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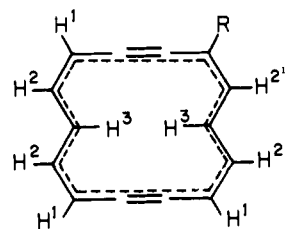
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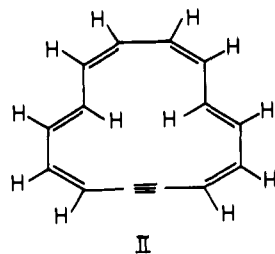
Electrophilic Substitution of Aromatic Fourteen-Membered Ring Cyclic Conjugated Systems¹

Sir:

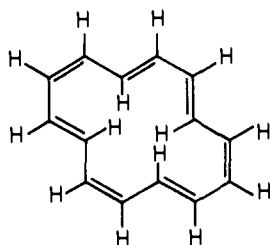
1,8-Bisdehydro[14]annulene (Ia)²⁻⁴ and monodehydro[14]annulene (II or III)^{2,5} have been shown to be aromatic compounds, since they sustain an induced ring current as demonstrated by nuclear magnetic resonance (n.m.r.) spectroscopy.^{3,5} On the other hand, [14]annulene (IV)^{2,6} on this basis is nonaromatic.^{1,5} Aromatic character has usually been associated with the ability to undergo electrophilic substitution reactions (although this need not necessarily be true for all aromatic systems^{1,5,7}). We now report that the two aromatic dehydroannulenes Ia and II (or III) in fact do undergo such substitution reactions, whereas the nonaromatic [14]annulene (IV) under analogous conditions does not.



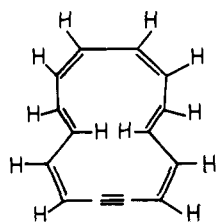
Ia, R=H Ic, R=SO₃Me
b, R=NO₂ d, R=COMe



II



III



IV

1,8-Bisdehydro[14]annulene (Ia) underwent substitution at the position adjacent to the acetylene. Nitration with cupric nitrate in acetic anhydride at room temperature yielded *ca.* 25% of mononitro compound Ib as black needles, which decomposed above 200° on heating [$\lambda_{\max}^{\text{isooctane}}$ 327, 467, and 605 μm (ϵ 85,500, 19,000, and 7800); $\lambda_{\max}^{\text{benzene}}$ 337, 476, and 608 μm ;

(1) This is Part XXXI in the series "Unsaturated Macroyclic Compounds"; for Part XXX, see F. Sondheimer, *Pure Appl. Chem.*, **7**, 363 (1963).

(2) F. Sondheimer and Y. Gaoni, *J. Am. Chem. Soc.*, **82**, 5765 (1960).

(3) F. Sondheimer, Y. Gaoni, L. M. Jackman, N. A. Bailey, and R. Mason, *ibid.*, **84**, 4595 (1962).

(4) N. A. Bailey and R. Mason, *Proc. Chem. Soc.*, 180 (1963).

(5) L. M. Jackman, F. Sondheimer, Y. Amiel, D. A. Ben-Efraim, Y. Gaoni, R. Wolovsky, and A. A. Bothner-By, *J. Am. Chem. Soc.*, **84**, 4307 (1962).

(6) J. Bregman, *Nature*, **194**, 679 (1962).

(7) F. Sondheimer, R. Wolovsky, and Y. Amiel, *J. Am. Chem. Soc.*, **84**, 274 (1962).

Anal. Found: N, 5.41]. The n.m.r. spectrum (100 Mc./sec., CDCl₃ solution) clearly points to structure Ib; it consists of two symmetrical 1-proton triplets at 15.25 and 14.85 τ ($J = 13.5$ c.p.s.) assigned to the inner H³ protons, a 3-proton multiplet at 1.30 τ assigned to H¹, a 3-proton multiplet at 0.33 τ due to H², and a 1-proton doublet at -0.43 τ ($J = 13.4$ c.p.s.) due to H^{2'} (the proton adjacent to the substituent).

Sulfonation of Ia with oleum in dioxane at room temperature gave a water-soluble sulfonic acid ($\lambda_{\max}^{\text{water}}$ 314, 440, and 590 μm), which was converted to the silver salt with aqueous silver nitrate and then methylated with methyl iodide. The resulting monomethyl sulfonate (Ic), formed in *ca.* 30% yield, crystallized as red needles, m.p. 168–169° dec. [$\lambda_{\max}^{\text{isooctane}}$ 315, 442, and 591 μm (ϵ 179,000, 20,400, and 7700); $\lambda_{\max}^{\text{benzene}}$ 321, 448, and 591 μm ; *Anal.* Found: C, 66.80; H, 4.73]. The n.m.r. spectrum (100 Mc./sec., CDCl₃ solution) consists of two incompletely resolved symmetrical 1-proton triplets at 14.95 and 14.71 τ ($J = 13.2$ c.p.s.) due to the inner H³ protons, a 3-proton singlet at 5.99 τ due to the methyl hydrogens, a 3-proton multiplet at 1.33 τ assigned to H¹, a 3-proton multiplet at 0.25 τ assigned to H², and a 1-proton doublet at -0.11 τ ($J = 13.4$ c.p.s.) due to H^{2'}.

Acylation of Ia with acetic anhydride and boron trifluoride etherate in methylene chloride at room temperature gave an acetyl compound in low yield, to which structure Id is tentatively assigned by analogy; it formed brown crystals [$\lambda_{\max}^{\text{ether}}$ 321, 451, and 608 μm (relative intensities, *ca.* 20:3:1); 2,4-dinitrophenylhydrazones: $\lambda_{\max}^{\text{benzene}}$ 505 and 619 μm]. The amount of material was insufficient for further investigation. Another acetyl compound with unusual ultraviolet properties was also formed, as will be described in a later publication.

Monodehydro[14]annulene (II or III) on nitration under the above-mentioned conditions gave *ca.* 20% of a mononitro compound as dark brown needles, m.p. 185–186° dec. [$\lambda_{\max}^{\text{isooctane}}$ 328 and 425 μm (ϵ 59,500 and 8300); $\lambda_{\max}^{\text{benzene}}$ 335 and 435 μm ; *Anal.* Found: N, 6.67]. The n.m.r. spectrum (56.4 Mc./sec., CDCl₃ solution) consists of two doublets at 10.61 and 10.72 τ assigned to the two inner protons, as well as a complex band in the 2.67–0.91 τ region due to the outer protons. Nitration must have resulted in substitution of one of the outer protons, but the exact point of attack has not been determined.

Sulfonation of monodehydro[14]annulene and subsequent methylation, as above, gave a *ca.* 4:1 mixture of two isomeric monomethyl sulfonates as dark red plates, m.p. 153–154° [$\lambda_{\max}^{\text{isooctane}}$ 314, 367, and 400 μm (ϵ 74,500, 6000, and 5300); $\lambda_{\max}^{\text{benzene}}$ 321, 371, and 406 μm ; *Anal.* Found: C, 65.32; H, 4.99]. That this was in fact a mixture was shown by thin layer chromatography (two spots of very similar polarity) and by the fact that the methyl proton signals in the n.m.r. spectrum (60 Mc./sec., CDCl₃ solution) appeared as two distinct peaks at 6.12 and 5.91 τ . Acylation of monodehydro[14]annulene with acetic anhydride, as above, led in low yield to an acetyl derivative [$\lambda_{\max}^{\text{ether}}$ 329 and 420 μm (relative intensities, *ca.* 7.5:1)].

[14]Annulene (IV) on attempted nitration, sulfonation, and acylation under the conditions used with the dehydro compounds gave no comparable substitution products. In no case did we observe the formation of a substance with a higher wave length maximum in the ultraviolet than the starting material, and decomposition of the latter usually resulted.

1,8-Bisdehydro[14]annulene (Ia) was found to form 1:1 π -complexes with compounds such as 1,3,5-trinitrobenzene; the complex with the latter crystallized as

dark red needles, m.p. 222–223° dec. (*Anal.* Found: N, 11.19). Similarly monodehydro[14]annulene (II or III) with 1,3,5-trinitrobenzene gave a 1:1 adduct as long red needles, m.p. 182–183° dec. (*Anal.* Found: C, 61.66; H, 3.80; N, 11.20). No comparable complex could be obtained from [14]annulene (IV).

The reaction of the 14-membered ring conjugated compounds with maleic anhydride also appears to be related to their aromatic nature. Thus, 1,8-bisdehydro[14]annulene on treatment with an excess of the anhydride in boiling benzene for 1 hr. was completely unchanged, monodehydro[14]annulene under these conditions was recovered to the extent of 85%, while less than 10% of the nonaromatic [14]annulene was unaffected.

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The Hyperfine Coupling Constants and Rates of Exchange for $C^{13}N^-$ with the Axial and Equatorial Positions in $Cr(CN)_5NO^{-3}$

Sir:

It has been recently reported^{1,2} that the magnetic hyperfine interaction of C^{13} was observable in the paramagnetic resonance spectrum of aqueous solutions of $Cr(CN)_5NO^{-3}$. It seemed probable that this interaction was only due to the equatorial CN^- , but the possible axial coupling remained unknown. In a preliminary report³ of the exchange with $C^{13}N^-$ we were also unable to differentiate between the axial and equatorial positions. We have now been able to prepare the complex by exchange with C^{13} substituted primarily in the axial position and by synthesis with every cyanide substituted by $C^{13}N^-$. Both the hyperfine interaction and the rates of exchange of the axial and equatorial positions have now been clearly resolved:

Samples of $K_3Cr(CN)_5NO$ were synthesized⁴ utilizing NaCN enriched to 55% in C^{13} isotope. The largest hyperfine splitting in the p.m.r. spectrum of $Cr(CN)_5NO^{-3}$ should arise from the species containing⁵ Cr^{53} , N^{14} , and five C^{13} . In the X-band spectrum of the enriched sample, clearly resolved lines occur 62.4 gauss above and below the center of the spectrum. Since these lines must be due to a combination of axial and equatorial C^{13} hyperfine interaction, this splitting can be combined with the previously assigned^{1,2} Cr^{53} , N^{14} , and C^{13} equatorial splittings to yield a value of 8.55 ± 0.4 gauss for the axial C^{13} coupling constant.

A prominent hyperfine line can also be observed between the C^{12} and the expected equatorial C^{13} lines when the complex is exchanged in solutions containing nearly equal amounts of C^{13} enriched CN^- and HCN. Direct measurement of this line gives 8.93 ± 0.2 gauss for the axial C^{13} coupling constant. Our values can be compared to the 8.43 ± 0.2 gauss reported by Kuska and Rogers⁶ from a resolution of the complex pattern observed for both axial and equatorial C^{13}

TABLE I
HYPERFINE COUPLING CONSTANTS

	A, gauss
Cr^{53}	18.39 ± 0.05
N^{14}	5.27 ± 0.05
C_e^{13}	12.64 ± 0.2
C_a^{13}	8.80 ± 0.3

substitution. A summary of our coupling constants is given in Table I.

In the temperature range 60–100°, the exchange with $C^{13}N^-$ can be observed without decomposition of the complex. We have followed the decrease in the signal due to unsubstituted complex and the increase in the signal resulting from equatorial C^{13} substitution while the samples were held at constant temperature in the microwave cavity of a p.m.r. spectrometer. In solutions ranging from 0.015 to 0.035 *F* in complex and 0.1–0.2 *F* in NaCN (55% in C^{13} isotope), we followed the adjacent lines for unsubstituted and C^{13} equatorial-substituted complex for the Cr^{53} species until approximately 50% of the complex was substituted with one $C^{13}N^-$. These experiments were conducted in the nearly complete darkness of the cavity. In separate experiments no pronounced light catalysis, as reported for other cyanide complexes,⁷ was observed.

These exchange data were fit by rate laws assuming first order in unsubstituted complex and zero order in total CN^- concentration. An integrated rate law was used which took into account the possible substitution of the axial and one of the four possible equatorial CN^- . The total rate constant $k_a + 4k_e$ can be directly obtained from the decrease in the unsubstituted complex and the equatorial rate constant k_e can be evaluated by successive approximation from the growth of the equatorial C^{13} signal. At 75° we obtain $k_a = 1 \times 10^{-4}$ sec.⁻¹ and $k_e = 7 \times 10^{-6}$ sec.⁻¹. Over the range of temperatures we get $\Delta H_a^* = 33.5 \pm 4$ kcal./mole, $\Delta S_a^* = 18 \pm 8$ e.u., $\Delta H_e^* = 30.5 \pm 4$ kcal./mole, and $\Delta S_e^* = 5 \pm 8$ e.u. In the solutions prepared by adding NaCN to neutral solutions of the complex, the ratio $k_a/4k_e = 4 \pm 2$ over the full range of temperature.

The apparent large positive value for ΔS_a^* indicates⁸ that the activated complex for axial exchange is a protonated species. The formation of $HCr(CN)_5NO^{-2}$ by the removal of the proton from HCN could contribute about 40 e.u. to the apparent entropy of activation. When exchange experiments are conducted in acidified solutions so that both CN^- and HCN have nearly equal concentrations, the axial rate is accelerated. In this case, as previously mentioned, a line due to axial substitution becomes prominent before the equatorial line is clearly observable. It seems probable that the formal charge of +1 on the NO group makes the axial CN^- more likely for protonation than the more adjacent equatorial CN^- . It is possible from our data, however, that the equatorial exchange is also partly acid-catalyzed.

The similar values for the N^{14} and both C^{13} coupling constants do not give any clear contradiction or support to the bonding scheme proposed⁹ for these complexes. The axial CN^- is more labile to exchange in aqueous solution primarily because of greater protonation at this position, and the enthalpies of activation are equally large for both positions. The theory for the isotropic hyperfine interaction in these compounds is necessarily complex, and both the signs of the coupling constants

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(8) We wish to thank Professor R. E. Connick for suggesting this possibility to us.

(9) H. B. Gray, I. Bernal, and E. Billig, *J. Am. Chem. Soc.*, **84**, 3404 (1962).

(1) R. G. Hayes, *J. Chem. Phys.*, **38**, 2580 (1963).

(2) I. Bernal and S. E. Harrison, *ibid.*, **38**, 2581 (1963).

(3) J. B. Spencer and R. J. Myers, presented before the Inorganic Division of the American Chemical Society, 144th National Meeting, Los Angeles, Calif., April, 1963.

(4) W. P. Griffith, J. Lewis, and G. Wilkinson, *J. Chem. Soc.*, 872 (1959).

(5) There is no observable hyperfine interaction from the N^{14} in the CN^- ; Cr^{53} is 9.5% abundant.

(6) H. A. Kuska and M. T. Rogers; we wish to thank Professor Rogers for sending us a pre-publication copy of their work.