Table II. Carbonyl Stretching Frequencies (cm^{-1}) in Iridium Complexes[a]

L in $[(L)IrCl(CO)(Ph_3P)_2]$	ν_{CO}
. . .	1956
O_2	2000
D_2	2003
H_2S	2013
SO_2	2020
HCl	2024
CH_3I	2054
I_2	2065
Br_2	2075
Cl_2	2078

[a] Crystals in Nujol or halocarbon mull.

Acknowledgment. Partial support of this work by the National Institutes of Health (Grant No. HE-09678) of the U. S. Public Health Service is gratefully acknowledged.

(22) Note Added in Proof. A recent paper describes a novel type SO_2 complex, a dimeric SO_2-bridged cobalt compound, $K_6[(CN)_5Co(SO_2)Co(CN)_5]$, which points to a further analogy between SO_2 and CO complexes of transition metals: A. A. Vlček and F. Basolo, *Inorg. Chem.*, **5**, 156 (1966).

(23) Deceased Oct 4, 1962.

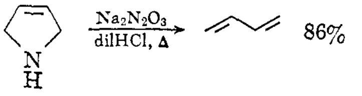
L. Vaska
Department of Chemistry, Clarkson College of Technology
Potsdam, New York 13676
S. S. Bath[23]
Mellon Institute
Pittsburgh, Pennsylvania 15213

Received January 25, 1966

Dienes from 3-Pyrrolines. A Stereospecific Deamination

Sir:

We wish to report that dienes are generated in high yield from 3-pyrrolines by treatment with nitrohydroxylamine, as illustrated by the prototype **1** → **2**. The availability of 3-pyrrolines from pyrroles makes this reaction potentially useful from a synthetic viewpoint, particularly because it proceeds with *complete stereospecificity.*



1 **2**

Concerted fragmentation of the five-membered ring might occur either with conrotation or with disrotation[1] of the ends of the developing diene system.[2] In Figure 1 these alternatives are illustrated for the presumed diazene intermediate[3] from 3-pyrroline. Since the process on the left (during which the entire molecule becomes twisted) is at every stage characterized by a twofold axis of symmetry and the right-hand process by a plane of symmetry, we choose to describe them as "axisymmetric" and "sigmasymmetric," respectively.[4]

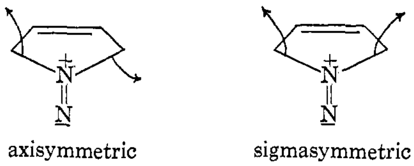
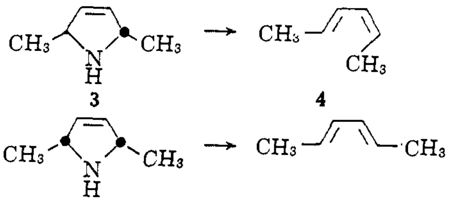


Figure 1. Possible fragmentation modes in 3-pyrroline deamination.

To distinguish between these possibilities it was necessary to obtain 2,5-disubstituted 3-pyrrolines of known stereochemistry. Thus the dimethyl derivative was prepared by zinc-hydrochloric acid reduction of 2,5-dimethylpyrrole.[5] Reported to be pure *trans*-2,5-dimethyl-3-pyrroline, the Δ^3 fraction of the product was shown in this laboratory to be a 1:3.5 *cis*:*trans* mixture.[6] The isomers were separated by fractional crystallization of their *p*-toluenesulfonamides and recovered by reductive cleavage with sodium in liquid ammonia.[7]

Deaminated in the manner described for **1**, *trans*-2,5-dimethyl-3-pyrroline (**3**) yielded *cis,trans*-2,4-hexadiene (**4**) and the *cis*-pyrroline **5** gave *trans,trans*-2,4-hexadiene (**6**); in neither experiment were traces of the other geometrical isomers detectable by vapor chromatography. *Hence both fragmentations occurred in the sigmasymmetric fashion.* Though in principle the *cis*-pyrroline was subject to a second sigmasymmetric mode of decomposition leading to *cis,cis*-2,4-hexadiene, the nonoccurrence of this process is not surprising in light of the severe methyl-methyl repulsion it would have entailed.



3 **4**
5 **6**

Woodward and Hoffmann's beautiful and far-reaching theory[1,8] regarding the influence of orbital symmetries over the course of organic reactions can be brought to bear on the present problem. Figures 2 and 3 are orbital correlation diagrams corresponding respectively to axisymmetric and sigmasymmetric decomposition of the diazene from 3-pyrroline.[9] Correlation of a bonding with an antibonding orbital characterizes the former, but not the latter process. Thus sigmasymmetric fragmentation should occur, in harmony with experiment.[10-12]

(1) R. B. Woodward and R. Hoffmann, *J. Am. Chem. Soc.*, **87**, 395 (1965).

(2) The literature on fragmentations related to **1** → **2** appears to be contradictory regarding the question of stereochemistry (*cf.* the discussion of this point by L. A. Carpino, *ibid.*, **84**, 2196 (1962)).

(3) D. M. Lemal and T. W. Rave, *ibid.*, **87**, 393 (1965).

(4) The terms "conrotatory" and "disrotatory," which aptly describe electrocyclic processes, would lose clarity if applied indiscriminately to fragmentation or cycloaddition reactions (particularly in cases more complex than the present one). "Axisymmetric" and "sigmasymmetric" are intended to describe *any* concerted reaction whose transition state possesses a twofold (or higher) axis or mirror plane, respectively. *Cf.* the less restrictive definition of the former term in Webster's Third New International Dictionary, G. and C. Merriam Co., Springfield, Mass., 1961.

(5) G. G. Evans, *J. Am. Chem. Soc.*, **73**, 5230 (1951).

(6) The nmr spectrum (D_2O) of the 3-pyrroline, free of double bond isomers, displayed a *pair* of doublets in the methyl region. Hydrogenation of this liquid over Adams catalyst in acetic acid gave a product resolvable into two peaks by vapor chromatography (though the 3-pyrrolines themselves were not separable on any of a variety of columns); the retention time of the minor component matched that of *cis*-2,5-dimethylpyrrolidine.[5]

(7) I. Photaki and V. du Vigneaud, *J. Am. Chem. Soc.*, **87**, 908 (1965), and references contained therein.

(8) R. Hoffmann and R. B. Woodward, *ibid.*, **87**, 2046, 4388, 4389 (1965); R. B. Woodward and R. Hoffmann, *ibid.*, **87**, 2511 (1965).

(9) Though the arrangement of orbital energy levels is only approximate, neither refinement of their spacing nor changes in the assumed hybridizations at nitrogen alter the argument based on Figures 2 and 3.

(10) The same theoretical conclusion was reached independently by Hoffmann and Woodward, who have derived selection rules for fragmentations of this type (Abstracts, 150th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1965, p 8S).

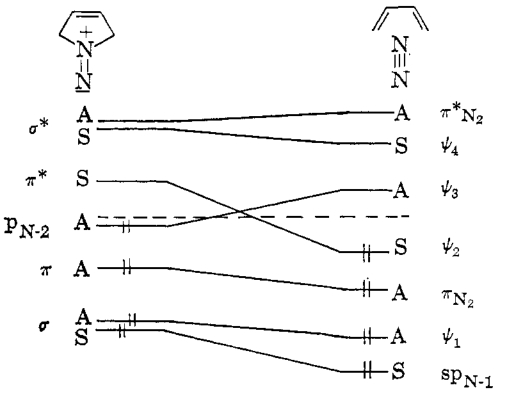


Figure 2. Axisymmetric fragmentation (orbital symmetries are given with respect to C_2).

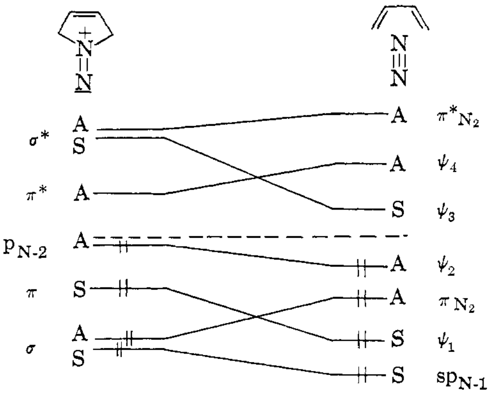
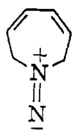


Figure 3. Sigmasymmetric fragmentation (orbital symmetries are given with respect to σ_v).

To be sure, the great majority of concerted cycloadditions and their *retro* counterparts should occur sigmasymmetrically because orbital overlap and steric problems make the axisymmetric transition state energetically inaccessible. The observed *cis* (sigmasymmetric) course of the Diels-Alder reaction, for example, is presumably attributable to these factors, for orbital symmetry considerations do not favor *cis* over *trans* addition. We wish to underline the possibility that *certain cycloadditions (or the corresponding fragmentations) may occur axisymmetrically*, *viz.*, those having (1) a bonding-antibonding correlation along the sigma-, and only the sigmasymmetric pathway, and (2) reasonable geometry for the axisymmetric transition state. A case in point is the decomposition of the yet unknown diazene 7, a vinylog of those discussed above.



7

The fragmentation stereochemistry of compounds which may elect the axially symmetric course is currently under investigation in our laboratory.

Acknowledgment. The authors are grateful to Dr. Roald Hoffmann for his comments on the manuscript, to Mr. Richard W. Harrington for skillful technical assistance, and to the National Science Foundation and the National Institutes of Health for generous financial support.

David M. Lemal
Stanley D. McGregor
Dartmouth College
Hanover, New Hampshire
University of Wisconsin
Madison, Wisconsin

Received December 27, 1965

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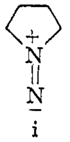
(11) Interestingly, decomposition of 3-cyclopentenones into carbon monoxide and dienes is predicted to occur in this fashion not only thermally, but in the photoexcited (n, π*) state as well.

(12) Concerted disintegration of i into ethylene and nitrogen (*via* a planar transition state) involves no bonding-antibonding correlation, and indeed the experimental evidence leaves little doubt that the three bond cleavages occur simultaneously (D. M. Lemal, T. W. Rave, and S. D. McGregor, *J. Am. Chem. Soc.*, **85**, 1944 (1963)).

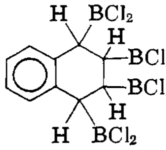


i

The Addition of B_2Cl_4 to 1,3-Cyclohexadiene and the Structural Similarity of the Adduct to That Formed between B_2Cl_4 and Naphthalene

Sir:

Until now, support for the structure proposed by Fox and Wartik[1] for the adduct between naphthalene and diboron tetrachloride ($C_{10}H_8 \cdot 2B_2Cl_4$) has been largely chemical in nature. The evidence was interpreted to favor a product involving four BCl_2 groups attached to a saturated ring, while the other ring retained its aromatic character. We have now prepared another organic polydichloroboryl compound using a synthetic route expected to lead to a molecule structurally similar to that postulated for the right-hand ring of I. The infrared and nuclear magnetic resonance spectra of the new molecule and of I lend strong support to the earlier structural views.



I

The new compound, 1,2,3,4-tetrakis(dichloroboryl)-cyclohexane, was produced by allowing a mixture of B_2Cl_4 (26.6 mmoles) and 1,3-cyclohexadiene (8.45 mmoles) to warm slowly from −80° to room temperature over a period of about 10 days in approximately 20° intervals. At the first appearance of the characteristic red color which signaled the decomposition of the excess B_2Cl_4, the reaction was terminated. Repeated molecular distillation of the crude product, an orange oil, yielded approximately 250 mg of a wet, orange, crystalline material which underwent rapid thermal decomposition above about 100° and which was extremely sensitive to air and moisture. The 2:1 reaction stoichiometry was supported both by the mole ratio of reactants consumed ($2.12B_2Cl_4$ to $1.00C_6H_8$) and, more reliably, by elemental analysis after treatment with fuming nitric acid at 350° in a sealed tube. *Anal.* Calcd for $C_6H_8 \cdot 2B_2Cl_4$: B, 10.6; C, 17.7; Cl, 69.7. Found: B, 10.9; C, 17.9; Cl, 70.0.

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[1] W. B. Fox and T. Wartik, *J. Am. Chem. Soc.*, **83**, 498 (1961).