chlorohexane-*1,1*-d_2 (**1a**)[8] and -*4,4*-d_2 (**1b**)[9] (Table I) this ion retains both deuterium atoms, consistent with the specific loss of the terminal C_2H_5 group as required by eq 1.

The collisional activation (CA) spectrum[12] of the $C_4H_8{}^{35}Cl^+$ ions from 1-chlorohexane (Table II) 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 $ClCH_2CH_2CH_2CH_2{}^+$ or most alternative structures is its axis of symmetry. Thus the $C_4H_6D_2Cl^+$ 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 $C_4H_6D_2{}^{35}Cl^+$ ions from **1a** and **1b** are virtually identical. Of course this would be true for even an open chain $C_4H_8Cl^+$ structure if complete H/D scrambling occurred before decomposition; the spectra indicate that H/D scrambling, although extensive, is not complete. Fortunately, there is a relatively small degree of scrambling in the $CH_2{}^{35}Cl^+$ ions (*m/e* 49 for d_0) formed by loss of C_3H_6.[15] If **1a** and **1b** gave the open chain ions $ClCD_2CH_2CH_2CH_2{}^+$ and $ClCH_2CH_2CH_2CD_2{}^+$, 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 spectra of the $C_4H_8{}^{35}Cl^+$ ions from both **1** and **1b**, the amounts of CH_2Cl^+ and CD_2Cl^+ formed are *equivalent*, and double that of $CHDCl^+$. This must result from decomposition of $C_4H_8Cl^+$ 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**.[16]

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

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(9) Phenyl propionate was reduced with $LiAlD_4$ in triethylene glycol dimethyl ether.[10] Treatment of the resulting $C_2H_5CD_2OH$ with PBr_3 yields $C_2H_5CD_2Br$ which was converted to $C_2H_5CD_2C_3H_6OH$ by treating its Grignard with trimethylene oxide.[11] This was converted to $C_2H_5CD_2C_3H_6Cl$ with $SOCl_2$ and purified by GC (2% d_1, 98% d_2).

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(15) Decomposition of completely H/D scrambled $C_4H_6D_2Cl^+$ ions would give $[CH_2Cl^+]$:$(CHDCl^+]$:$[CD_2Cl^+]$ of 15:12:1.

(16) It is possible that the $CHDCl^+$ ions in the CA spectrum are due to the formation of an additional $C_4H_8Cl^+$ isomer, not just to scrambling accompanying the decomposition of **2**. Such a $C_4H_8Cl^+$ isomer would be expected to give abundant CH_2Cl^+ ions in its CA spectrum also, however, so that the proportion present should be small in comparison to that for **2**.

(17) Postdoctoral Fellow, 1974; on leave from the NFWO, Belgium.

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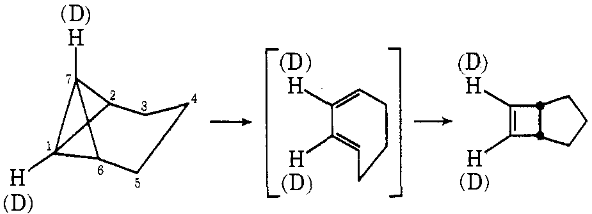
Thermal Rearrangement of Some Endo-Endo'-Bridged Bicyclo[1.1.0]butanes

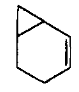
Sir:

The thermal rearrangement of bicyclo[1.1.0]butane to butadiene is considered to be a concerted $[_{\sigma}2_s + _{\sigma}2_a]$ type reaction.[1,2] Recently Dewar and Kirschner[3] on the basis of 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[1,2] formation of the products. Wiberg and Szeimies[4] 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** → **3** is forbidden,[1] 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**.[5]



1 (1a) 2 (2a) 3 (3a)

We wish to report the results of a study, in which **1**, tricyclo[4.1.0.0^{2,7}]hept-3-ene (**5**), tricyclo[3.1.0.0^{2,6}]hexane (**9**), and tetracyclo[4.1.0.0^{2,4}.0^{3,5}]heptane (**12**) were rearranged in solution. Since in toluene-d_8 thermolysis of **1** produces only a small amount of **3** and mainly 2-norcarene (**4**), the formation of which is probably acid catalyzed,[6] we used tetramethylethylenediamine (TMEDA) as solvent and obtained after heating to 200° for 24 hr 40% **3** and 60% **4**.



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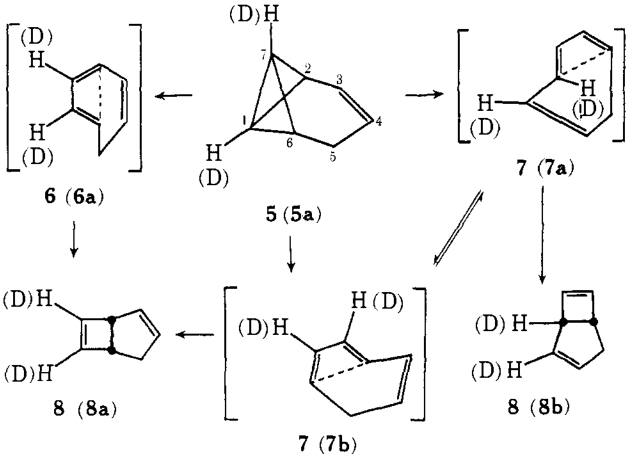
Recently the preparation of (**5**) and its thermolysis to bicyclo[3.2.0]hepta-2.6-diene (**8**) were reported.[7] The byproduct cycloheptatriene does not appear, if the reaction is carried out in the presence of TMEDA. At 135° the half-life was determined to be 1 hr, the yield more than 90%. An overall pathway analogous to the **1** thermolysis is indicated by the reaction product **8**. Being less symmetric than **1**, **5**

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

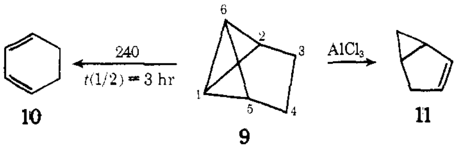
Compound	Temp range (°C)	$k_{200°}$, sec^{-1}	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu	E_A, kcal/mol	Log A
5[a]	120–145	$(4.6 \pm 0.2) \times 10^{-2}$[b]	31.5 ± 0.6	1.1 ± 1.1	32.4 ± 0.6	13.6 ± 0.4
1[c,d]	190–210	$(1.7 \pm 0.1) \times 10^{-5}$	37.9 ± 1.5	−1.1 ± 3.0	38.8 ± 1.5	13.2 ± 0.7
12[c]	180–210	$(9.4 \pm 0.4) \times 10^{-5}$	37.6 ± 1.0	1.5 ± 1.0	38.5 ± 1.0	13.7 ± 0.5
9[c]	230–250	$(2.1 \pm 0.1) \times 10^{-6}$[b]	40.7 ± 1.0	0.6 ± 1.5	41.7 ± 1.0	13.6 ± 0.5

[a] Solvent toluene-d_8–TMEDA. [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 disected in the ratio of the products 3 and 4.

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 interconvertable 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**,[8] **7a** and **7b** are distinguished by the position of the deuterium 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**. Since we did not find any **8b**, **6a** remains as the most probable intermediate. Involving the double bond π 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 deuterium distribution on thermolysis of **5a**.

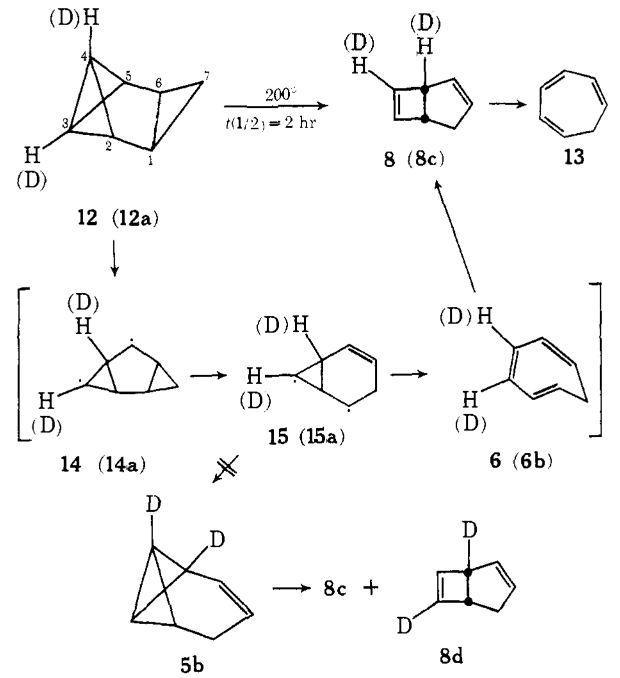


Tricyclo[3.1.0.0^{2,6}]hexane (**9**) became easily accessible recently.[9] It thermolyzes in the gas phase[9] as well as in TMEDA solution to produce only cyclohexa-1,3-diene (**10**). No acid catalysis is involved as shown by the treatment of **9** in dioxane with aluminum chloride, which gives bicyclo[3.1.0]hex-2-ene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



Preparation and pyrolysis of tetracyclo[4.1.0.0^{2,4}.0^{3,5}]heptane (**12**) were described previously.[7] The rearrangement in tetrachloroethylene[7] seems to be an acid catalyzed process, because in TMEDA the reaction rate is slower and the bicycloheptadiene **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).[11] From products vs. time plots it can be concluded, that **12** rearranges completely via **8**. After a conversion of 70-80% the yield of **8** plus **13** was determined to be greater than 90%.

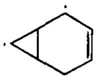
Scheme I

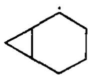


Although other mechanistic pathways, e.g., a [$_\sigma2_s$ + $_\sigma2_s$ + $_\sigma2_s$] bond relocation, cannot be ruled out, we favor the one including the diradical **14**, which should undergo a cyclopropylcarbinyl-homoallyl rearrangement, a generally very easily occurring reaction,[12] to produce **15**. Its stabilization would lead to **6** and finally to the observed **8**. As shown in Scheme I this sequence satisfies the experimental deuterium distribution on thermolysis of the dideuterio compound **12a**.[13] According to the NMR analysis **8c** is the only product, which should be transformed to 3,4-dideuteriocycloheptatriene. Because of the rapid hydrogen shifts in **13**[14] this expectation could not be proved. The ring closure of **15a** to **5b** does not take place, since a 1:1 mixture of **8c** and **8d** would be the result of the rapid rearrangement of **5b** at the high reaction temperature.

The decomposition rates of **1**, **5**, **9**, and **12** were determined by means of NMR spectroscopy. From the first-order rate constants the activation parameters, shown in Table I, were calculated. While **9** has about the same activation energy as bicyclo[1.1.0]butane itself (E_A = 40.6,[15a] 41.3[15b] kcal/mol), **1**, **5**, and **12** rearrange faster. The vinyl substituted bicyclobutane **5** shows the largest effect, since it thermolyzes 2700 times more rapidly than its saturated analog **1**. The diradical intermediate **16** can explain the high reaction rate of **5** based on the allyl stabilization of one radical center,[16] which is absent in **17**. The exclusive formation of **6** from **16** might be connected with the fact that **6** in contrast to **7** has the two cis double bonds in conjugation.

12 thermolyzes 45 times faster than **9**, which would be in accord with the intermediate **14**, since cyclopropylcarbinyl radicals dispose of a stabilization energy of several kilocalories per mole.[17] Furthermore an easy ring enlargement[12] as **14** → **15** is not available to **18**, the rearrangement of which should therefore be encumbered with more constraints.


16


17


18

Another recent finding seems to support the intermediacy of diradicals in bicyclobutane rearrangements. Naphtho-[1.8]tricyclo[4.1.0.0^{2,7}]heptene transforms to the corresponding *cis*-cyclobutene at temperatures[18] 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.

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

Sir:

The reactions of O_2 with low-spin pentacoordinate 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]

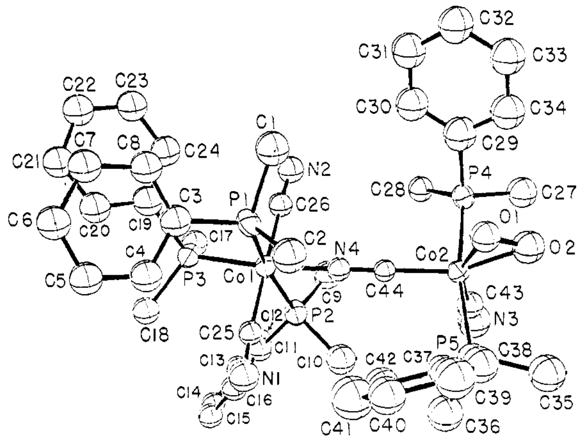
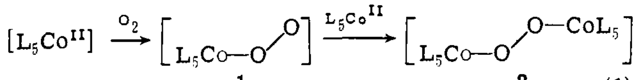


Figure 1. Molecular structure of $[Co_2(CN)_4(PMe_2Ph)_5(O_2)]$.



$$[L_5Co^{II}] \xrightarrow{O_2} \left[L_5Co{-}O{-}O\right] \xrightarrow{L_5Co^{II}} \left[L_5Co{-}O{-}O{-}CoL_5\right] \qquad (1)$$

1 **2**

While the bonding in such adducts is still a subject of active discussion (formulation 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.[1-6] Such structures have, accordingly, also been generally assumed for other cobalt(II)-O_2 adducts.[1] 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 $[Co^{II}(CN)_2(PMe_2Ph)_3]$ (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.[7,8]

Passing a stream of O_2 through a benzene solution of $[Co(CN)_2(PMe_2Ph)_3]$ 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), λ_{max} 295 nm (ϵ 2.1 × 10^4 M^{-1} cm^{-1}); infrared (Nujol), ν_{CN}, 2085 and 2105 cm^{-1}, ν_{O_2}, 881 cm^{-1}.

$$2[Co(CN)_2(PMe_2Ph)_3] + O_2 \longrightarrow \underset{\textbf{3}}{[Co_2(CN)_4(PMe_2Ph)_5(O_2)]} + PMe_2Ph \qquad (2)$$

Crystals of $[Co_2(CN)_4(PMe_2Ph)_5(O_2)]\cdot\frac{1}{2}C_6H_6$, grown from benzene-acetone, belong to the *Fdd*2 space group with cell dimensions a = 33.583 (4), b = 30.471 (4), and c = 19.449 (2) Å and ρ_{obsd} = 1.317 and ρ_{calcd} = 1.313 g/cm^3 for 16 formula units per unit cell. Data were collected on a Picker FACS-I diffractometer, using Mo Kα radiation and a graphite monochromater. A total of 2212 independent reflections ($2\theta \leq 40°$, relative structure factors $>3\sigma_F$) were used in the solution and refinement of the structure. The structure was solved by direct methods using a modified version of MULTAN.[9] 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 Å 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).