The thermal rearrangement of bicyclo[1.1.0]butane was studied to understand its reaction behavior. The thermal rearrangement of bicyclo[1.1.0]butane is considered to be a concerto reaction. Recently, Dewar and Kirschner® on the basis of the MINDO/3 calculations concluded, that a two-step mechanism with a diradical intermediate is more favorable and not in contradiction with the allowed and stereoselective formation of the products. Wiberg and Szeilimèt® obtained bicyclo[3.2.0]hept-6-ene (3) on gas phase pyrolysis of tricyclo[4.1.0.0\(^2\)7]heptane (1). Since the direct conversion 1 â†’ 3 is forbidden, the authors proposed cis,trans-cyclohepta-1,3-diene (2) as intermediate, which on conrotatory ring closure forms the cis substituted cyclobutene (3). As expected 1a is transformed to 3a.

We wish to report the results of a study, in which 1, tricyclo[4.1.0.0\(^2\)7]hept-6-ene (5), tricyclo[3.1.0.0\(^3\)6]hexane (9), and tetracyclo[4.1.0.0\(^2\)4.0\(^3\)6]heptane (12) were rearranged in solution. Since in toluene-\(\delta\) thermolysis of 1 produces only a small amount of 3 and mainly 2-norcarane (4), the formation of which is probably acid catalyzed, we used tetramethylhexadeuteriol (TMEDA) as solvent to obtain after heating to 200° for 24 hr 40%, 3 and 60% 4.

Recently the preparation of (5) and its thermolysis to bicyclo[3.2.0]hepta-2,6-diene (8) were reported. The byproduct cycloheptatriene does not appear, if the reaction is carried out in the presence of TMEDA. At 135° the half-life was determined to be 1 hr, the yield more than 90%. An overall pathway analogous to the 1,3 thermolysis is indicated by the reaction product 8. Being less symmetric than 1, 5

*Prepared by reductlon of 1 (la) 2 (lb) 3 (Table I) this ion retains both deuterium atoms, consistent with the specific loss of the terminal CH₃ group as required by eq 1.

The collisional activation (CA) spectrum of the C₄H₈₃Cl⁺ ions from 1-chlorohexane (Table I) is not affected by lowering the electron energy, indicating that a single ion structure is formed. The same CA spectrum is observed for these ions from 1-chloroheptane, consistent with a common mechanism of formation. A unique feature of the chloronium ion 2 in comparison to CICH₂CH₂CH₂CH₂⁺ or other alternative mechanisms is its basis of symmetry. Thus the C₄H₈₂Cl⁺ ion produced from 1a should be identical with that from 1b, while open chain ion products would differ in their position of deuterium substitution. The CA spectra of the C₄H₈₂Cl⁺ ions from 1a and 1b are virtually identical. In fact, there is a relatively small degree of scrambling in the CH₃Cl⁺ ions (m/e 49 for d₀) formed by loss of C₂H₆. If 1a and 1b gave the open chain ions ClC₂H₅CH₂CH₂⁺ and ClCH₂CH₂CH₂CD₂⁺, respectively, the m/e 49 peak of 1 should appear largely at m/e 51 and 49 in 1a and 1b, respectively. However, in the CA spectrum of the C₄H₈₂Cl⁺ ions from both 1a and 1b, the amounts of CH₃Cl⁺ and CD₂Cl⁺ formed are equivalent, and double that of CHDCI⁺. This must result from decomp­osition of C₄H₈₂Cl⁺ ions in which carbons 1 and 4 have become equivalent to each other but not to carbons 2 and 3, completely consistent with the chloronium ion structure 2.¹⁸

Acknowledgment. We are grateful to the Army Research Office, Durham, and to the National Institutes of Health for generous financial support.

References and Notes

8. © Prepared by reduction of n-C₆H₁₃COOH to n-C₆H₁₃COH with LiAlH₄ and conversion to n-C₆H₁₃CD₂COH with SOCl₂ with purification by gas chromatography (30% d₃; 97% d₀).
9. Phenyl propionate was reduced with LiAlH₄ in triethylamine glycol dimethyl ether.⁶ Treatment of the resulting C₆H₅CD₂OH with Pb(OAc)₂ yields C₆H₅CD₂Br which was converted to C₆H₅CD₂OH by treating with Gläser with trimethylamine oxide.¹⁰ This was converted to C₆H₅CD₂COHCl with SOCl₂ and purified by GC (9% d₃; 98% d₀).
13. Measurements were made on a Hitachi RMU-7 double-focusing mass spectrometer in which the positions of ion source and electron multiplier were interchanged as described previously.¹⁴ An ion accelerating potential of 7.8 kV, ionizing electron energy of 50 eV and lower were noted, and a sample reservoir and source temperature of 150° were used. IE spectra of the precursor ions selected by the magnetic field decomposing in the field-free drift region between the magnetic and electrostatic (ESA) analyzers are measured by scanning the ESA potential. The pressure in the field-free drift region between the magnetic and ESA is then increased with helium until the precursor ion intensity is reduced to 50% of its original value, and the CA ion product abundances are determined in the same manner in a second ESA scan.¹⁵ The data are the computer averaged composites of at least 16 separate scans. The contributions from M₁ products (corrected as de­scribed) are subtracted from these voltages to obtain the CA spectrum. Corrections have been made for the contribution of large peaks to neighboring peaks caused by incomplete resolution; reproducibility of the abundance values are at least ±5% relative or ±0.3 absolute, whichever is the larger.
15. © A comparison of completely H/D scrambled C₄H₈₂Cl⁺ ions would give [CH₃CD⁺]CH₂CDCl⁺ [(CD₂)³⁺] of 15:12:1. (CHDCI⁺) should give the decomposition of 2. Such a CHDCI⁺ isomer would be expected to give its abundance in the CA spectrum also, however, so that the proportion present should be small in comparison to that for 2.
16. © Postdoctoral Fellow, 1974; on leave from the NSFWO, Belgium.

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Communications to the Editor
can convert into two different intermediates, either trans, cis, cis- (6) or cis, trans, cis-cycloheptatriene (7). 7 should consist of two identical conformers, which are interconvertible on rotation of the trans substituted ethylenic unit. Because of the rather high strain energy of 7, this process should need only low activation. Molecular models even allow the assumption that the $c_2$ symmetric transition state between the conformers, having the trans double bond perpendicular on the cis double bonds, might be the most stable form. Starting with the dideuterio compound 5a, 7a and 7b are distinguished by the position of the deuteron labels. Provided that 7a and 7b are in equilibrium and isotope effects can be neglected, ring closure according to the dotted lines should lead to a 1:1 mixture of 8a and 8b.

We did not find any 8b. 6a remains as the most probable intermediate. Involved the double bond is electrons in 5 a series of concerted six-electron rearrangements are allowed, which directly or via other $C_7H_8$ isomers could produce 8. All these processes, however, do not satisfy the experimental deuteron distribution on thermolysis of 5a.

Tricyclo[3.1.0.0$^{2,6}$]hexane (9) became easily accessible recently. It thermolyzes in the gas phase as well as in TMEDA solution to produce only cyclohexa-1,3-diene (10). No acid catalysis is involved as shown by the treatment of 9 in dioxane with aluminum chloride, which gives bicyclo[3.1.0]hexa-2-ene (11), a molecule thermally more stable than 9.

Preparation and pyrolysis of tetracyclo[4.1.0.0$^{2,5}$]heptane (12) were described previously. The rearrangement in tetrachloroethylene 8 is observed by NMR as an intermediate, which builds up a maximum concentration of about 18%. Its thermal rearrangement to cycloheptatriene (13) is well known ($E_A = 39.5$ kcal/mol). From products vs.

Table I. Kinetics of the Thermal Rearrangement of Endo-Endo'-Bridged Bicyclo[1.1.0]butanes

<table>
<thead>
<tr>
<th>Compound</th>
<th>Temp range (°C)</th>
<th>$k_{600}$, sec$^{-1}$</th>
<th>$\Delta H^\ddagger$, kcal/mol</th>
<th>$\Delta S^\ddagger$, eu</th>
<th>$E_A$, kcal/mol</th>
<th>Log $A$</th>
</tr>
</thead>
<tbody>
<tr>
<td>5a</td>
<td>120-145</td>
<td>(4.6 ± 0.2) x 10$^{-6}$</td>
<td>31.5 ± 0.6</td>
<td>1.1 ± 1</td>
<td>32.4 ± 0.6</td>
<td>13.6 ± 0.4</td>
</tr>
<tr>
<td>126</td>
<td>190-210</td>
<td>(1.7 ± 0.1) x 10$^{-4}$</td>
<td>37.9 ± 1.5</td>
<td>-1.1 ± 3</td>
<td>38.8 ± 1.5</td>
<td>13.2 ± 0.7</td>
</tr>
<tr>
<td>12c</td>
<td>180-210</td>
<td>(9.4 ± 0.4) x 10$^{-3}$</td>
<td>37.6 ± 1.0</td>
<td>1.5 ± 1</td>
<td>38.5 ± 1.0</td>
<td>13.7 ± 0.5</td>
</tr>
<tr>
<td>9c</td>
<td>230-250</td>
<td>(2.1 ± 0.1) x 10$^{-4}$</td>
<td>40.7 ± 1.0</td>
<td>0.6 ± 1</td>
<td>41.7 ± 1.0</td>
<td>13.6 ± 0.5</td>
</tr>
</tbody>
</table>

a) Solvent toluene-d$_4$. b) Extrapolated. c) Solvent TMEDA. d) To obtain the rate constants for the conversion 1→3, the overall rate constants for the decrease of the 1 concentration were dissected in the ratio of the products 3 and 4.

Scheme I

[Diagram of cycloheptatriene rearrangement]

Preparation and pyrolysis of tetracyclo[4.1.0.0$^{2,5}$]heptane (12) were described previously. The rearrangement in tetrachloroethylene 8 is observed by NMR as an intermediate, which builds up a maximum concentration of about 18%. Its thermal rearrangement to cycloheptatriene (13) is well known ($E_A = 39.5$ kcal/mol). From products vs.
radicals disposes of a stabilization energy of several kilocalories per mole. Furthermore an easy ring enlargement as $14 \rightarrow 15$ is not available to $18$, the rearrangement of which should therefore be encumbered with more constraints.

Another recent finding seems to support the intermediary of diradicals in bicylobutane rearrangements. Naphthalene-1,8-tricycle[4.1.0.02,7]heptene transforms to the corresponding cis-cyclobutene at temperatures as low as those necessary to decompose 5. In this case the benzyl type stabilization of one radical center in the intermediate would account for the easy reaction.

**Acknowledgment.** We are indebted to Drs. G. Szeimies and G. Boche, Universität München, for stimulating discussions, Professor M. J. S. Dewar, The University of Texas at Austin, for providing us with his results prior to publication, and the Deutsche Forschungsgemeinschaft for generous support.

**References and Notes**


(3) M. J. S. Dewar and S. Kraschner, submitted for publication.


(9) Prepared from $5$, n-BuLi, ether, CuO twice, >95% deuterated.


(13) From 12 analogous to the conversion $5 \rightarrow 5a$ given in ref 5.


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**Reaction of Oxygen with Dicyanoguanidinium(dimethylphenylphosphine)cobalt(II). Synthesis, Structure, and Reactivity of a Novel Cobalt–Dioxygen Adduct**

**Stir.**

The reactions of $O_2$ with low-spin pentacordinate cobalt(II) complexes are of widespread occurrence and characteristically follow the course of eq 1 to form either terminally bonded mononuclear or $O_2$-bridged binuclear adducts (types 1 and 2, respectively). $^1$

$$[L_2CoCl^II] + O_2 \rightarrow \left[ L_2CoO \right] + \left[ L_2CoCl^II \right]$$

While the bonding in such adducts is still a subject of active discussion (formation as cobalt(III) complexes being generally favored) several complexes of each type have been structurally characterized and found to be in accord with the above representations. Such structures have, accordingly, also been generally assumed for other cobalt(II)–$O_2$ adducts. In view of this, our finding of a rather different, previously unrecognized, structure for the 1:2 adduct formed by reaction of $O_2$ with $\left[ Co(CN)\left( PMe_2Ph \right) \right](Me = CH_3, Ph = C_6H_5)$, which together with the characterization of this adduct are the subjects of this communication, represents a quite unexpected result. This finding also prompts reexamination of hitherto accepted assignments of the structures of certain other cobalt(II)–$O_2$ adducts. $^7$

Passing a stream of $O_2$ through a benzene solution of $\left[ Co(CN)\left( PMe_2Ph \right) \right]$ for about 8 hr resulted in formation of the adduct (3) in accord with the stoichiometry of eq 2. Addition of hexane resulted in precipitation of brown crystals of 3: electronic spectrum of 3 (in methanol), $\lambda_{max} 295$ nm ($E 2.1 \times 10^4 M^{-1} cm^{-1}$); infrared (Nujol), $\nu_C= 2085$ and 2105 cm$^{-1}$, $\delta_D 881$ cm$^{-1}$.

$$2 \left[ Co(CN)\left( PMe_2Ph \right) \right] + O_2 \rightarrow \left[ Co_2(CN)_2\left( PMe_2Ph \right) \left( O_2 \right) \right]$$

Crystals of $\left[ Co_2(CN)_2\left( PMe_2Ph \right) \left( O_2 \right) \right]$ grown from benzene–acetone, belong to the Fdd2 space group with cell dimensions $a = 33.583$ (4), $b = 30.471$ (4), and $c = 19.449$ (2) $\AA$ and $\beta = 1.317$ and $\rho_{calc} = 1.313$ g/cm$^3$ for 16 formula units per unit cell. Data were collected on a Picker FACs-1 diffractometer, using Mo Kα radiation and graphite monochromator. A total of 2212 independent reflections ($2\theta < 40^\circ$, relative structure factors $> 3\sigma$) were used in the solution and refinement of the structure. The structure was solved by direct methods using a modified version of MULTAN. $^7$ In the refinement by full-matrix least-squares methods, the benzene molecule and phenyl groups were treated as rigid bodies, the Co and P atoms were assigned anisotropic thermal parameters, and the other atoms were assigned isotropic thermal parameters. H atoms were included as fixed atom contributions assuming $r_C-H = 0.95$ $\AA$ and normal geometries (the orientation of the methyl groups being determined by a least-squares fit of the difference-Fourier at the final stages of refinement).