

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) spectrum¹² 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

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- Prepared by reduction of $n-C_8H_{17}COOH$ to $n-C_8H_{17}CD_2OH$ with $LiAlD_4$ and conversion to $n-C_8H_{17}CD_2Cl$ with $SOCl_2$ with purification by gas chromatography (3% d_1 , 97% d_2).
- 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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- 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 electrons of 100 μ A and 70 eV (or lower where noted), and a sample reservoir and source temperature of 150° were used. MI 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 magnet and ESA is then increased with helium until the precursor ion intensity is reduced to 35% of its original value, and the CA ion product abundances are determined in the same manner in a second ESA scan.¹² The data are the computer averaged composites of at least 16 separate scans. The contributions from MI products (corrected as de-

scribed¹²) are subtracted from these values 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 $\pm 5\%$ relative or ± 0.3 absolute, whichever is the larger.

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- Decomposition of completely H/D scrambled $C_4H_6D_2Cl^+$ ions would give $[CH_2Cl^+]:[CHDCl^+]:[CD_2Cl^+]$ of 15:12:1.
- 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**.
- Postdoctoral Fellow, 1974; on leave from the NFWO, Belgium.

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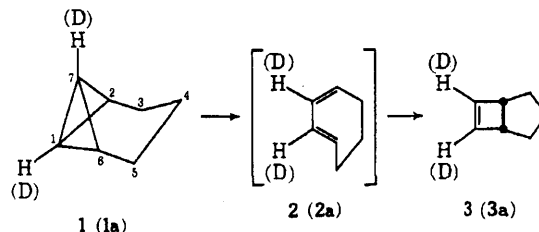
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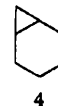
Thermal Rearrangement of Some Endo-Endo'-Bridged Bicyclo[1.1.0]butanes

Sir:

The thermal rearrangement of bicyclo[1.1.0]butane to butadiene is considered to be a concerted [$\sigma_2s + \sigma_2a$] type reaction.^{1,2} Recently Dewar and Kirschner³ 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 Szeimies⁴ 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** \rightarrow **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



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**.

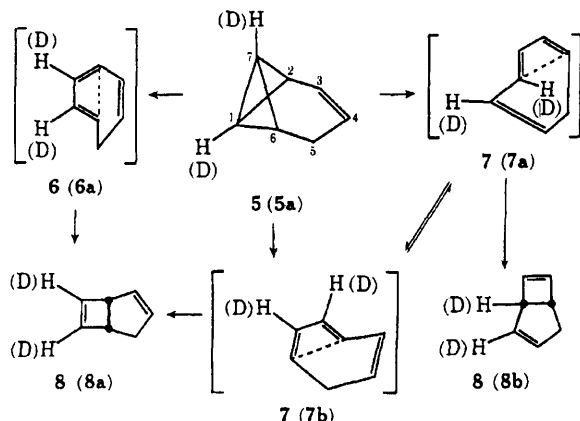
Recently the preparation of (**5**) and its thermolysis to bicyclo[3.2.0]hepta-2,6-diene (**8**) were reported.⁷ The by-product cycloheptatriene does not appear, if the reaction is carried out in the presence of TMEDA. At 135° the half-life was determined to be 1 hr, the yield more than 90%. An overall 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	ΔH^\ddagger , kcal/mol	ΔS^\ddagger , eu	E_A , kcal/mol	Log A
5a	120–145	$(4.6 \pm 0.2) \times 10^{-2b}$	31.5 ± 0.6	1.1 ± 1.1	32.4 ± 0.6	13.6 ± 0.4
1c,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
12c	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
9c	230–250	$(2.1 \pm 0.1) \times 10^{-6b}$	40.7 ± 1.0	0.6 ± 1.5	41.7 ± 1.0	13.6 ± 0.5

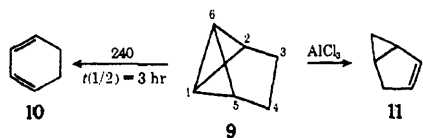
^a Solvent toluene-*d*₆-TMEDA. ^b Extrapolated. ^c Solvent TMEDA. ^d To obtain the rate constants for the conversion 1→3, the overall rate constants for the decrease of the 1 concentration were dissected in the ratio of the products 3 and 4.

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 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 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

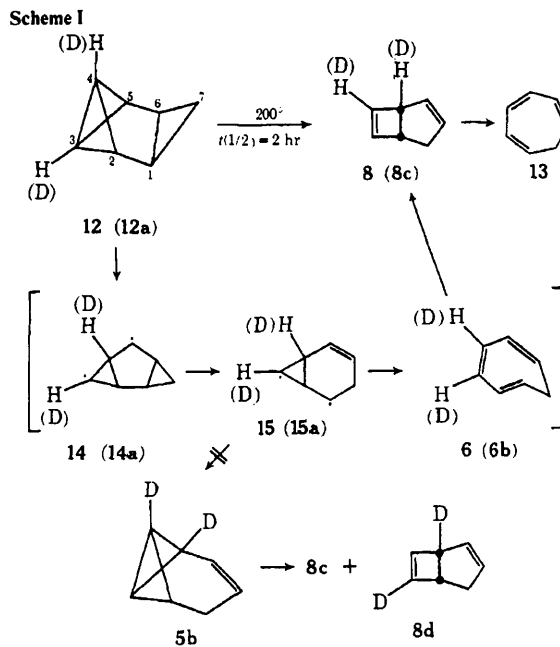


we did not find any 8b, 6a remains as the most probable intermediate. Involving the double bond π electrons in 5 a series of concerted six-electron rearrangements are allowed, which directly or via other C₇H₈ isomers could produce 8. All these processes, however, do not satisfy the experimental deuterium distribution on thermolysis of 5a.

Tricyclo[3.1.0.0^{2,6}]hexane (9) became easily accessible recently.⁹ It thermolyzes in the gas phase⁹ 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 tetrachloroethylene⁷ 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.



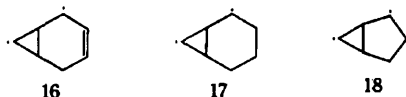
time plots it can be concluded, that 12 rearranges completely via 8. After a conversion of 70–80% the yield of 8 plus 13 was determined to be greater than 90%.

Although other mechanistic pathways, e.g., a [$\sigma_2 + \sigma_2 + \sigma_2$] bond relocation, cannot be ruled out, we favor the one including the diradical 14, which should undergo a cyclopropylcarbonyl-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 13¹⁴ 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 cyclopropylcarbonyl

radicals dispose of a stabilization energy of several kilocalories per mole.¹⁷ Furthermore an easy ring enlargement¹² as **14** → **15** is not available to **18**, the rearrangement of which should therefore be encumbered with more constraints.



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 temperatures¹⁸ 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 O₂ with low-spin pentacoordinate cobalt(II) complexes are of widespread occurrence and characteristically follow the course of eq 1 to form either termi-

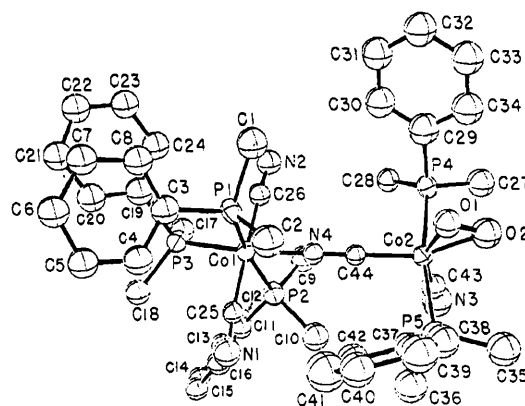
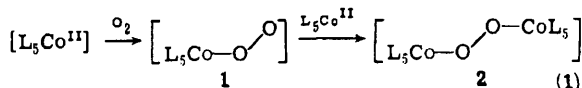


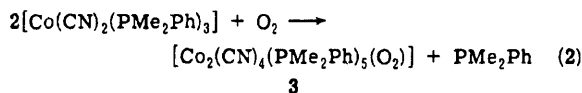
Figure 1. Molecular structure of [Co₂(CN)₄(PMe₂Ph)₅(O₂)].

nally bonded mononuclear or O₂-bridged binuclear adducts (types 1 and 2, respectively).¹



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)-O₂ adducts.¹ In view of this, our finding of a rather different, previously unrecognized, structure for the 1:2 adduct formed by reaction of O₂ with [Co^{II}(CN)₂(PMe₂Ph)₃] (Me = CH₃, Ph = C₆H₅), 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)-O₂ adducts.^{7,8}

Passing a stream of O₂ through a benzene solution of [Co(CN)₂(PMe₂Ph)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 × 10⁴ M⁻¹ cm⁻¹); infrared (Nujol), ν_{CN}, 2085 and 2105 cm⁻¹, ν_{O2}, 881 cm⁻¹.



Crystals of [Co₂(CN)₄(PMe₂Ph)₅(O₂)] · ½C₆H₆, 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) Å and ρ_{obsd} = 1.317 and ρ_{calcd} = 1.313 g/cm³ for 16 formula units per unit cell. Data were collected on a Picker FACS-I diffractometer, using Mo Kα radiation and a graphite monochromator. A total of 2212 independent reflections (2θ ≤ 40°, relative structure factors >3σ_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).