

berg with regard to exact force field calculations is most gratefully acknowledged.

Appendix

Averaging of Computed Isotope Effects. The observed oxygen isotope effect, k_{16}/k_{18} , is the average of that resulting from substitution at O-3 (Figure 2), denoted as k_{16}/k_{18}^3 and that from substitution at O-5, k_{16}/k_{18}^5 . One must consider not only the proper formulation of this average but also its sensitivity to an unequal distribution of O¹⁸ between the two non-equivalent oxygens.

We define r , the initial isotopic inhomogeneity, to be the initial concentration of O-3-labeled adduct divided by that of O-5-labeled material and then derive equation A.1 by conventional means. Expansion about $f = 0$ produces eq. A.2 which is further simplified to eq. A.3 so long as the isotope effects are small.

$$(1+r) \left[1 - \frac{R_f}{R_i} f \left(\frac{1+R_1}{1+R_f} \right) \right] = r \left[1 - f \left(\frac{1+R_1}{1+R_f} \right) \right]^{k_{18}^3/k_{16}} + \left[1 - f \left(\frac{1+R_1}{1+R_f} \right) \right]^{k_{18}^5/k_{16}} \quad (\text{A.1})$$

$$\left(\frac{k_{18}}{k_{16}} \right)_{\text{obsd}} = \frac{R_f}{R_i} = \frac{r(k_{18}^3/k_{16}) + (k_{18}^5/k_{16})}{r+1} \quad (\text{A.2})$$

$$\left(\frac{k_{16}}{k_{18}} \right)_{\text{obsd}} = \frac{r(k_{16}/k_{18}^3) + (k_{16}/k_{18}^5)}{r+1} \quad (\text{A.3})$$

Isotopic Inhomogeneity. Although every reaction used to prepare the adduct proceeds in high yield, at least one of them, the acid-catalyzed, decarbonylative condensation of malic to coumalic acid, provides ample opportunity for an intramolecular isotope effect.

This must result in a value of r equal to it in magnitude and independent of yield.

The problem is least ambiguously evaluated by first assuming isotopic homogeneity and then inquiring how large a discrepancy in isotopic composition might be tolerated before the resulting error reaches the experimental uncertainty. The error is defined as

$$\epsilon \equiv (k_{16}/k_{18})_r - (k_{16}/k_{18})_{r=1}$$

Substitution in eq. A.3 produces eq. A.4 which shows ϵ to depend both on r and on the difference between the

$$\epsilon = \frac{1}{2} \left(\frac{r-1}{r+1} \right) \left(\frac{k_{16}}{k_{18}^3} - \frac{k_{16}}{k_{18}^5} \right) \quad (\text{A.4})$$

two isotope effects to be averaged. Predicted differences between the two ratios have never exceeded 0.026. With $\epsilon \leq 0.0019$ (the standard deviation), r (or its reciprocal) becomes dangerous only if greater than 1.34, a value to be compared with 4.5%, the maximum variation of natural O¹⁸ thus far detected,^{7a} and 19%, the (unrealistically high) room temperature maximum value of an O¹⁸ isotope effect as evaluated by Bigeleisen some time ago.¹² Isotopic homogeneity is a comfortable assumption.

Supplementary Data

These have been deposited with the American Documentation Institute, c/o Library of Congress, Washington 25, D. C., as Document No. 8266 and may be obtained by remitting \$1.75 for microfilms and \$2.50 for photographs. They include the assignments of atomic cartesian coordinates, valence coordinate, selected moments of inertia and frequencies, a complete list of essential data obtained for the 23 transition state force fields and two reactant force fields investigated, and details of auxiliary corrections.²³

Cyclononatetraenide. A Ten- π -Electron Aromatic System

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Received December 2, 1964

Cyclononatetraenide, isolated and characterized as the tetraethylammonium salt, shows aromatic character as established from ¹H and ¹³C n.m.r. data and intense absorption in the ultraviolet. Reaction of C₉H₉⁻ with water leads to a mixture of products including indene, dihydroindene, and presumably the labile cyclononatetraene. Evidence for the existence of the tetraene was found in partial reconversion of the water-treated product to C₉H₉⁻ and hydrogenation to cyclononane. Cyclononatetraenide undergoes electron transfer with tetracyanoethylene and proton exchange with cyclopentadiene.

Validation of the Hückel ($4n + 2$) π -electron rule¹ for aromaticity in carbomonocyclic systems has been well established where $n = 1$. In spite of several attempts to uncover systems where $n = 2$, the cyclooctatetraene dianion until recently constituted the single example² of a ten- π -electron carbomonocyclic system. A second example has been found in the

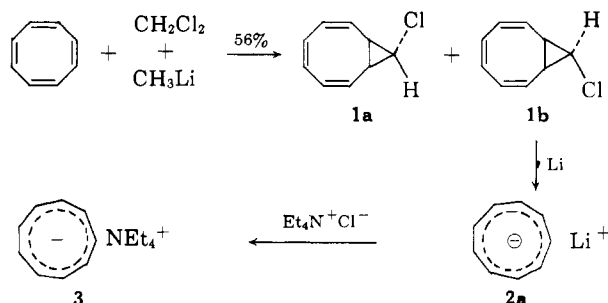
(1) E. Hückel, *Z. Physik*, **70**, 204 (1931).

(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).

synthesis of cyclononatetraenide, reported from two laboratories.^{3,4} Very recently, the synthesis of 1,6-methano-1,3,5,7,9-cyclodecapentaene⁵ and the 1,6-oxa analog⁶ has been described. Preliminary reports indicate aromatic character for these compounds.

The present paper reports the details of the synthesis of cyclononatetraenide together with the chemical properties of this unusual monocycle.

Upon treating cyclooctatetraene with methylene chloride and methyllithium under the general conditions described by Closs and Closs⁷ for preparing chlorocyclopropanes, a 3:1 mixture of *syn*- and *anti*-9-chlorobicyclo[6.1.0]nona-2,4,6-triene (**1a** and **1b**) is obtained.



The stereochemical assignment is based on the magnitude of the coupling constants for the triplets attributable to $-CHCl$.⁸ On this basis the major fraction is assigned the *syn* structure **1a** ($CHCl$ as triplet, $J_{AX_2} = 7.6$ c.p.s. vs. $J_{AX_2} = 4.3$ c.p.s. for **1b**).

When the chlorocyclopropane mixture **1a** and **1b** is treated in tetrahydrofuran (THF) solution with a 30% lithium dispersion containing 2% sodium, the multiplet at 6.0 p.p.m. in the 1H n.m.r. disappears and a sharp line at 6.72 p.p.m. (width at half-height no greater than 0.8 c.p.s.) is observed.⁹ The position of the 1H resonance line establishes that the compound supports a ring current and on this basis **2a** can be regarded as having aromatic character. In addition, the absorption line is narrow and this, together with the fact that no pronounced line broadening is observed at temperatures from -40 to $+60^\circ$, suggests that the molecule is approximately planar, or is oscillating sufficiently rapidly to give a narrow line representing the "averaged" resonance frequency.

(3) E. A. LaLancette and R. E. Benson, *J. Am. Chem. Soc.*, **85**, 2853 (1963).

(4) T. J. Katz and P. J. Garratt, *ibid.*, **85**, 2852 (1963). Since our manuscript was submitted for publication, the full paper has appeared: *ibid.*, **86**, 5194 (1964).

(5) E. Vogel and H. D. Roth, *Angew. Chem.*, **76**, 145 (1964).

(6) F. Sondheimer and A. Shani, *J. Am. Chem. Soc.*, **86**, 3168 (1964).

(7) G. L. Closs and L. E. Closs, *ibid.*, **82**, 5723 (1960).

(8) It is now believed that in three-membered rings *cis* coupling constants are larger than *trans* coupling constants: (a) H. M. Hutton and T. Shaefer, *Can. J. Chem.*, **40**, 875 (1962); (b) J. D. Graham and M. T. Rogers, *J. Am. Chem. Soc.*, **84**, 2249 (1962); (c) G. L. Closs, R. A. Moss, and J. J. Coyle, *ibid.*, **84**, 4985 (1962); (d) D. Seyferth, H. Yamazaki, and D. L. Alleston, *J. Org. Chem.*, **28**, 703 (1963).

(9) From the relationship¹⁰ $\delta = k\Delta\rho$ ($k = 10.7 \pm 1.0$ p.p.m./electron) cyclononatetraenide would be predicted to absorb in the n.m.r. at 71 ± 7 c.p.s. to high field from benzene. Actually, the 1H chemical shift for LiC_9H_9 in tetrahydrofuran from internal benzene is found at $+30.5$ c.p.s. The chemical shift was noted to increase upon dilution ($+27.3$ c.p.s. at ca. 3 mole % to $+30.5$ c.p.s. at ca. 0.4 mole %). It should be noted that inclusion of the data for $C_9H_9^-$ and $C_9H_9^{2-}$ with that for $C_7H_7^-$, C_6H_6 , and $C_8H_8^{2-}$ would further decrease the previously¹⁰ recommended values of k .

(10) (a) G. Fraenkel, R. E. Carter, A. McLachland, and J. H. Richards, *J. Am. Chem. Soc.*, **82**, 5846 (1960); (b) H. Spiesscke and W. G. Schneider, *Tetrahedron Letters*, No. 14, 468 (1961); (c) T. Shaefer and W. G. Schneider, *Can. J. Chem.*, **41**, 966 (1963).

Further evidence regarding the aromatic nature of $C_9H_9^-$ was obtained through ^{13}C n.m.r. studies. The spectrum consists of a doublet at $+19.0$ p.p.m. from benzene with $J = 137$ c.p.s. The ^{13}C chemical shift is in excellent agreement with the simple linear correlation between chemical shift and π -electron density as found recently^{10b} for the aromatic series $C_7H_7^+$, C_6H_6 , $C_5H_5^-$, and $C_8H_8^{2-}$. Calculations using the least-squares method to include the published data together with that found for $C_9H_9^-$ gives the equation $\delta^{13}C = 167.8\rho - 169.9$, where ρ is the π -electron density per carbon atom.

Chemical evidence for the presence of the nine-membered ring in **2a** was obtained by catalytic hydrogenation to give a mixture of products including cyclononane, as shown by vapor phase chromatography and mass spectrometry.

Metathesis of lithium cyclononatetraenide with tetraethylammonium chloride yields tetraethylammonium cyclononatetraenide (**3**) as white needles, m.p. 318° dec. In addition to the absorption attributable to the ethyl groups, the 1H n.m.r. spectrum of **3** in dimethyl- d_6 sulfoxide solution displays a singlet at 6.82 p.p.m. having a width at half-height no greater than 0.6 c.p.s.

The infrared (Experimental) and ultraviolet absorption spectra of the tetraethylammonium salt are very simple as expected¹¹ for a highly symmetrical molecule having a ninefold rotational axis. As reported⁸ earlier, some difficulty was experienced in determining the exact extinction coefficient, presumably because of reaction with impurities present in the solution in trace amounts. The use of highly purified acetonitrile has given slightly higher extinction coefficients: 250 μ (ϵ 66,300) and a doublet at 317 (6630) and 322 (6750).

Although the lithium salt **2a** in solution is very sensitive to both moisture and oxygen, the compound is stable in an inert atmosphere. Furthermore, **2a** survives to the extent of 70% on heating in bis(2-methoxyethyl) ether at 163° for 30 hr.

The tetraethylammonium salt **3** is sensitive to moisture, but appears to be inert to anhydrous oxygen. In solution, however, **3** is fairly readily oxidized. Polarographic studies in acetonitrile solution containing 0.1 *M* lithium perchlorate as the supporting electrolyte with a rotating platinum electrode show what appears to be a one-electron oxidation at $E_{1/2} = -0.03$ v. (vs. s.c.e.). In 1,2-dimethoxyethane solution the tetraethylammonium salt **3** is oxidized with tetracyanoethylene (TCNE) or 7,7,8,8-tetracyanoquinodimethane. After oxidation with TCNE, no success was achieved in detecting by e.s.r. a radical species derived from **3** at either 25 or -80° , although the spectrum of $TCNE^-$ was readily observed. No electron exchange occurred between **2a** and cyclooctatetraene.³

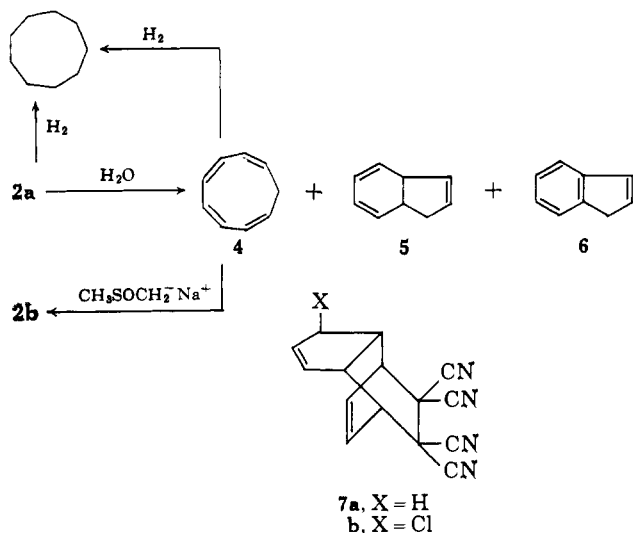
Some evidence implying the existence of the conjugate acid of cyclononatetraenide, *i.e.*, cyclononatetraene (**4**), has been obtained although efforts to isolate the tetraene have been unsuccessful. The quenching of lithium cyclononatetraenide with water leads to a yellow oil (87%) containing two volatile products. By vapor phase chromatography the two products were separated and identified by mass spectrometry as 8,9-

(11) H. E. Simmons, D. B. Chesnut, and E. A. LaLancette, *J. Am. Chem. Soc.*, **87**, 982 (1965).

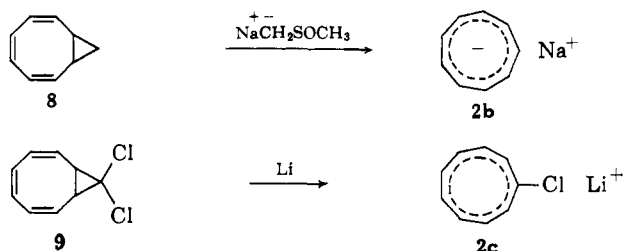
dihydroindene (**5**, 12%) and indene (**6**, 12%). The identity and amount of 8,9-dihydroindene was confirmed chemically by isolation of the adduct **7a** formed upon treating the distillate with TCNE.

Further evidence for the formation of the tetraene **4** in the solution was obtained by hydrogenation of the yellow oil resulting from the action of water on the lithium salt **2a** with a Pt-on-C catalyst to give a mixture of products in which cyclononane was established to be the major component by vapor phase chromatography and mass spectrometry. In addition, treatment of the yellow oil with sodium methylsulfinyl carbanion¹² led to sodium cyclononatetraenide (**2b**, 13%). It was further established that 8,9-dihydroindene was not converted to cyclononatetraenide **2b** by reaction with sodium methylsulfinyl carbanion.

These results are consistent with the concept that cyclononatetraene **4** is formed on treatment of the lithium salt **2a** with water and that the tetraene is highly reactive, converting readily to the valence tautomer **5** and to nonvolatile products, presumably by Diels-Alder reactions. No evidence was uncovered for the existence of a second valence tautomer bicyclo[6.1.0]nona-2,4,6-triene (**8**) in the reaction product. The presence of this tautomer, in excess of 10% yield, was excluded by n.m.r. studies, since no absorption was found at 0 p.p.m., where the triene **8** shows absorption for one of the cyclopropyl hydrogens.

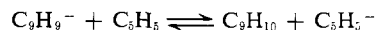


Cyclononatetraenide can also be prepared from bicyclo[6.1.0]nona-2,4,6-triene (**8**) albeit in lower yield (38%). The base of choice appears to be the methylsulfinyl carbanion. N.m.r. evidence has been obtained suggesting that the chlorocyclononatetraenide **2c** is obtained (ca. 50%) upon treating 9,9-dichlorobicyclo[6.1.0]nona-2,4,6-triene (**9**) with lithium.



(12) E. J. Corey and M. Chaykovsky, *J. Am. Chem. Soc.*, **84**, 866 (1962).

Information regarding the relative acidity of cyclononatetraene was sought through n.m.r. studies of the reaction of **2a** with cyclopentadiene. It is not possible to obtain an accurate equilibrium value in this case

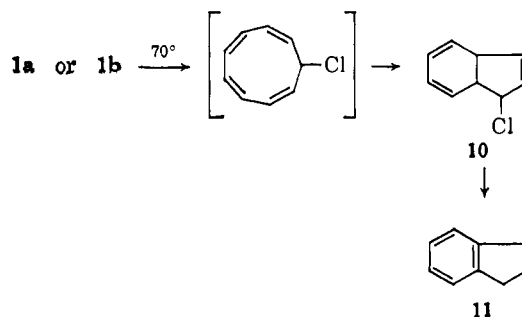


because of the reactivity of both cyclopentadiene and cyclononatetraene. However, from the integrated areas of the absorption in the n.m.r. of $C_5H_5^-$, $C_9H_9^-$, and C_5H_6 , an "apparent" equilibrium constant of less than 0.4 was observed over $C_5H_6/C_9H_9^-$ concentration ratios of 3.75 to 17.5, and reaction periods of up to 100 hr. This result suggests that $C_9H_9^-$ is more thermodynamically stable than $C_5H_5^-$.

On the other hand, no proton exchange between the lithium salt **2a** and indene was observed over a 42-day period. Since proton exchange of cyclononatetraenide occurs with cyclopentadiene but not with indene, it appears that the pK of cyclononatetraene lies between 16 and 21 on the scale proposed by Streitwieser.¹³

Some comment regarding the synthesis and properties of the intermediate 9-chlorobicyclo[6.1.0]nona-2,4,6-triene (**1**) should be made. The best conditions involve slowly adding the methyl lithium solution (1 mole) to a stirred mixture of cyclooctatetraene (3 moles) and methylene chloride (2 moles). We have also prepared the chlorocyclopropane **1** in 52% yield by using the cyclooctatetraene dianion-chloroform method of Katz and Garratt,⁴ since this preparation is more easily carried out on a larger scale. Although they report⁴ that the higher boiling *syn* isomer **1a** appears not to be formed in this reaction, we have noted its presence (16%) as would be expected from a simple bis-nucleophilic displacement reaction.

The chlorocyclopropane mixture **1** is best stored under nitrogen at -30° or lower since it slowly isomerizes to 1-chloro-8,9-dihydroindene (**10**). At 70° this transformation can be carried out in good yield within 5 hr. Since both **1a** and **1b** undergo thermal isomeriza-



tion to chlorodihydroindene (**10**) of the same, though unestablished stereochemistry, chlorocyclononatetraene may be the common intermediate in these transformations. Prolonged heating of **1** at 70° (48 hr.) resulted in formation of a mixture consisting of 1-chloro-8,9-dihydroindene (**10**, 41%), indene (**11**, 44%), and unchanged **1** (15%). It is of interest that both 9-chlorobicyclo[6.1.0]nonatriene (**1a** and **1b**) and 1-chloro-8,9-dihydroindene (**10**) react at room temperature with tetracyanoethylene to give the same adduct **7b** although, as indicated above, higher temperatures are required to effect the isomerization of **1** to **10** within the reaction period involved.

(13) A. Streitwieser, Jr., *Tetrahedron Letters*, **6**, 23 (1960).

Experimental¹⁴

9-Chlorobicyclo[6.1.0]nona-2,4,6-triene (*syn-anti*, 3:1) (**1a** and **1b**). To a magnetically stirred solution of 20 g. (0.192 mole) of cyclooctatetraene and 16.5 ml. (0.256 mole) of dry methylene chloride there was added dropwise 38 ml. of a 1.27 *M* solution of methyl-lithium¹⁵ in ether. More cyclooctatetraene (20 g., 0.192 mole) was then added, and the dropwise addition of methyl-lithium solution was continued (total 101 ml., 0.128 mole of CH₃Li). The addition of methyl-lithium took place over a period of 125 min. after which the reaction mixture was stirred at ambient temperature for 30 min. The product was taken up in ether and washed with water until the washings were no longer basic. The ether was removed from the filtered, dried (MgSO₄) solution by distillation *in vacuo* using an 18-in. spinning band column. Continued distillation at a bath temperature of 40° gave 26 g. of unreacted cyclooctatetraene, b.p. 28° (10 mm.), *n*^{24D} 1.5342. The remaining product was distilled through a 3-in. Vigreux column to give 5.41 g. (28% conversion, 56% yield) of a *syn-anti* (3:1) mixture of **1a** and **1b**, b.p. 26° (0.35 mm.) to 40° (0.25 mm.). The *anti* isomer has the lower boiling point. The product is best stored under nitrogen at -30° or lower.

Anal. Calcd. for C₉H₉Cl: C, 70.82; H, 5.94; mol. wt., 152.63. Found: C, 70.76; H, 6.14; mol. wt., 152 (mass spectrometry).

¹H n.m.r. (CDCl₃ solution) showed a multiplet 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 multiplet at 1.83 (allylic cyclopropane H); $\lambda_{\text{max}}^{\text{isooctane}}$ 248 m μ (ϵ 3080); $\lambda_{\text{max}}^{\text{CCl}_4}$ 1.67 μ ($\log \epsilon$ 0.79) and 1.71 μ ($\log \epsilon$ 1.50); $\lambda_{\text{max}}^{\text{neat}}$ 3.30, 3.34, 6.08, 6.18, 7.85, 12.36, 12.65, 12.9, 13.98, and 14.78 μ .

Lithium Cyclononatetraenide (2a). The reaction was carried out under an argon atmosphere using a magnetic stirrer. A 30% lithium-wax dispersion containing 2% sodium (0.313 g., 13.5 mg.-atoms of lithium) was stirred with 5 ml. of dry tetrahydrofuran to dissolve the wax matrix. The tetrahydrofuran (THF) was then removed by pressure filtration through a fritted glass cylinder. After a total of three extractions, 1 g. (6.5 mmoles) of a *syn-anti* (3:1) mixture of 9-chlorobicyclo[6.1.0]nona-2,4,6-triene in 5 ml. of dry THF was added through a serum cap by means of a syringe. The reaction mixture was cooled for 15 min. with an ice-water bath to compensate for the mild exothermic reaction which occurs within 5-10 min. The reaction is usually complete after stirring at ambient temperature for 2 hr. (60-65% yield based on ¹H n.m.r.). The reaction is slower when a mechanical paddle-type stirrer is used or when small pieces of lithium are used; ¹H n.m.r. 6.72 (width at half-height no greater than 0.8 c.p.s.); ¹³C n.m.r., doublet at +19.0 with benzene as external reference, *J* = 137 c.p.s.¹⁶

(14) Unless otherwise indicated, n.m.r. data are reported as δ in p.p.m. from internal tetramethylsilane which is taken as 0.

(15) The reagent, prepared from methyl chloride, was purchased from the Foote Mineral Co.

(16) We are indebted to Dr. H. Foster for the C¹³ n.m.r. studies, which were carried out at 14.2 Mc./sec. with solutions twice as concentrated as that described above. The chemical shift and coupling constant were determined by measuring the chart distance between the C₉H₉⁻ resonance and the low-field triplet of the tetrahydrofuran solvent

Lithium cyclononatetraenide was also prepared in 1,2-dimethoxyethane or bis(2-methoxyethyl) ether. Although solutions of lithium cyclononatetraenide rapidly react with oxygen, they are quite stable under an inert atmosphere. Thus, upon heating a solution of the anion in diethylene glycol dimethyl ether at 160° for 30 hr., 70% of the lithium cyclononatetraenide remains unchanged.

Tetraethylammonium Cyclononatetraenide (3). To a stirred solution of **2a** in THF solution there was added a solution of 1 g. (6.03 mmoles) of anhydrous tetraethylammonium chloride in 10 ml. of dry chloroform. After stirring for 3 min., 10 ml. of chloroform was added and the precipitate was collected by filtration under nitrogen and washed with more chloroform to give 1.02 g. of crude, white tetraethylammonium salt **3**. An analytical sample was prepared by recrystallizing the product under nitrogen two times from anhydrous acetonitrile (10 ml./100 mg. of salt), m.p. 318° (dec., sealed capillary).

Anal. Calcd. for C₁₇H₂₉N: C, 82.52; H, 11.81; N, 5.66. Found: C, 82.30; H, 11.55; N, 5.75.

Although it was subsequently found that **3** reacts with chloroform, the above conditions have thus far led to the most readily purifiable product; ¹H n.m.r. (dimethyl-*d*₆ sulfoxide) 6.82 (width at half-height no greater than 0.6 c.p.s.), quartet at 3.03 (CH₂, *J* = 7 c.p.s.), and triplet of triplets at 1.05 p.p.m. (CH₃, *J* = 7 and *ca.* 1.5 c.p.s.); $\lambda_{\text{max}}^{\text{CH}_3\text{CN}}$ 250 m μ (ϵ 66,300), and doublet at 317 and 322 m μ (ϵ 6630 and 6750, respectively); $\lambda_{\text{max}}^{\text{KBr}}$ 3.25 (w), 3.31 (m), 3.34 (s), 3.43 (s), 3.48 (m), 5.18 (w), 5.28 (w), 5.61 (w), 6.26 (w), 6.77 (s), 6.88 (m), 6.96 (s), 7.20 (s), 7.28 (m), 7.48 (w), 8.55 (s), 9.18 (w), 9.40 (w), 9.48 (w), 9.99 (s), 11.06 (w), 11.87 (s), and 12.78 (s) μ .

Hydrogenation of Lithium Cyclononatetraenide (2a) to Cyclononane. To a solution of **2a** prepared from 4 g. (27 mmoles) of 9-chlorobicyclo[6.1.0]nona-2,4,6-triene, 1.25 g. (54 mg.-atoms) of 30% lithium dispersion in wax containing 2% sodium and 20 ml. of THF, there was added 4 g. of 5% platinum-on-carbon catalyst and 20 ml. of THF. The reaction mixture was shaken overnight in a Parr apparatus with hydrogen at 30 p.s.i. The solvent was removed by distillation at atmospheric pressure, and the residue was distilled (to a pot temperature of 300° at 35 mm.) using a short-path apparatus to give 1.339 g. of a pale yellow liquid. Analysis by g.l.c. using a 6 ft. \times 0.25 in. column containing 20% 1,9-dicyano-3,7-dioxo-5,5-bis(2-cyanoethoxymethyl)nonane on 60-80 mesh firebrick indicated a complex mixture of 14 compounds. The compound present in the largest amount whose peak had a relative area of 31.3% was found to be cyclononane (characterized by comparison of retention time with that of an authentic sample¹⁷ and by mass spectrometry).

Reaction of Lithium Cyclononatetraenide with Water to Give Oil A. A solution of lithium cyclononatetraenide in 5 ml. of THF, prepared from 1 g. (6.53 mmoles) of 9-chlorobicyclo[6.1.0]nona-2,4,6-triene, was

and comparing this value with the observed chart distance between the benzene doublet and the low-field THF triplet (δ = 61 p.p.m.) as determined at identical instrument settings for a benzene-tetrahydrofuran solution.

(17) We are grateful to Drs. A. T. Blomquist and G. Denning for providing an authentic sample of cyclononane.

cooled with a Dry Ice-acetone bath. Water (3 ml.) was added and the reaction mixture was stirred in the cold for 12 min., allowed to warm slightly, and taken up in ether. The ether solution was washed with water until the washings were no longer basic. The dried (MgSO₄) ether solution was concentrated under slightly reduced pressure to give a yellow oil (672 mg., 87%). All of the above operations were carried out within 36 min. from the time of the addition of water; $\lambda_{\text{max}}^{\text{hexane}}$ 258 μ (ϵ 2690 assuming C₉H₁₀).

Anal. Calcd. for C₉H₁₀: C, 91.46; H, 8.53. Found: C, 89.07; H, 8.46.

Analysis (g.l.c.) using a 6 ft. \times 0.25 in. column containing 20% Apiezon L on firebrick at a temperature of 150° and a preheater temperature of 172° (flow rate of 66 ml./min.) showed the presence of two volatile compounds at retention times of 9.9 and 15.7 min. which were characterized by mass spectroscopy. The 9.9-min. peak was shown to be due to 8,9-dihydroindene (12% of the yellow oil), and the compound having the 15.7-min. peak was characterized as indene (*ca.* 12%). The amount of indene in the yellow oil appeared to increase upon standing at ambient temperature. Moreover, the relative amounts of 8,9-dihydroindene and indene varied somewhat from experiment to experiment.

The amount of 8,9-dihydroindene present could be confirmed chemically. Distillation of the oil obtained from the reaction involving 5.237 g. of 9-chlorobicyclo[6.1.0]nona-2,4,6-triene gave 1 g. of liquid, b.p. 60–80° (26 mm.), which was dissolved in 20 ml. of THF and treated with 0.8 g. of tetracyanoethylene. The reaction mixture quickly turned red and then became amber in color. After 1.5 hr. at ambient temperature, the solvent was removed using a gentle stream of nitrogen, and the residue was crystallized from methylene chloride-ether to give 0.97 g. (equivalent to 12% of 8,9-dihydroindene in the yellow oil A) of adduct **7a**. An analytical sample, m.p. 235–236° dec., was obtained after two recrystallizations from methylene chloride-ether.

Anal. Calcd. for C₁₅H₁₀N₄: C, 73.15; H, 4.09. Found: C, 73.16, 73.52; H, 4.33, 4.52.

This Diels-Alder product **7a** was identical with that prepared in quantitative yield from 8,9-dihydroindene and tetracyanoethylene in THF.

The following evidence suggests the presence of cyclononatetraene in the yellow oil A obtained upon treating **2a** with water.

A. Conversion of A to Sodium Cyclononatetraenide. The yellow oil A (1.05 g.) prepared as above was dissolved in 2 ml. of dimethyl sulfoxide and added at 25° to a solution of methylsulfinyl carbanion prepared by stirring 0.49 g. (10.9 mmoles) of a 53.5% sodium hydride dispersion in mineral oil in 8 ml. of dimethyl sulfoxide at 65° for 1 hr. The reaction mixture immediately turned dark. Within 50 min. sodium cyclononatetraenide **2b** had formed (13%, ¹H n.m.r. 6.90) along with the same anion that is obtained from 8,9-dihydroindene and methylsulfinyl carbanion. No further change in the n.m.r. spectrum of the reaction mixture was observed after 2–3 hr.

B. Reduction of A to Cyclononane. An ether solution of the yellow oil A prepared from 3 g. of 9-chlorobicyclo[6.1.0]nona-2,4,6-triene was hydrogenated for 2

hr. in a Parr apparatus at 30 p.s.i. using 3 g. of 5% platinum-on-carbon catalyst. The reaction mixture was filtered, the ether was removed, and the residue was distilled through a short-path still to give 1.75 g. of a liquid, b.p. to 190°, which was analyzed by g.l.c. using a 6 ft. \times 0.25 in. column containing 20% 1,9-dicyano-3,7-dioxa-5,5-bis(2-cyanoethoxymethyl)nonane on 60–80 mesh firebrick. Twelve peaks were noted. The largest peak having a relative area of 46% was found to be due to cyclononane (identified by mass spectroscopy).

Sodium Cyclononatetraenide (2b) from Bicyclo[6.1.0]nona-2,4,6-triene and Methylsulfinyl Carbanion. A mixture of 0.4 g. (8.92 mmoles) of 53.5% sodium hydride dispersion in mineral oil in 10 ml. of dry dimethyl sulfoxide was stirred at 65° for 1 hr. and then treated with 1 g. (8.44 mmoles) of bicyclo[6.1.0]nona-2,4,6-triene whereupon the reaction mixture immediately turned green. After stirring for 3.3 hr. at 65–70°, the presence of **2b** (38% yield) was established by ¹H n.m.r. (6.90, width at half-height no greater than 1 c.p.s.).

9,9-Dichlorobicyclo[6.1.0]nona-2,4,6-triene (9). This compound was prepared by adding dichlorocarbene to cyclooctatetraene,^{18,19} b.p. 46° (0.2 mm.); lit.¹⁹ b.p. 56° (0.2 mm.); ¹H n.m.r. (neat) multiplet centered at 5.85 (olefinic H) and 2.25 (allylic cyclopropane H); $\lambda_{\text{max}}^{\text{isooctane}}$ 243 μ (ϵ 3070).

Anal. Calcd. for C₉H₈Cl₂: C, 57.78; H, 4.31; Cl, 37.90. Found: C, 57.51; H, 4.59; Cl, 37.57.

Lithium Chlorocyclononatetraenide (2c). 9,9-Dichlorobicyclo[6.1.0]nona-2,4,6-triene (0.892 g., 4.76 mmoles) was added to a magnetically stirred mixture of 0.25 g. (10.8 mg.-atoms) of 30% lithium dispersion in wax containing 2% sodium (which had been extracted with THF to remove the wax matrix) in 5 ml. of THF. After stirring at ambient temperature for 3 hr. lithium chlorocyclononatetraenide was formed in *ca.* 50% yield (¹H n.m.r. 6.73). The yield appeared to decrease upon allowing the reaction to proceed for a longer time.

N.m.r. Study of Proton Exchange of LiC₉H₉. A. With Cyclopentadiene. A solution of **2a** in tetrahydrofuran was stirred with 0.5 ml. of mercury for 0.5 hr. in order to remove any unreacted lithium. Aliquots (0.3 ml.) were subsequently withdrawn from the refiltered solutions with a hypodermic syringe and added to n.m.r. tubes. Freshly distilled cyclopentadiene was then introduced in varying amounts and more tetrahydrofuran was added as needed to bring the total volume to 0.6 ml. The n.m.r. tubes were then sealed. Concentration ratios of C₅H₆/C₉H₉⁻ from 3.75 to 17.5 were examined. The concentrations of C₉H₉⁻, C₅H₆, and C₅H₅⁻ were easily followed with time by integrating the intensities of their respective peaks.

Apparent equilibrium constants were calculated using the equation $K = [\text{C}_5\text{H}_5^-]^2 / [\text{C}_9\text{H}_9^-][\text{C}_5\text{H}_6]$. Although reproducible results were not achieved, the apparent equilibrium constant was consistently less than 0.4 for reaction periods of up to 100 hr.

B. With Indene. To three n.m.r. tubes containing 0.3-ml. aliquots of LiC₉H₉ in tetrahydrofuran, there were added 0.05 ml., 0.10 ml., and 0.30 ml. of indene.

(18) E. Vogel, *Angew. Chem.*, **74**, 829 (1962).

(19) W. Sanne and O. Schlichting, German Patent 1,029,370 (1957), assigned to Badische Anilin und Soda-Fabrik.

More tetrahydrofuran was then added to bring the total volume to 0.7 ml., and the tubes were sealed. No proton exchange took place within 42 days as determined by n.m.r.

Isomerization of 9-Chlorobicyclo[6.1.0]nona-2,4,6-triene (syn-anti, 3:1) to 1-Chloro-8,9-dihydroindene. A sealed ampoule containing 1.186 g. of a mixture (*syn-anti*, 3:1) of 9-chlorobicyclo[6.1.0]nona-2,4,6-triene was heated at 70° for 5 hr. and the product was distilled to give 0.95 g. (80%) of 1-chloro-8,9-dihydroindene, b.p. 28.5° (0.18 mm.); ¹H n.m.r. (neat) multiplet at 5.72 (6 olefinic), multiplet at 4.78 (>CHCl), and quartet of multiplets at 3.45 (2 bridgehead CH).

Satisfactory analytical values were not obtained, but in view of the marked similarity of the n.m.r. spectrum with that of the product resulting from the rearrangement of *anti*-9-chlorobicyclo[6.1.0]nona-2,4,6-triene, there is little question regarding the formation of 1-chloro-8,9-dihydroindene.

Anal. Calcd. for C₉H₉Cl: C, 70.82; H, 5.94. Found: C, 71.93; H, 6.23.

Isomerization of anti-9-Chlorobicyclo[6.1.0]nona-2,4,6-triene. A sealed ampoule containing 11.6 g. of 9-chlorobicyclo[6.1.0]nona-2,4,6-triene (mainly the *anti* isomer) was heated at 70° for 5 hr., and the product was distilled to give 10.6 g. (92%) of 1-chloro-8,9-dihydroindene, b.p. 30° (0.20 mm.); ¹H n.m.r. (neat) multiplet at 5.67, multiplet at 4.73, and quartet of multiplets at 3.47. The multiplets had identical fine structure as observed for the product obtained upon isomerizing the *syn-anti-1a* and *-1b* (3:1) mixture.

Anal. Calcd. for C₉H₉Cl: C, 70.82; H, 5.94; Cl, 23.24. Found: C, 70.90; H, 6.05; Cl, 22.96.

If the heating was carried out at 70° for 48 hr. under a slow stream of nitrogen, a mixture resulted consisting of 1-chloro-8,9-dihydroindene (41%), indene (44%), separated by g.l.c. using 1,9-dicyano-3,7-dioxo-5,5-bis(2-cyanoethoxymethyl)nonane (20%) on 60–80 mesh firebrick, and characterized by mass spectrometry) and 9-chlorobicyclo[6.1.0]nona-2,4,6-triene (15%).

Reaction of 1-Chloro-8,9-dihydroindene with Tetracyanoethylene to Give 7b. To a solution of 1.73 g. (13.5 mmoles) of TCNE in 20 ml. of THF was added 2.06 g. (13.5 mmoles) of 1-chloro-8,9-dihydroindene.

The reaction mixture which immediately turned red was allowed to stand at ambient temperature for 3.75 days and taken to dryness, and the product was crystallized from methylene chloride-ether to give 2.16 g. (57%) of the adduct **7b**, m.p. 230.5–231° dec. This product was identical with that obtained from 9-chlorobicyclo[6.1.0]nona-2,4,6-triene and TCNE.

Reaction of 9-Chlorobicyclo[6.1.0]nona-2,4,6-triene with Tetracyanoethylene to Give 7b. A solution of 1.73 g. (13.5 mmoles) of TCNE and 2.06 g. (13.5 mmoles) of 9-chlorobicyclo[6.1.0]nona-2,4,6-triene in 20 ml. of THF immediately turned amber. After standing for 3 days at ambient temperature the reaction mixture was taken to dryness, and the residue was crystallized from methylene chloride-ether to give 1.90 g. (50%) of the adduct **7b**. An analytical sample, prepared by two recrystallizations from methylene chloride-ether, had m.p. 230–231° dec.

Anal. Calcd. for C₁₃H₉ClN₄: C, 64.17; H, 3.23; Cl, 12.63; N, 19.96. Found: C, 64.13; H, 3.21; Cl, 12.35; N, 19.97.

9-Chlorobicyclo[6.1.0]nona-2,4,6-triene (syn-anti, 1:5.3) (1a and 1b) from Cyclooctatetraene Dianion. To a solution of 80 g. (0.758 mole) of cyclooctatetraene in 1000 ml. of dry THF there was added under nitrogen over a period of 45 min. 60 g. (1.53 g.-atoms) of potassium. The reaction mixture was cooled with a Dry Ice-benzene bath as required to keep the temperature at 20–25°. After stirring at ambient temperature for 1.75 hr., 110 ml. of dry chloroform was added over a period of 28 min., cooling with a Dry Ice-acetone bath as necessary to maintain the temperature at 20–25°. The reaction mixture was stirred for 5 min., 200 ml. of water was added, and the mixture was poured into 4000 ml. of water. The product was taken up in ether and the ether solution was washed with water and dried (MgSO₄). Distillation of the residue obtained after removal of the ether gave 15.2 g. of recovered cyclooctatetraene and 48.82 g. (52% based on recovered cyclooctatetraene) of 9-chlorobicyclo[6.1.0]nona-2,4,6-triene, b.p. 26 (0.25 mm.) to 35° (0.35 mm.). The product consisted of 16% of the *syn* isomer and 84% of the *anti* isomer as determined from n.m.r. studies. The inverse addition of the cyclooctatetraene dianion to chloroform gave similar results (22% *syn*).