spectra show the formation of $H_2Ru(CO)(PPh_3)_3$ and $H_2Ru(CO)_2(PPh_3)_2$, presumably due to decarbonylation of aldose sugars present (vide infra).[12] This does not immediately lead to loss of catalytic activity, however, since $H_2Ru(CO)(PPh_3)_3$ also hydrocracks fructose (expt 5, footnote *e*).

Clues to the hydrocracking mechanism are provided by the cleavage products and intermediate sugars observed. The primary C–C cleavage site (especially at low base concentrations) is always β to the sugar carbonyl group; the major product of fructose cleavage being glycerol, of glucose cleavage ethylene glycol and erythritol (expt 7), and of *manno*-2-heptulose cleavage glycerol and erythritol (expt 8). This cleavage site selectivity, together with the strong base catalysis observed, suggests that a retro-aldol reaction (possibly metal-enhanced) may be involved (Figure 1).[13,14]

Sugars are known to undergo a complex set of reactions in aqueous alkaline solution including isomerization (e.g. fructose → glucose), retro-aldolization, and degradation.[15] The same reactions take place in the nonaqueous solvent used here. Thus fructose heated to 100 °C in the presence of catalytic amounts of potassium hydroxide or potassium *tert*-butoxide yields a complex mixture of C_2–C_6 sugars consistent with that expected for fructose isomerization and multiple, reversible aldol reactions.[16] A very similar mixture of sugars is observed in the early stages of the Ru/KOH-catalyzed hydrogenation of fructose.

The final product distributions in these hydrocracking reactions appear to be controlled by a competition between sugar hydrogenation and retro-aldol cleavage. The carbonyl groups in short chain C_2–C_4 sugars are more readily hydrogenated than those in C_5–C_6 sugars since the former are less involved in hemiacetal and hemiketal formation.[17] Increasing the base concentration accelerates the cleavage to small retro-aldol derived sugars, thereby raising the ultimate percentage of hydrocracked products.[18] Higher base concentrations also cause the sugar isomerization and reversible aldol scrambling reactions to compete more effectively with hydrogenation, resulting in the decline in selectivity amongst the hydrocracked products.

The chemistry observed here therefore appears to be a combination of a sugar retro-aldol reaction and a metal-catalyzed carbonyl group hydrogenation. The net result of these otherwise ordinary reactions is the strikingly facile hydrocracking of specific C–C single bonds, a reaction with virtually no precedent in homogeneous transition-metal catalysis,[19] even for functionalized substrates[14] such as sugars. These findings furthermore provide one of the first fundamental bases for the rational development of nonbiological approaches to biomass conversion.

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Supplementary Material Available: Experimental details and a sample GC analysis (5 pages). Ordering information is given on any current masthead page.

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(18) The selectivity for hydrocracking decreases as the reaction proceeds, however, since the hydroxide concentration drops rapidly due to its consumption in the formation of carboxylate salts.[5]

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ESR Evidence for the Stereospecific Formation of the Chair Cyclohexane-1,4-diyl Radical Cation from Both Bicyclo[2.2.0]hexane and 1,5-Hexadiene

Ffrancon Williams* and Qing-Xiang Guo*

Department of Chemistry, University of Tennessee Knoxville, Tennessee 37996-1600

Deborah C. Bebout and Barry K. Carpenter*

Baker Laboratory, Department of Chemistry Cornell University Ithaca, New York 14853-1301

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Cyclohexane-1,4-diyl has assumed considerable interest as a prototype structure associated with the hypothetical biradical pathway in the Cope rearrangement and in the cleavage of bicyclo[2.2.0]hexanes,[1] largely because of the stereochemical requirement for *chairlike* structures at the product-determining stage of these isomerizations.[2,3] These elusive biradicals have resisted further characterization, however, and thermal generation of an identical parent diyl from both 1,5-hexadiene (**1**) and bicyclo[2.2.0]hexane (**2**) has been questioned on the basis of the discordant free energies of formation obtained for the transition states derived from these two reactants.[1f] Similar questions of conformation and of a common identity from different precursors naturally arise for the radical cation (**3**),[4-8] and here we report spectroscopic evidence that the chair form of **3** is produced stereospecifically by the oxidation of both **1** and **2**.

As shown in Figure 1, virtually identical ESR spectra were obtained by the radiolytic oxidation of **1** and **2** in a haloethane matrix, the binomial seven-line pattern (A(6 H) = 12.0 (1) G; g = 2.0026 (4)) from **1** having previously been assigned to **3**.[6] That the spectral correspondence represents a true identity of signal carriers and not just a verisimilitude[9] was established by the exact parallelism observed in the growth of the spectrum from the cyclohexene radical cation (**4**) when the two samples were annealed or photobleached.[6] Furthermore, while the seven-line pattern was also generated from solid solutions of **1** and **2** in $CF_2ClCFCl_2$, only the spectrum of **4** was revealed from the corresponding $CFCl_3$ solutions. All these results accord with the conclusion that **3** is a common intermediate along the oxidation pathways from **1** and **2** to **4**.

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0002-7863/89/1511-4133$01.50/0

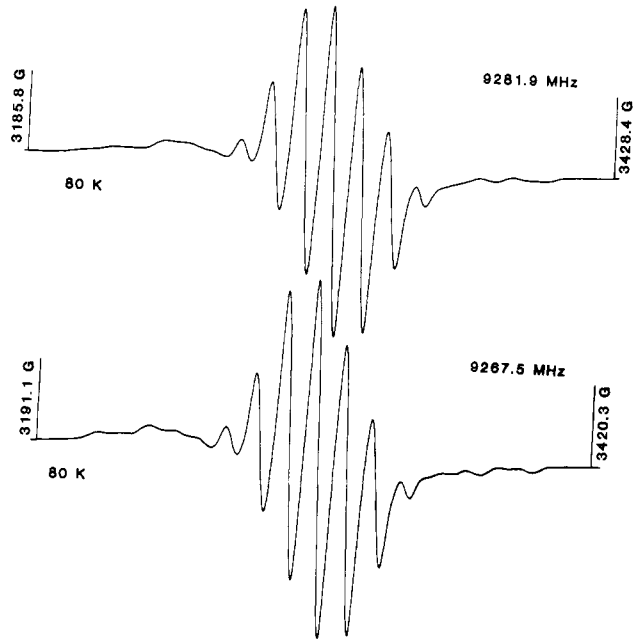


Figure 1. ESR spectra obtained from γ-irradiated CF_3CCl_3 solutions of bicyclo[2.2.0]hexane (upper) and 1,5-hexadiene (lower) at 80 K before annealing.

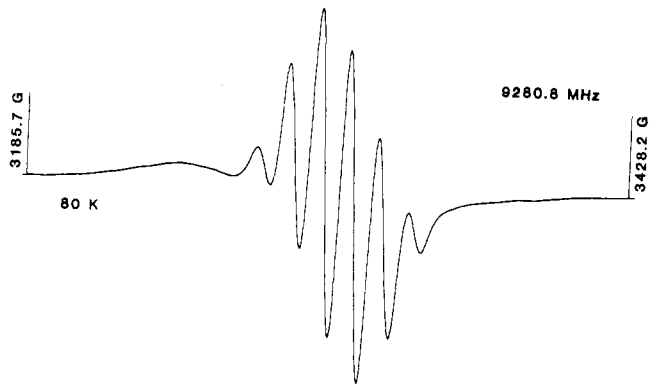
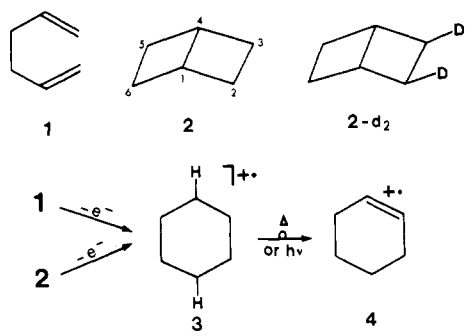


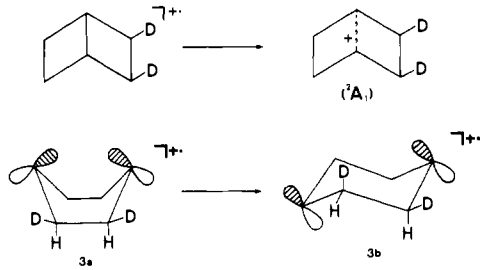
Figure 2. ESR spectrum obtained from a γ-irradiated CF_3CCl_3 solution of *exo-cis*-2,3-dideuteriobicyclo[2.2.0]hexane at 80 K before annealing.

Scheme I



Information about the stereochemistry of the formation of **3** from **2** was obtained through the use of *exo-cis*-2,3-dideuterio-**2** (**2-d_2**).[10,11] The six-line spectrum obtained in this case (Figure 2) shows that one of the six interacting hydrogens in **3** ($2H_\alpha$ and $4H_{\beta a}$)[6] has been replaced by deuterium, and this must be in an axial position considering that the two α-hydrogens originate from the bridgehead positions in **2**. The boat structure **3a**[12,13] formed from **2-d_2** would place both deuterium atoms into equatorial positions, and therefore neither this (e,e) stereoisomer nor its (a,a) conformational diastereomer is compatible with the ESR result. On the other hand, a conformational flip of **3a** to the chair form produces either the (a,e) stereoisomer **3b** or its conformational (e,a) enantiomer which both satisfy the six-line spectrum, whereas the trans isomers consisting of the enantiomeric pairs of (a,a) and (e,e) conformational diastereomers are now excluded, again in keeping with the result. Thus, **2-d_2** is specifically oxidized to the cis enantiomers of the chair form of **3-d_2**.

Scheme II



A clean six-line spectrum was also obtained from the oxidation of an ca. 50:50 mixture of *meso*-3,4-dideuterio-**1** and (*E*,*Z*)-1,6-dideuterio-**1** prepared by thermal cleavage of **2-d_2**.[3c,14] For cyclization of the meso stereoisomer, the chiral centers should be unaffected to produce the erythro C_2–C_3 form of **3-d_2**, so only the chair (a,e) structure is again consistent with the ESR spectrum. Since the (*E*,*Z*)-1,6-dideuterio-**1** isomer must likewise give a chair structure for **3**, we obtain in this case the additional information that the chirality produced in the bond-forming cyclization step is directed by a chair *transition state* to give the required erythro configuration in chair **3-d_2**. Had a boat transition state intervened, the resulting threo configuration would have given the (a,a) and (e,e) forms of chair **3-d_2** with 5- and 7-line spectra. To summarize, the ESR result for the mixture of **1-d_2** isomers establishes that the chair form of **3** is also produced from **1** and that this cyclization reaction proceeds stereospecifically through a chairlike transition state.

The pathways from **1** and **2** to chair **3** contrast, therefore, in that cyclization involves uniquely chairlike structures, whereas cleavage necessarily proceeds through an incipient boatlike geometry. Consequently, it seems reasonable to attribute the predominance at 80 K of the chair form of **3** over a possible boat form to thermodynamic rather than kinetic factors.

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(10) **2-d_2** was prepared from bicyclo[2.2.0]hex-2-ene[11] using D_2 instead of H_2 in the hydrogenation procedure.[11]

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(12) This $^2A_1$ state of the boat structure is not necessarily formed by the vertical ionization of **2**. In this regard, both MO calculations and comparison of relevant photoelectron spectra[11] indicate that the $8a_1$ orbital responsible for most of the C_1–C_4 bonding in **2** is not the HOMO, the orbital energy sequence being $4a_2 > 6b_1 > 8a_1 > 3a_2$. Considerable electron reorganization could therefore be involved on ionization resulting in a different orbital sequence for **2**$^{+\cdot}$. We thank Professor Heilbronner for his detailed and enlightening comments on this question.

(13) Relaxation from **2**$^{+\cdot}$ may also occur through a twist-boat structure of D_2 symmetry. However, it is unlikely to be the equilibrium structure because of the relatively small value of the angular-dependent hfc to the axial hydrogens.[6]

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