

Figure 2. One of the four $\text{Co}^{\text{II}}\text{-Cl}_2\text{-Na}^+$ complexes in the large cavity of each unit cell. Selected bond lengths (in ångströms) are $\text{Co}^{\text{II}}\text{-Cl}(1)$, 2.24 (1); $\text{Cl}(1)\text{-Cl}(2)$, 2.52 (2); $\text{Cl}(2)\text{-Na}^+$, 2.54 (8); $\text{Co}^{\text{II}}\text{-O}(3)$, 2.244 (6). Co^{II} is in a tetrahedral environment: $\text{O}(3)\text{-Co}^{\text{II}}\text{-O}(3)$, 109.6 (3) $^\circ$; $\text{Cl}(1)\text{-Co}^{\text{II}}\text{-O}(3)$, 109.3 (4) $^\circ$.

cations to accommodate the four $\text{Cl}(2)$ atoms, one ion at $\text{Na}(2)$ associates itself symmetrically with two $\text{Cl}(2)$ atoms and remains in the 8-ring plane. Consistent with this are the two $\text{Na-Cl}(2)$ distances: $\text{Na}(1)\text{-Cl}(2)$, 2.54 (8) Å, and $\text{Na}(2)\text{-Cl}(2)$, 2.85 (2) Å.

The cobalt(II) ions are four coordinate; three 6-ring oxide ions of the zeolite framework at $\text{O}(3)$, and a chlorine atom at $\text{Cl}(1)$, are tetrahedrally disposed about cobalt(II) (see Figure 2). The $\text{Co-Cl}(1)\text{-Cl}(2)$ angle, 114 (1) $^\circ$, is quite bent, and the $\text{Co-Cl}(1)$ distance, 2.24 (1) Å, is comparable with that found in chloride complexes of cobalt(II).⁸ The Cl-Cl bond length is 2.52 (2) Å, 0.53 Å longer than the bond in free Cl_2 .⁹

In this structure, the cobalt(II) ion lies further from the plane of its three coordinated $\text{O}(3)$ framework oxide ions than it does in other cobalt(II)-exchanged zeolite A structures (see Table II). The $\text{Co}^{\text{II}}\text{-O}(3)$ distance of 2.244 (6) Å found in this structure is significantly longer than the same distance reported in dehydrated $\text{Co}_4\text{Na}_4\text{-A}$ or in its complexes with C_2H_4 ,¹¹ C_2H_2 ,¹² C_3H_6 ,¹³ NO_2 ,¹⁰ and CO^4 (see Table II). This indicates that cobalt(II) interacts more strongly with Cl_2 than it does with the other ligands.

The X_2 bond lengths ($\text{X}_2 = \text{I}_2, \text{Br}_2, \text{Cl}_2$)^{3,15,16} are significantly longer in their intrazeolitic charge-transfer complexes than in the uncomplexed molecules.⁹ Each halogen molecule forms an axial complex with a framework oxide ion.

In this work, however, instead of oxide ions, dichlorine complexes to cobalt(II); the relatively short $\text{Co}^{\text{II}}\text{-Cl}$ distance observed, 2.24 Å, as compared with the sum of the appropriate ionic and van der Waals radii,¹⁷ $0.72 + 1.80 = 2.52$ Å, indicates a strong interaction.

The long Cl-Cl bond indicates that its bond order has been reduced upon complexation to cobalt(II). This can occur (1) when charge is delocalized from an occupied bonding orbital on Cl_2 into an empty cobalt(II) orbital, or (2) when charge on cobalt(II) delocalizes into an empty antibonding dichlorine orbital. The highest occupied molecular orbitals in dichlorine are $3p\pi_g^*$, $3p\pi_u$, and $3p\sigma_g$.¹⁸ Dichlorine could be acting as a σ donor from $3p\pi_u$ to, perhaps, the empty cobalt(II) 4s orbital, the lowest unoccupied cobalt(II) orbital of proper symmetry. The order of the dichlorine bond might also be decreased by a $3d\pi_{\text{Co}} \rightarrow 3d\pi_{\text{Cl}_2}$ back-bonding interaction.

The observations, (1) that the color of the crystal did not change upon the sorption of Cl_2 and (2) that the approach distances between the cobalt ion and the zeolite framework are relatively long, indicate that cobalt(II) has not been oxidized to cobalt(III) by Cl_2 . The first observation indicates also that the 3d structure of cobalt(II) has not been qualitatively altered by coordination to Cl_2 .

The $\text{Na}^+\text{-Cl}(2)$ distances (2.54 and 2.85 Å) average to less than the sum of the corresponding ionic and van der Waals

radii,¹⁷ $0.97 + 1.80 = 2.77$ Å. The $\text{Na}^+\text{-O}$ distances (2.96 and 2.57 Å) are both more than the sum of the corresponding radii, $0.97 + 1.32 = 2.29$ Å. This indicates that the larger Cl^0 atoms, which are more polarizable than oxide ions, can interact strongly with Na^+ .

Acknowledgments. This work was supported by the National Science Foundation (Grant No. CHE76-81586). We are indebted to the University of Hawaii Computing Center.

Supplementary Material Available: Final positional, thermal, and occupancy parameters for the structure at -165 (3) $^\circ\text{C}$ (Supplementary Table 1) and listings of the observed and calculated structure factors for both structures (Supplementary Tables 2 and 3) (8 pages). Ordering information is given on any current masthead page.

References and Notes

- (1) The nomenclature refers to the contents of the unit cell. For example, $\text{Co}_4\text{Na}_4\text{-A}$ represents $\text{Co}_4\text{Na}_4\text{Al}_{12}\text{Si}_{12}\text{O}_{48}$ with the zeolite A structure.
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V. Subramanian, Karl Seff*

Chemistry Department, University of Hawaii
Honolulu, Hawaii 96822

Tor Ottersen

Department of Chemistry, University of Oslo
Oslo, Norway

Received October 31, 1977

A Stereoelectronic Effect in Hydrogen Atom Abstraction from a Substituted Cyclohexyl Radical

Sir:

Since the pseudoaxial and pseudoequatorial protons of the β positions of cyclohexyl radical in its chair-like conformation are stereochemically nonequivalent with respect to the semi-occupied p orbital, they should exhibit different reactivity toward reagents capable of abstracting hydrogen atoms. Two reports of such reactivity differences have recently appeared. Agosta and Wolff¹ observed preferential intramolecular transfer of the pseudoaxial β -hydrogen atom in biradicals generated photochemically from bicyclo[3.2.1]octan-6-ones. A contrary result was reported by Livant and Lawler² who studied the disproportionation of cyclohexyl radicals by the CIDNP technique and obtained evidence for the selective loss of pseudoequatorial β -hydrogen atoms. The discord between these reports prompted the present study of the stereochemical course of reactions of an appropriately substituted, conformationally locked³ cyclohexyl radical **4**.

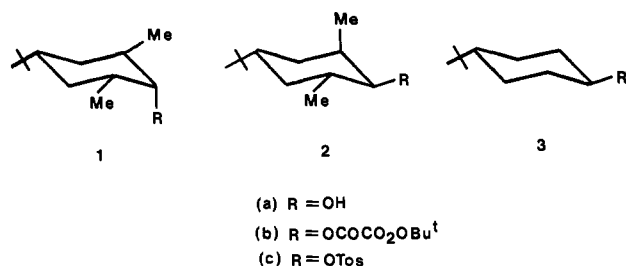
The radical **4** was generated by thermolysis of the *tert*-butyl peroxyglyoxalate **2b**. Catalytic hydrogenation of 4-*tert*-

Table I. Products of Thermolysis of Peroxyglyoxalates **1b** and **2b**

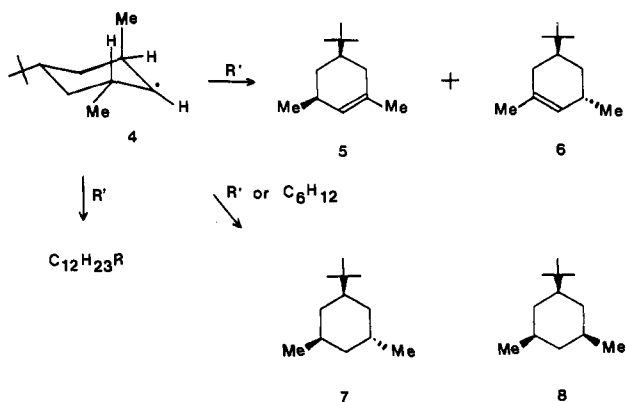
Peroxy ester	Yields of products, %			
	5	6	7	8
1b	22	0	0	69
2b	1.7	14	72	1 ^a

^a Formed from 1% isomeric impurity in starting material.

butyl-2,6-dimethylphenol⁴ over rhodium on alumina gave the triequatorially substituted cyclohexanol **1a**. Oxidation of **1a**



gave the related ketone which was converted via the semicarbazone⁵ into its stereoisomer containing one pseudoaxial and one pseudoequatorial methyl substituent. The alcohol **2a** obtained by reduction with lithium aluminium hydride was converted into the radical precursor **2b** by successive treatment with oxalyl chloride and *tert*-butyl hydroperoxide.⁶ The peroxy ester **2b** was then heated in cyclohexane under nitrogen at 100 °C for 2 h and the mixture was analyzed by GLC, using as reference compounds samples of the cyclohexanes, **7** and **8**, and cyclohexenes, **5** and **6**, synthesized by unambiguous routes.



Stereochemical assignments for all these compounds were consistent with the methods of their preparation and were supported by ¹³C NMR, ¹H NMR, and infrared spectral data.

Homolysis^{6,7} of **2b** initially affords the trisubstituted cyclohexyl radical **4** and *tert*-butoxy radicals, but the latter should be rapidly consumed by reaction with solvent to afford cyclohexyl radicals. Cyclohexene was detected in the reaction mixture in sufficient yield (>0.6 mol/mol of **2b**) to indicate that decomposition of the peroxy ester **2b** induced by direct abstraction of β hydrogen from *tert*-butoxy radicals is unlikely to be a significant reaction pathway.

Disproportionation of **4** affords the olefin **5** by loss of the pseudoequatorial β -hydrogen atom or its isomer **6** by loss of the pseudoaxial hydrogen. Of these two competing processes the former should be favored on steric and thermodynamic grounds, for nonbonded interactions are less severe in the diequatorially substituted cyclohexene **5** than in its isomer **6**. However, the data are not in accord with this simple view, for the high yield of **6** relative to **5** clearly shows that loss of the

pseudoaxial hydrogen atom from **4** is the preferred process and occurs approximately eight times more rapidly than loss of the pseudoequatorial hydrogen atom. Our results thus agree nicely with those of Agosta and Wolff.¹ They support the hypothesis that homolysis of the β -C-H bond, like β -C-C bond fission in cycloalkylcarbinyl radicals,⁸ is subject to stereoelectronic control: the bond which preferentially undergoes fission is that which lies closest to the plane of the adjacent semioccupied p orbital. Their relatively large ESR hyperfine splittings⁹ show that it is the pseudoaxial β protons in cyclohexyl radicals which best satisfy this criterion.

Of the other processes available to **4**, radical coupling is clearly unimportant, for a high yield (~90%) of monomeric products was obtained. The major product from the thermolysis of **2b** is the cyclohexane **7**. Undoubtedly some of it arises by disproportionation between **4** and cyclohexyl radicals. However, in view of the high relative yield of **7**, it seems likely that it is also formed by hydrogen atom abstraction from solvent cyclohexane.

For comparative purposes thermolyses of **3b** and of the triequatorially substituted peroxy ester **1b** were also studied. The former gave *tert*-butylcyclohexane (70%) and 4-*tert*-butylcyclohexene (14%), whilst the latter gave **5** and **8**. Interestingly, the ratio of yields of olefin and cycloalkane, % **5** to % **8**, from decomposition of **1b** is considerably higher than the equivalent ratio, % (**5** + **6**) to % **7** for decomposition of **2b**. This reflects the fact that the intermediate radical **4** has only one pseudoaxial β proton, whereas the radical derived from **1b** has two.

Separate experiments were conducted to test the possible importance of alternative routes to the observed products of decomposition of **2b**. Thus, solvolysis of the tosylate **2c** afforded **5** (53%) and rearranged olefins, but no trans olefin **6**. We conclude that formation of **6** from **2b** cannot involve a cationic intermediate. Also, the acetate and chloroglyoxalate of the alcohol **2a** were each found to be completely stable under the thermolysis reaction conditions: it appears unlikely, therefore, that the peroxy ester **2b** decomposes by intramolecular concerted elimination of *tert*-butyl alcohol and carbon dioxide.

In summary, the results outlined above, and those reported previously, conform to a general pattern: homolysis of a C-H bond adjacent to a semioccupied p orbital, a lone pair,¹⁰ or a π orbital,¹¹ or of a C-C bond adjacent to a semioccupied p orbital,⁸ will occur most readily when the bond undergoing fission and the orbital can assume coplanarity.

Acknowledgment. We thank Dr. R. G. Lawler for helpful discussion and comment.

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A. L. J. Beckwith,* C. Easton

Organic Chemistry Department, University of Adelaide
G.P.O. Box 498, Adelaide, South Australia 5001

Received December 28, 1977