$ ,  $J = 7$  c.p.s. and *ca.* 1.5 c.p.s.). The ultraviolet absorption spectrum is very simple, as expected for a molecule having a ninefold rotational axis:  $\lambda_{max}^{CH_3CN}$  250  $m\mu$  ( $\epsilon > 61,700$ ) and doublet at 317 and 322  $m\mu$  ( $\epsilon > 6,170$ ).<sup>14</sup>

Polarographic analysis of the tetraethylammonium salt IV in acetonitrile containing  $LiClO_4$  (0.1 *M*) as the supporting electrolyte with a rotating platinum electrode shows what appears to be an irreversible one-electron oxidation at  $E_{0.5} = -0.03$  v. (*vs.* s.c.e.). As expected from this result, the tetraethylammonium salt IV can be oxidized by either tetracyanoethylene or 7,7,8,8-tetracyanoquinodimethan. Attempts to detect the resulting radical<sup>15</sup> in 1,2-dimethoxyethane solution *via* e.p.r. at ambient temperature or at  $-80^\circ$  have been unsuccessful although the spectrum of TCNE $\cdot^-$  is observed.

Lithium cyclononatetraenide (III) does not undergo detectable electron exchange over a period of 45 days with cyclooctatetraene to give cyclooctatetraene dianion. However, the salt III reacts with cyclopentadiene to give lithium cyclopentadienide.

On the basis of the  $H^1$  and  $C^{13}$  n.m.r. data and the strong absorption in the ultraviolet, it is concluded that cyclononatetraenide has aromatic character. Further studies are in progress.

(12) J. Meinwald, A. Lewis, and P. G. Gassman, *ibid.*, **84**, 977 (1962), and references therein.

(13) We are grateful to Dr. H. Foster for the  $C^{13}$  N.m.r. studies. The  $C^{13}$  chemical shift is in excellent agreement with the simple linear correlation between chemical shift and  $\pi$ -electron density as found recently for the aromatic series  $C_7H_7^-$ ,  $C_8H_8$ ,  $C_8H_8^-$  and  $C_8H_8^{2-}$  [H. Spiesscke and W. G. Schneider, *Tetrahedron Letters*, No. 14, 468 (1961)]. Calculations using the least-squares method for their published data together with that found for  $C_8H_8^-$  gives the equation  $\delta C^{13} = 167.8\rho - 169.9$ . Although the value reported for  $C_8H_8^-$  appears to be anomalous, it has been confirmed by Dr. Foster.

As previously noted [T. Schaefer and W. G. Schneider, *Can. J. Chem.*, **41**, 966 (1963)] the prediction of the  $H^1$  chemical shift from the  $\pi$ -electron density is less satisfying for larger ring aromatic compounds due to the difficulty of applying ring size corrections. The  $H^1$  chemical shift for  $LiC_9H_9$  from internal benzene was found to increase upon dilution (27.3 c.p.s. at *ca.* 3 mole % to 30.5 c.p.s. at *ca.* 0.4 mole %) as expected for decreasing ion association.

(14) Some difficulty was experienced in determining the exact value of the extinction coefficients since Beer's law was not followed upon carrying out the necessary dilutions, presumably because of reaction with trace impurities in the solvent.

(15) We are indebted to Dr. M. T. Jones for this experiment.

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