fluences of base type upon ring puckering, at least for the more common systems. Altona and co-workers have recently reached similar conclusions through analyses of the β-D-furanoside fragments of various X-ray crystal structures.[62]

Acknowledgment. The author is grateful to the National Institute of Health (USPHS Grant GM-20861) and to the Charles and Johanna Busch Memorial Fund of Rutgers University for laboratory support, to Professor Joachim Seelig for his hospitality at the Biozentrum of the University of Basel, Switzerland, where this work was initiated, to the J. S. Guggenheim Memorial Foundation for a fellowship, to the University of Basel Computer Center and the Center for Computer and Information Services of Rutgers University for computer time, and to the USPHS for a Research Career Development Award (Grant GM-00155).

Registry No. Ribose, 79681-15-5; 2'-deoxyribose, 79681-16-6; 3'-deoxyribose, 79681-17-7; 2'-*F*-2'-deoxyribose, 79681-18-8.

Supplementary Material Available: Pseudorotation coordinates of ribose (Table I-S) (2 pages). Ordering information is given on any current masthead page.

(62) H. P. M. de Leeuw, C. A. G. Haasnoot, and C. Altona, *Isr. J. Chem.*, **20**, 108-126 (1980).

Communications to the Editor

Small Ring Heterocycles. Role of Azabenzvalenes in the Thermolysis of 3-Cyclopropenyl Substituted Oxazolinones

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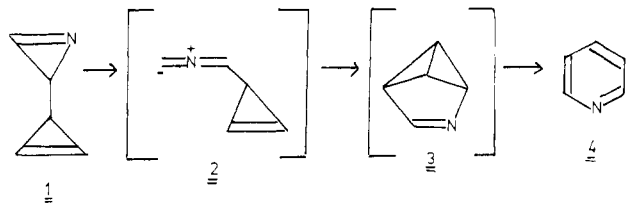
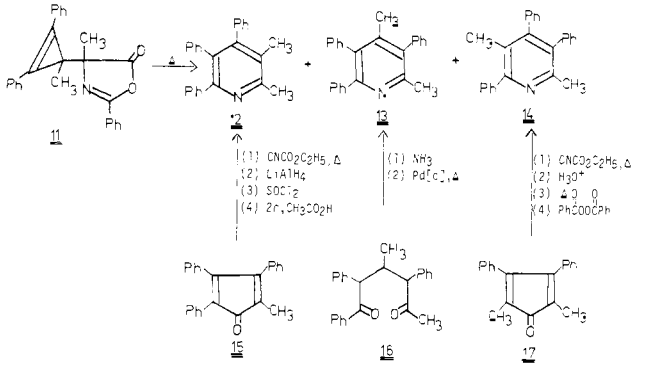
Received August 3, 1981

The rearrangement of 3,3'-bicyclopropenyls to benzene derivatives is one of the most exothermic unimolecular isomerizations known.[1-8] Its mechanism has been a source of controversy over the years. At various times the rearrangement has been postulated to proceed through Dewar benzene,[3] benzvalene,[9] prismane,[1] diradical[6] and ionic intermediates.[3] The most recent data are consistent with a path involving initial homolytic cleavage of one of the cyclopropene rings followed by expansion of the other ring, closure to a Dewar benzene, and finally opening of the Dewar intermediate to form aromatic products.[7,8] The conversion of the closely related 3-azirinylcyclopropene system (**1**) to a pyridine derivative **4** represents a more complicated transformation since several different possibilities are available. One of the more attractive paths involves the initial formation of a nitrile ylide intermediate[10] **2** followed by intramolecular dipolar cycloaddition[11] to give azabenzvalene (**3**) which subsequently rearranges to pyridine (**4**). In this communication we report the results of our investigations dealing with the conversion of cyclopropenyl substituted nitrile ylides to pyridines according to the mechanism outlined in Scheme I.

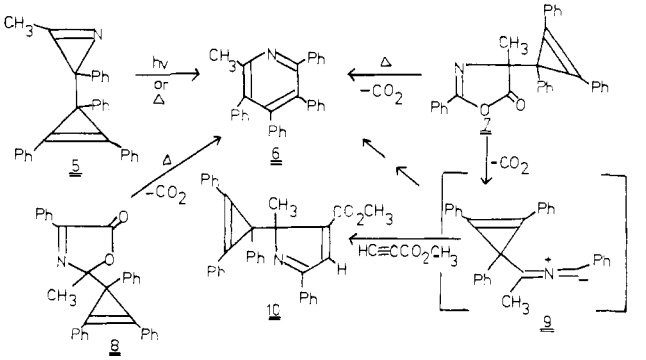
Scheme I



Scheme II



Thermolysis or photolysis of a sample of the 3-cyclopropenyl-substituted 2*H*-azirine **5**[12] produced 2-methyl-3,4,5,6-tetraphenylpyridine (**6**),[13] mp 160-161 °C, in quantitative yield.



We believe that the rearrangement of **5** to **6** occurs via the se-

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‡ Agricultural Chemical Research Group, FMC Corporation, Princeton, New Jersey 08540.

(1) Breslow, R.; Gal, P.; Chang, H. W.; Altman, L. J. *J. Am. Chem. Soc.* **1965**, *87*, 5139.

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(10) Padwa, A. *Acc. Chem. Res.* **1976**, *9*, 371.

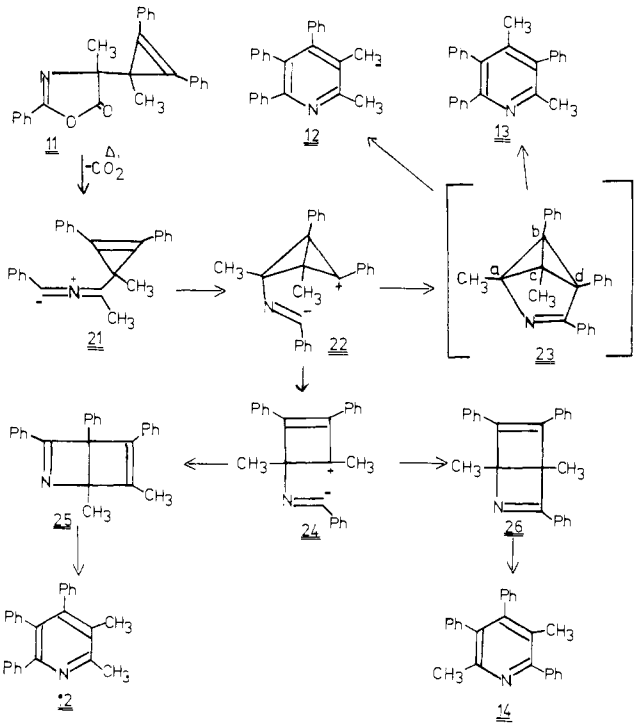
(11) For leading references of intramolecular cycloadditions of nitrile ylides, see: Padwa, A.; Ku, A.; Carlsen, P. H. J. *J. Am. Chem. Soc.* **1978**, *100*, 3494.

(12) 2*H*-Azirine **5** was prepared by treating triphenylcyclopropenyl perchlorate with the anion derived from phenylacetone *N,N*-dimethylhydrazone followed by quaternarization with methyl iodide and treatment with sodium isopropoxide. Complete details will be provided in a later publication.

(13) Wakatsuki, Y.; Yamazaki, H. *Tetrahedron Lett.* **1973**, 3383.

0002-7863/82/1504-0286$01.25/0

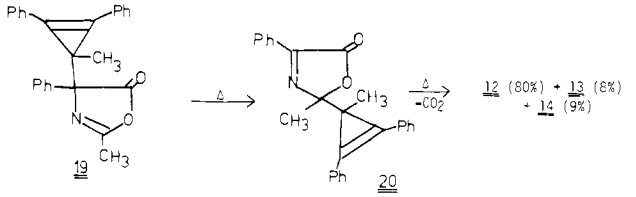
Scheme III



quence of reactions described in Scheme I. In order to provide additional support for this mechanism, we investigated the thermal chemistry of the cyclopropenyl substituted oxazolinones **7** and **8**.[14] Earlier results in the literature have shown that oxazolinones undergo a thermally induced 1,3-dipolar cycloreversion reaction with elimination of carbon dioxide to generate nitrile ylides.[15,16] Heating a sample of Δ^2-oxazolinone **7** at 150 °C for 24 h resulted in a quantitative yield of pyridine **6**. When the thermolysis of **7** was carried out in xylene in the presence of methyl propiolate, 2*H*-pyrrole **10**, mp 159–160 °C, was isolated in good yield. The formation of this compound is readily interpreted in terms of 1,3-dipolar cycloaddition of the intially generated nitrile ylide intermediate **9** with the added dipolarophile. In the absence of an added trapping agent, **9** rearranges to pyridine **6**. The thermal behavior of the isomeric Δ^3-oxazolinone system **8** was also studied and was found to give **6** upon heating in toluene at 180 °C for 35 h.

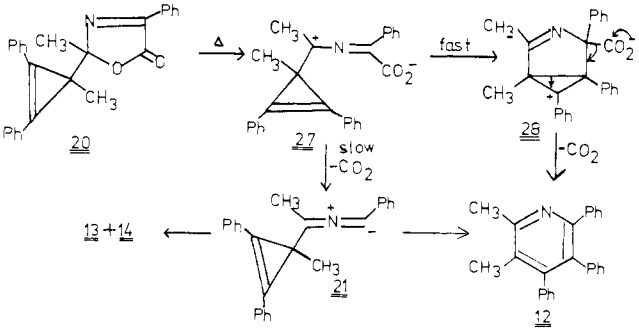
Although the rearrangement of **5** to **6** can be accommodated by the reactions outlined in Scheme I, several other plausible routes were considered as likely alternatives. To aid in distinguishing among these pathways, we have examined the thermal behavior of a more extensively labeled system. Heating a sample of Δ^2-oxazolinone **11** at 150 °C for 24 h afforded a mixture of 2,3-dimethyltriphenylpyridine (**12**) (45%) 2,4-dimethyltriphenylpyridine (**13**) (20%), and 2,5-dimethyltriphenylpyridine (**14**) (35%). Assignment of the various isomers was made by comparison with independently synthesized samples. Preparation of an authentic sample of 2,3-dimethyl-4,5,6-triphenylpyridine (**12**) was accomplished by allowing 2-methyl-3,4,5-triphenylcyclopentadienone (**15**) to undergo [4 + 2] cycloaddition with ethyl cyanoformate.[17] Reduction of the resulting ester to the alcohol and then conversion to the chloride followed by treatment with zinc in acetic acid gave pyridine **12**. The 2,4-isomer **13** was prepared by the conjugate addition of 1-phenyl-2-(trimethylsiloxy)-1-propene to 1,2-diphenyl-2-buten-1-one according to the method of Mukaiyama to give **16**.[18] Treatment of **16** with ammonia followed by oxidation gave **13** in high yield. Pyridine **14** was prepared from the Diels–Alder reaction of 2,5-dimethyl-3,4-diphenylcyclopentadienone (**17**) with ethyl cyanoformate. The resulting [4 + 2] cycloadduct was converted to the corresponding acid which was thermally decarboxylated at 200 °C to give 2,5-dimethyl-3,4-diphenylpyridine (**18**). Treatment of this material with benzoyl peroxide in refluxing acetic acid gave the 2,5-substituted isomer **14** in 35% yield.[19]

We have also examined the thermal extrusion of carbon dioxide from the closely related Δ^2-oxazolinone **19**. Upon heating at 80 °C for 90 min, **19** was found to rearrange to the isomeric Δ^3-oxazolinone **20** in quantitative yield. Further heating of **20** at 170 °C for 25 h gave pyridines **12–14**. In this case, however, the ratio of the three dimethyl substituted pyridines is substantially different from that encountered in the thermolysis of Δ^2-oxazolinone **11**.



We believe that the thermal reaction of **11** begins with a 1,3-cycloelimination of carbon dioxide, yielding nitrile ylide **21**. Stepwise cycloaddition[11] of **21** produces the bicyclobutyl zwitterion **22** which can either collapse to give azabenzvalene **23** or undergo rearrangement to the cyclobutenyl cation **24**. Applying the concepts of Closs and Pfeffer[20] to the thermal rearrangement of azabenzvalene **23**, it can be seen that **12** results from cleavage of the a–b and c–d bonds, while **13** is derived from a similar cleavage of the a–c and b–d bonds. The cyclobutenyl cation **24** will give two different aza(Dewar benzenes) **25** and **26**, which, in turn, will produce pyridines **12** and **14**. The ring expansion of **21** is undoubtedly facilitated by release of strain in the three-membered ring and is analogous to similar reactions reported by Breslow and co-workers.[21] Alternate mechanisms based on a concerted intramolecular cycloaddition reaction of nitrile ylide **21** do not account reasonably for the observed product ratio. It should be pointed out that classical forms of carbonium ions have been drawn for simplicity, although it is recognized that in all of them considerably more delocalization of charge is probable.

The significant difference in product distribution formed in the thermolysis of **20** vs. that found with **11** indicates that the reaction does not proceed via simple loss of carbon dioxide. The preferential formation of the 2,3-dimethyl substituted isomer from **20** can be understood in terms of (1) opening of the Δ^3-oxazolinone ring to produce zwitterion **27**, (2) cyclization of this species to azabicyclo[3.1.0]hexene **28**, and (3) simultaneous or stepwise extrusion



(14) Δ^2-Oxazolinone **7** was prepared by treating the anion derived from 2-phenyl-4-methyl-Δ^2-oxazolinone with triphenylcyclopropenyl perchlorate. Δ^3-Oxazolinone **8** was obtained from the thermal rearrangement of 2-methyl-4-phenyl-4-cyclopropenyl-Δ^2-oxazolinone.

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(19) Bonnier, J. M.; Court, J.; Gelus, M. *Bull. Soc. Chim. Fr.* **1970**, 139. Dou, H. J. M.; Lynch, B. M. *Tetrahedron Lett.* **1965**, 897.

(20) Closs, G. L.; Pfeffer, P. E. *J. Am. Chem. Soc.* **1968**, *90*, 2452.

(21) Breslow, R.; Battiste, M. *J. Am. Chem. Soc.* **1960**, *82*, 3626. Breslow, R.; Lockhart, J.; Small, A. *Ibid.* **1962**, *84*, 2793.

of carbon dioxide from **28** to give pyridine **12**. Loss of CO_2 from the initial ring opened intermediate **27** also occurs to produce nitrile ylide **21** which ultimately affords pyridines **12-14**. A strong argument can be made that the cyclization of **27** to **28** is faster than loss of carbon dioxide. This is predicated on the fact that Δ^2-oxazolinones lose CO_2 at a much faster rate than the isomeric Δ^3-oxazolinone system.[16]

We are continuing to investigate the more intriguing mechanistic aspects of these interesting extrusion reactions and will report additional findings at a later date.

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Stable Monomeric Complexes of Molybdenum(III) and Tungsten(III)

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In recent years various facets of the inorganic chemistry of molybdenum have been closely scrutinized in order to provide models for the molybdenum-containing enzymes.[1,2] Enzyme intermediates containing molybdenum in the +3 oxidation state have been proposed many times, although no definitive evidence for molybdenum(III) biological systems has ever been produced.[3] The inorganic chemistry of molybdenum(III) is also sparse in comparison to that of the more fully developed chemistry of the +4, +5, and +6 oxidation states.[2] Complexes of molybdenum (III) which have been characterized are readily oxidized by air and a variety of mild oxidizing reagents.[2] We report that the coordination of tridentate polypyrazolylborate ligands[4] can stabilize molybdenum(III) complexes with respect to oxidation to such an extent that the +3 oxidation state becomes predominate.

The reaction of $KHB(3,5\text{-}Me_2pz)_3$ with $MoCl_3(THF)_3$ gives the yellow crystalline compounds $K(THF)_3HB(3,5\text{-}Me_2pz)_3MoCl_3$ (**1**). Its magnetic susceptibility (3.69 μ_B), electronic spectrum, and ESR spectrum are consistent with a d^3, $S = {}^3/_2$ ground state. An X-ray diffraction study (Figure 1) of $[Et_4N][HB(3,5\text{-}Me_2pz)_3MoCl_3]CH_3CN$ (**2**) reveals a monomeric anion with near octahedral coordination about the metal. The facial C_{3v} geometry imposed by the ligand is in contrast to the meridional structure established for $MoCl_3(pyridine)_3$ and believed to exist in other MoX_3L_3 compounds.[2] Compound **2** undergoes two one-electron

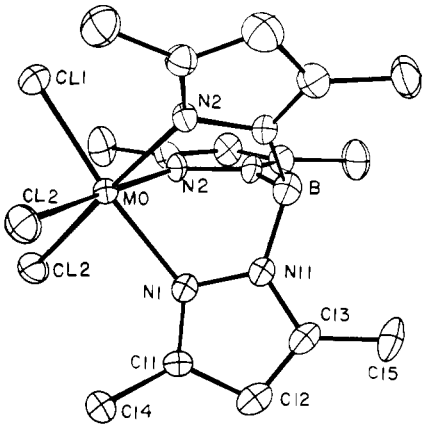

Figure 1. ORTEP view of the structure of the anion of **2**. Selected bond lengths (Å) and bond angles (deg) are as follows: Mo-Cl(1), 2.433 (1); Mo-N(1), 2.198 (5); N(1)-Mo-N(2), 85.67 (13); N(1)-Mo-Cl(2), 91.27 (9); Cl(1)-Mo-Cl(2), 93.10 (4).

oxidations at +0.49 V [Mo(III)/Mo(IV)] and +1.55 V [Mo(IV)/Mo(V)] vs. SCE. Oxidation of **2** by ceric ammonium nitrate or by controlled potential electrolysis gives the red monomeric Mo(IV) compound $HB(3,5\text{-}Me_2px)_3\ MoCl_3$[6] in excellent yield. Interestingly, this product can be directly obtained by the reaction of $(Et_4N)[HB(3,5\text{-}Me_2pz)_3Mo(CO)_3$ thionyl chloride.[7a] As anticipated from the quite positive Mo(III)/Mo(IV) couple, the Mo(IV) compound is readily reduced to the Mo(III) anion by such mild reductants as sulfide and alcohols. Solutions containing $[HB(3,5\text{-}Me_2pz)_3Mo^{III}Cl_3]^-$ react with air only very slowly (over a period of several months) to give the green oxomolybdenum(V) complex $HB(3,5\text{-}Me_2pz)_3MoCl_2O$.[7b] The stabilizing effect of polypyrazolylborate coordination on the +3 oxidation state results from the interaction of the Mo $d\pi$ orbitals with the ligand π^* orbitals.

Further evidence for this effect comes from our observation that a Mo(III) complex, $HBpz_3MoCl_2$(pyrazole) (**4**) is obtained from the reaction of molybdenum(V) chloride with $KHBpz_3$ in aqueous HCl solution without the addition of a reducing agent. The structure of **4**[8] is similar to that of **2** with a pyrazole replacing one of the chlorides. Presumably this product is formed by the disproportionation reaction of Mo(V)[9]; a driving force for this reaction may well be the stability of the Mo(III) compound.

Analogous polypyrazolylborate chemistry of tungsten provides synthetic access to monomeric W(III) complexes. The first definitive example of this class of compounds has only recently been obtained.[10,11] The chemistry of W(III) monomers has been precluded by their oxidative instability and/or their strong tendency to form metal-metal bonded dimers.[11] The reaction of $(Et_4N)[LW(CO)_3]$ [where L = $HBpz_3^-$ and $HB(3,5\text{-}Me_2pz)_3^-$] with thionyl chloride gives $LW^{IV}Cl_3$[6] in 80-90% yield. $HB(3,5\text{-}Me_2pz)_3WCl_3$ exhibits a reversible one-electron reduction at -0.33 V and a one-electron oxidation at +1.02 V. The 0.8-V difference in the M(III)/M(IV) couples for M = Mo and W is a quantitative measure of a known periodic trend, the instability of the lower

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(4) Hydrotris(1-pyrazolyl)borate ≡ $HBpz_3^-$; hydrotris(3,5-dimethyl-1-pyrazolyl)borate ≡ $HB(3,5\text{-}Me_2pz)_3^-$.
(5) Compound **2** is orthorhombic (*Pnma*) with a = 16.242 (2) Å, b = 10.931 (4) Å, c = 18.219 (2) Å and V = 3235 Å^3. This and the subsequent structures were solved by Patterson and difference Fourier methods. Final refinement using 2002 reflections with $I > 3.0\sigma(I)$ gave R = 0.0458 and R_w = 0.0748. Full details for the structures described in this paper will be published at a latter date.
(6) Mass spectroscopy indicates a momomeric formulation.
(7) (a) This reaction was reported by Trofimenko[6b] to give an unidentified red compound which in fact is **3**. (b) Trofimenko, S. *Inorg. Chem.* **1971**, *10*, 504-507.
(8) Compound **4** crystallized in the monoclinic space group $P2_1/n$ with a = 8.705 (1) Å, b = 12.889 (2) Å, c = 15.684 (3) Å, β = 104.01, and V = 1707.3 (10) Å^3. All hydrogens including the pyrazole N-H were located in a difference Fourier map and were included in final structure factor calculations. Final refinement using 2063 reflections with $I > 3.0\sigma(I)$ gave R = 0.026 and R_w = 0.037.
(9) Lamache-Duhameaux, M. "Proceeding of the Climax Third International Conference on the Chemistry and Uses of Molybdenum"; Barry, H. F., Mitchel, P. C. H., Eds.; Climax Molybdenum Co.: Ann Arbor, MI, 1979; p 253-258.
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