Donovan and Hussain[4b] of a rather efficient conversion of the electronic energy of $CO(a\,^3\Pi)$ to vibrational energy in CO(X) in the presence of H_2 suggests the lack of a chemical reaction leading to products which incorporate CO into their structure. Another argument against a chemical interaction for hydrogen is the very small isotope effect for quenching by deuterium (see Table I).

Acknowledgments. We thank the National Air Pollution Control Administration Public Health Service, Grant No. AP-00391, and the U. S. Army Research Office (Durham) for financial support. We also thank Dr. Tom Slanger, Stanford Research Institute, for correspondence concerning the reactions and properties of $N_2(A)$ and CO(a).

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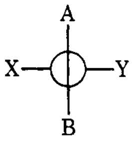
The Absolute Configuration of (+)-1,2-Cyclononadiene[1]

Sir:

Relatively few allenes of established absolute configuration are known and methods for determining configuration are fewer still.[2] Based on the original helical model of optical activity which Brewster proposed[3] and has subsequently amplified,[4] Lowe[5] proposed the rule summarized below for predicting the absolute configuration of an allene from its rotation[6] at the sodium D line and the relative polarizabilities of the substituents on the allenic linkage. For a 1,3-dialkylallene, Lowe's rule predicts that the *R* enantiomer (A = X = R; B = Y = H) will be levorotatory. We note that Lowe[5] was careful to restrict his rule to allenes with substituents "...which present no problems of conformational asymmetry."

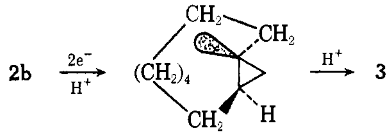


Polarizability	Sign of rotation at the D line
A > B; X > Y	(−)
A > B; X < Y	(+)

1,2-Cyclononadiene (**1**), the smallest isolable cyclic allene, presents a most interesting system for consideration. While at first inspection **1** may appear to be a fitting case for application of Lowe's rule, further reflection makes evident the fact that the *allenic linkage induces dissymmetry into the methylene chain by restricting it conformationally.* Our suspicion that, as a consequence of this additional dissymmetry, the absolute configuration of **1** might not be predictable by Lowe's rule was increased on comparing the optical rotatory dispersion (ORD) and circular dichroism (CD) of **1** with the corresponding curves of allenes which lack conformational dissymmetry and thus should follow Lowe's rule. Thus, (+)-**1** shows a *positive* Cotton effect in the same region of the ultraviolet where (+)-1,3-dimethylallene[7a] and (+)-1,3-di-*tert*-butylallene[7a] show *negative* Cotton effects.[7b]

Since the configuration of **1** is of interest with respect to both optical properties and mechanistic studies,[2b] we sought to establish it in a way which, hopefully, would also develop principles of general significance. The method we now describe consists of a stereospecific addition, a stereospecific reduction, and a clear-cut ORD-CD correlation.

Addition of dibromocarbene to (+)-**1** gives the adduct **2a**.[8] This addition can occur *only from the "outside" of the molecule* since the topology is such that the methylene chain effectively screens one side of each double bond (*i.e.*, the double bond of **2a** is cis). Reduction of **2a** with sodium in liquid ammonia with ether as a cosolvent and *tert*-butyl alcohol as a necessary proton donor gives (+)-*trans*-bicyclo[7.1.0]decane (**3**) as the main product along with some *cis*- and *trans*-cyclodecene.[9] The cis isomer of **3** is not formed. This reaction must proceed by initial reductive replacement of the bromine atoms to give **2b**.[10] Subsequent reduction of **2b** by a sequence of electron addition–protonation–electron addition must generate a trans carbanion as the immediate precursor of **3**. The remarkable specificity indicates that a substantial thermodynamic preference for trans over cis substituents on a cyclopropane ring[11] is not diminished at the carbanion stage.[12]



This scheme establishes that **1**, **2**, and **3** are configurationally related as shown in the accompanying formulas. (Although absolute configurations are given, at this point only relative configurations are known.)

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(1) Acknowledgment is made to the National Science Foundation for support of this research (GP 25216).

(2) (a) For a review, see G. Krow, *Top. Stereochem.*, **3**, 31 (1970). Krow has assigned the incorrect configuration to (−)-**1** (pp 38–39) based on the assumption that the opening of the three-membered ring of the carbenoid precursor[2b,14] occurred in the same sense as that found by Jones[2c] for cyclopropylidenes leading to acyclic allenes. (b) W. R. Moore and R. D. Bach, *J. Amer. Chem. Soc.*, in press. (c) W. M. Jones and J. M. Walbrick, *Tetrahedron Lett.*, 5229 (1968), and references cited therein.

(3) J. H. Brewster, *J. Amer. Chem. Soc.*, **81**, 5475 (1959).

(4) J. H. Brewster, *Top. Stereochem.*, **2**, 33 (1967).

(5) G. Lowe, *Chem. Commun.*, 411 (1965).

(6) Following convention, subsequent designation of a compound as (+) or (−) refers to the rotation at the D line.

(7) (a) The ORD and CD measurements employed the (−)-enantiomers; (b) CD $\lambda_{\max}^{\text{pentane}}$ nm ($\Delta\epsilon$), (+)-**1**, 236 (1.2); (+)-1,3-dimethylallene, 223 (−0.6); (+)-1,3-di-*tert*-butylallene, 219 (−1.0). The $\Delta\epsilon$ values are not corrected for optical purity; P. Crabbe, A. F. Drake, S. F. Mason, H. W. Anderson, S. D. Clark, and W. R. Moore, *Chem. Commun.*, in press.

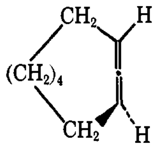
(8) Racemic **2a** has been described: W. R. Moore and T. M. Ozretich, *Tetrahedron Lett.*, 3205 (1967).

(9) These olefins appear to result from reduction of 1,2,3-cyclodecatriene formed by reductive opening of the three-membered ring.[8]

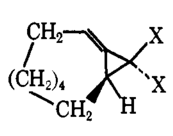
(10) Under these conditions **2b** is reduced to **3**. We have prepared racemic **2b** by reduction of racemic **2a** with tri-*n*-butyltin hydride and by application of the Simmons–Smith reaction to **1**.

(11) While experimental data are lacking, SCF-MO calculations have lead to an estimate that *trans*-1,2-dimethylcyclopropane is 2.6 kcal/mol more stable than the cis isomer: N. C. Baird and M. J. S. Dewar, *J. Amer. Chem. Soc.*, **89**, 3966 (1967).

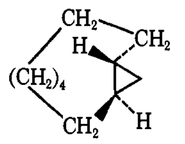
(12) The formally related reduction of derivatives of vinylidenecyclopropane (R. W. Mills, R. D. H. Murray, and R. A. Raphael, *Chem. Commun.*, 555 (1971)) probably involves protonation of allylic (planar) carbanions from either side except when the protonation is intramolecular.



(R)-(+)-1

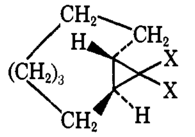


2a, X = Br
b, X = H

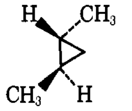


(1R,9R)-(+)-3

As reference compounds, we have prepared (1*R*,8*R*)-(+)-*trans*-bicyclo[6.1.0]nonane (**4b**)[13] by reduction of (1*S*,8*S*)-(+)-8,8-dibromo-*trans*-bicyclo[6.1.0]nonane (**4a**)[14] with sodium in liquid ammonia[15] and (1*R*,2*R*)-(−)-*trans*-1,2-dimethylcyclopropane (**5**) by the method of Doering and Kirmse.[16]



4a, X = Br; (1S,8S)-(+)
b, X = H; (1R,8R)-(+)



(1R,2R)-(−)-5

The ORD and CD curves for (+)-**3**, (+)-**4b**, and (−)-**5**[17] in the ultraviolet are given in Figure 1. It is evident that all three compounds show a positive Cotton effect in the same region of the far ultraviolet.[18] The fact that (+)-**4b** and (−)-**5**, which have the same absolute configuration, show similar ORD–CD behavior in the accessible ultraviolet region yet have rotations of opposite sign at the D line indicates that the observed Cotton effect must mainly reflect the dissymmetry arising from the stereochemical relationship of the substituents (CH_2 or CH_3) immediately attached to the cyclopropane ring rather than more remote substituents. Clearly there must be a negative Cotton effect at shorter wavelengths which is dominant for (−)-**5** (but not for (+)-**4b**) in determining the rotation at the D line.

While **3** and (to a greater extent) **4b** are conformationally mobile, it is evident from examination of molecular models that the most probable conformations retain the local C_2 symmetry of the trans-substituted cyclopropane ring and that the related conformations of **3** and **4b** are topologically very closely similar. Thus, on the basis of its ORD–CD behavior, it is quite clear that (+)-**3** has the same absolute configuration as (+)-**4b**. *Therefore, (+)-**3** can be assigned the 1R,9R configuration, a finding which leads to the conclusion that (+)-**1** has the R configuration.*[19]

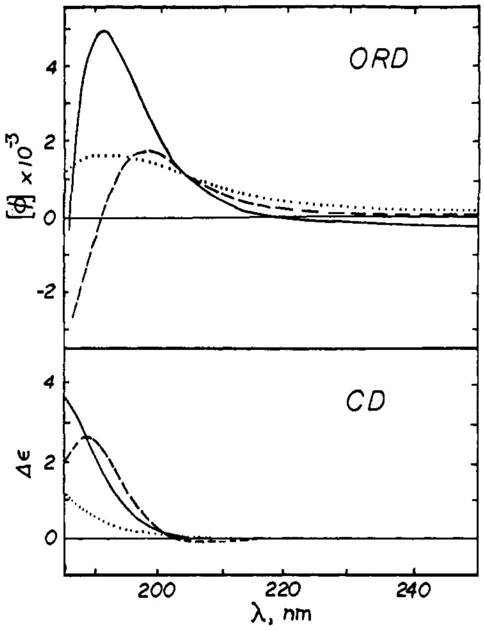


Figure 1. The optical rotatory dispersion and circular dichroism of (+)-**3** (· · ·), (+)-**4b** (---), and (−)-**5** (—).

It is most significant that this assignment is in agreement with a recently formulated sector rule for chiral allenes which predicts, as is observed,[7] a positive CD band for the lowest energy transition of (*R*)-**1**.[20]

It is important to note that if one were to apply Lowe's rule to (+)-**1** the *wrong S* configuration would be predicted. This result emphasizes that Lowe's rule *must* be restricted to chiral allenes having substituents X,Y and A,B which have actual or conformationally averaged symmetry about the X–C–Y and A–C–B planes, respectively.

On the other hand, **1** would appear to provide a fair test for Brewster's more general helical model.[4] To apply this model, one must sum the estimated contributions to the rotatory power from consecutive three-bond helical units over the *entire* molecule. Our calculations indicate that those conformations which appear most probable do correctly predict the sign, if not the magnitude, of the rotation of (*R*)-(+)-**1**.[21]

Finally, we note that the ORD–CD behavior of chiral cyclopropanes in the far-ultraviolet should prove to be useful in other systems to establish absolute configurations. Trans dialkyl-substituted cyclopropanes and, in general, any polyalkylated chiral cyclopropane maintaining at least local C_2 symmetry

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(13) (a) E. J. Corey and J. I. Shulman, *Tetrahedron Lett.*, 3655 (1968); (b) A. C. Cope and J. K. Hecht, *J. Amer. Chem. Soc.*, **85**, 1780 (1963).

(14) A. C. Cope, W. R. Moore, R. D. Bach, and H. J. S. Winkler, *ibid.*, **92**, 1243 (1970).

(15) Professor R. D. Bach has informed us that reduction of **4a** with tri-*n*-butyltin hydride also gives **4b**.

(16) W. von E. Doering and W. Kirmse, *Tetrahedron*, **11**, 272 (1960).

(17) Observed $[\alpha]^{25}$D (*c* 0.5, pentane): (+)-**3**, +36°; (+)-**4b**, +31°; (−)-**5**, −42°.

(18) Saturated hydrocarbons lacking a cyclopropane ring are transparent and show no circular dichroism in this region. The Cotton effect must be associated with a magnetic-dipole allowed–electric-dipole forbidden transition since these cyclopropanes show only relatively weak end absorption (no maxima above 188 nm). Torsional strain in **4b** probably causes this transition to shift somewhat toward the visible and may also account for the very weak negative CD band at *ca.* 208 nm (less than 4% of the principal band). It is noteworthy that **4a** has a CD spectrum similar to that of **4b**, but the *gem*-dibromide (a chromophore) leads to a further red shift and greatly enhanced intensities: λ_{max} 191 nm ($\Delta\epsilon$ +9.9); λ_{min} 221 nm ($\Delta\epsilon$ −1.0).

(19) (a) This assignment is supported by our conclusion (in preparation) based on ORD–CD analysis that partial asymmetric reduction (W. L. Waters, W. S. Linn, and M. C. Caserio, *J. Amer. Chem. Soc.*, **90**, 6741 (1968)) of several 1,3-dialkylallenes including **1** occurs in the same stereochemical sense for all.

(20) (a) The general problem of chiral allenes and the basis of the sector rule are considered elsewhere (see Crabbe, *et al.*, ref 7b). (b) We wish to acknowledge a correspondence concerning chiral allenes with Professor S. F. Mason which has been most stimulating and informative to us.

(21) (a) Calculated values of $[\phi]$D are in the range of +50 to +130° for conformations having C_2 symmetry. (b) Unfortunately the significance of this prediction is clouded by the fact that in another key cyclic system the helical model leads to the incorrect prediction that (*R*)-(−)-*trans*-cyclooctene should be *dextrorotatory*. This discrepancy may in some way be a reflection of an inherently dissymmetric chromophore although Scott[22] has questioned the importance of the latter in his extensive considerations of chiral olefins. Professor Brewster has suggested that one may have to consider longer range helicity (more than three bond units) in this and other cases (including that of **1**).

(22) A. I. Scott and A. D. Wrixon, *Chem. Commun.*, 43 (1970); *Tetrahedron*, **26**, 3695 (1970).

should exhibit ORD–CD behavior analogous to that of the present examples.

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Electrophilic Behavior of Nitrene Coordinated to Iridium(III)

Sir:

It has been proposed[1] that acid-catalyzed decomposition of ruthenium(III) azides proceeds by a mechanism involving an intermediate coordinated nitrene,[2] Ru(III)–NH, which then reacts *via* two separate pathways to yield dinitrogen complexes of Ru(II).

The facile reduction of Ru(III) to Ru(II) makes possible the internal redox reactions which yield these products. We were interested in studying the reactions of coordinated nitrenes where these redox reactions were not possible. The absence of Ir(II)–amine complexes[3] indicated that decomposition of Ir(III) azides (where nitrogen evolution has been previously observed[4]) might yield nitrenes which behaved differently from the Ru(III) systems.

We wish to report the production of an Ir(III) nitrene intermediate from the acid decomposition of $[Ir(NH_3)_5N_3]^{2+}$ salts. An Ir(III)–chloramine complex and an Ir(III)–hydroxylamine complex have been characterized as products of reaction of the Ir(III) nitrene.

Treatment of $[Ir(NH_3)_5N_3]Cl_2$ (1.0 g) in H_2O (20 ml) with concentrated H_2SO_4 (7 ml) resulted in the vigorous evolution of gas and the precipitation of a while solid, A. A solution of $BaCl_2$ (2.0 g) in H_2O (10 ml) was added to a suspension of A (1.25 g) in 0.1 *M* HCl (80 ml). The precipitated $BaSO_4$ was removed by filtration. On addition of 70% $HClO_4$ (40 ml) and cooling, white crystals of $[Ir(NH_3)_5NH_2Cl](ClO_4)_3$ (B) separated, which were collected, washed with ethanol and ether, and air-dried. The yield was 1.25 g, 80% based on $[Ir(NH_3)_5N_3]Cl_2$. *Anal.* Calcd for $[Ir(NH_3)_5NH_2Cl](ClO_4)_3$: N, 13.40; H, 2.73; ClO_4^-, 47.58; Cl, 5.65. Found: N, 13.2; H, 2.8; ClO_4^-, 47.6; Cl, 5.8.

Quantitative measurements showed that 1.01 mol of gas was liberated per mole of $[Ir(NH_3)_5N_3]Cl_2$ and the gas was shown to be nitrogen by mass spectrometry.

Compound B is an air-stable, diamagnetic, white crystalline solid which is stable in aqueous acid but decomposes in neutral or basic solutions. Compound B was characterized by a determination of its charge as 3+ using ion-exchange techniques. On reaction of B with I^-, I_2 is liberated quantitatively (eq 1), a reaction

$$[Ir(NH_3)_5NH_2Cl]^{3+} + 2I^- + H^+ \longrightarrow [Ir(NH_3)_6]^{3+} + Cl^- + I_2 \quad (1)$$

characteristic of free[5] and coordinated[6] NH_2Cl. Decomposition of B in basic solution followed by acidification and treatment with Ag^+ gave a quantitative yield of AgCl. However, treatment of B in acid solution with Ag^+ gave no precipitate. Similar behavior is observed for free NH_2Cl.[5]

Decomposition of $[Ir(NH_3)_5N_3](ClO_4)_2$ with 4.5 *M* H_2SO_4 in the complete absence of Cl^- for 2 days, followed by addition of 70% $HClO_4$, yielded a white solid, C, which was identified as $[Ir(NH_3)_5NH_2OH](ClO_4)_3$. *Anal.* Calcd for $[Ir(NH_3)_5NH_2OH](ClO_4)_3$: N, 13.81; H, 2.98. Found: N, 13.4; H, 3.0.

Compound C was characterized by a determination of its charge as 3+ using ion-exchange techniques. Titration of C with base showed the presence of 1.0 mol of ionizable protons with $pK_a = 9.4$ (literature pK_a values for NH_2OH complexes of Pt(II) are 8–9).[7] The ir spectrum of C showed bands characteristic of NH_2OH at 2890 (ν_{OH}) and 939 cm^{-1} (ν_{NO})[8] in addition to the expected amine and perchlorate bands.

Kinetic studies of the reaction of 10^{-3} *M* solutions of $[Ir(NH_3)_5N_3]Cl_2$ with 4.5 *M* H_2SO_4 showed that the azide complex decomposed rapidly (monitored by the decreasing intensity of the 279-nm band of this complex), and that this reaction was accompanied by the quantitative loss of nitrogen. However, the formation of $[Ir(NH_3)_5NH_2Cl]^{3+}$ under these conditions is a much slower reaction, as shown by the gradual increase of the 258-nm band characteristic of this product. If the reaction products from the decomposition of $[Ir(NH_3)_5N_3](ClO_4)_2$ in 4.5 *M* H_2SO_4 were isolated by precipitation with 70% $HClO_4$ after 40 min, a different product, D, was obtained, contaminated with some C.

Compound D reacts with HCl to give $[Ir(NH_3)_5NH_2Cl]^{3+}$ and with H_2O to give $[Ir(NH_3)_5NH_2OH]^{3+}$, and appears to be an intermediate in the production of B and C. Preliminary characterization of D shows the presence of 1 mol of bisulfate ion per mole of complex. Addition of Ba^{2+} to an acidic solution of D precipitates only a small portion of the HSO_4^-. However, decomposition of D in basic solution followed by acidification and treatment with Ba^{2+} gives an almost quantitative yield of $BaSO_4$. On this basis, D is formulated as $[Ir(NH_3)_5NH_2OSO_3](ClO_4)_2$ (containing bound sulfate). Free NH_3OSO_3 and D undergo similar reactions.[9]

The formation of B, C, and D can be rationalized in terms of Scheme I, which involves the intermediacy of a coordinated nitrene. The dependence of the rate of decomposition of $[Ir(NH_3)_5N_3]^{2+}$ on sulfuric acid strength is a function of h_0, similar to the behavior observed by Davis and Lalor[10] for $[Rh(NH_3)_5N_3]^{2+}$. In HCl where $[Ir(NH_3)_5NH_2Cl]^{3+}$ is formed, and in $HClO_4$, at the same h_0, the rate of decomposition of the azido complex is almost identical with the rate in H_2SO_4. The independence of this rate on the anion of the acid shows the absence of nucleophilic-assisted loss of nitrogen, and gives strong support to the intermediacy of a coordinated nitrene.

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[1] L. A. P. Kane-McGuire, P. S. Sheridan, F. Basolo, and R. G. Pearson, *J. Amer. Chem. Soc.*, **92**, 5865 (1970).

[2] The term nitrene throughout this paper refers to the molecule NH.

[3] W. P. Griffith, "The Chemistry of the Rare Platinum Metals," Interscience, New York, N. Y., 1967, p 269.

[4] R. A. Bauer and F. Basolo, *Inorg. Chem.*, **8**, 2231 (1969).

[5] R. S. Drago, *J. Chem. Educ.*, **34**, 541 (1957), and references therein.

[6] I. I. Chernyaev, G. S. Muraveiskaya, and L. S. Korablina, *Zh. Neorg. Khim.*, 10, 300 (1965); *Russ. J. Inorg. Chem.*, 10, 158 (1965); *Zh. Neorg. Khim.*, **11**, 1365 (1966); *Russ. J. Inorg. Chem.*, **11**, 728 (1966).

[7] A. A. Grinberg, A. I. Stetsenko, and N. C. Mitkinova, *Zh. Neorg. Khim.*, **11**, 2075 (1966); *Russ. J. Inorg. Chem.*, **11**, 1110 (1966).

[8] K. Nakamoto, "Infrared Spectra of Inorganic Coordination Compounds," 2nd ed, Wiley, New York, N. Y., 1970, p 107.

[9] P. A. S. Smith, H. R. Alul, and R. L. Baumgarten, *J. Amer. Chem. Soc.*, **86**, 1139 (1964); H. J. Matsuguma and L. T. Audrieth, *J. Inorg. Nucl. Chem.*, **12**, 186 (1959).

[10] C. S. Davis and G. C. Lalor, *J. Chem. Soc. A*, 445 (1970).