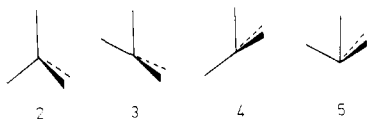


Figure 1. Dependence of structural stability of the 22 dipolar wurtzite-like structures on the number of shared edges per unit cell containing eight formula units: results from a purely point charge electrostatic model, ●, and a one-electron tight-binding approach, ○.

packing with cations (A), for cells of different size. The result is a series of structures containing AX_4 tetrahedra that point either parallel or antiparallel to the crystallographic c axis. If all the tetrahedral point in the same direction, then none share edges, all share vertices, and the wurtzite structure (found for BeO for example) results. If both up and down pointing tetrahedra are present, then edge sharing is required. We have performed both Madelung calculations and one-electron tight-binding based band structure computations⁵ on the set of 22 possible structures of this type with the 8-atom (1,1) cell or the 16-atom (2,1) cell of ref 4a. For the latter Be and O atoms were used for A and X. The results are shown in Figure 1 and, perhaps surprisingly, indicate a good energetic correlation with the number of shared edges per formula unit for *both* sets of calculations. The success of the "molecular orbital" model indicates that Pauling's third rule may have an orbital explanation too.

The reasons behind the band structure results are not hard to find. We focus on the energetic contributions from different local geometrical arrangements in the solid, a technique we have used effectively before.^{6,7} The number of cation-anion or anion-anion interactions at any given distance will be equal in any of these 22 structures, so the interpretation of the ionic results must rely on a comparison of cation-cation distances. The angular relations among the four cations coordinated to any anion can differ, however, and an orbital approach will look at the coordination around the anions since this is where the valence electron density will be largest. Structures 2-5 show the four different geometrical



arrangements found at the anion sites in these crystal structures. Molecular orbital calculations on isolated OBe_4^{6+} units with these geometries (to mimic the local crystal energetics) show that their energy increases in this order, i.e., as the distortion from tetrahedral increases. This of course is just what is expected from traditional ideas of *molecular* structure. Consideration of the Be-Be and Be-O bond overlap populations in these distorted molecules shows

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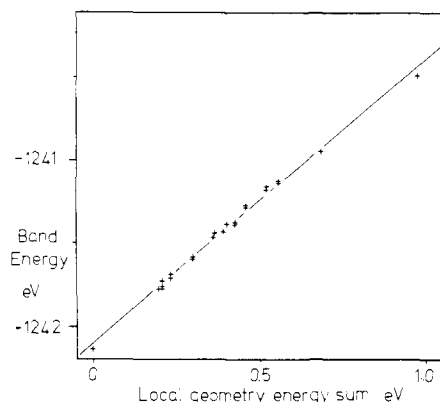


Figure 2. Matching of the calculated band structure energy to the weighted sum of local geometry energy contributions (2-5).

that the energetic differences arise from variations in direct central atom-ligand interactions and not from ligand-ligand (i.e., Be-Be) effects. Figure 2 shows how the computed band structure energy of the 22 possibilities compares with the weighted sum of the four energies of the molecular units 2-5. The truly excellent correlation is good evidence for the importance of such anion coordination variations via an orbital model.

Our results do not of course disprove the traditional explanation behind Pauling's third rule but show in an interesting way an isomorphism between orbital and ionic models⁸ of solid-state structure. The ideas will be extended to other, more complex structures in the near future.

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for their partial support of this research, which was also supported by the National Science Foundation under NSF DMR8019741.

(8) We should point out in this context that the ill- (or un-) defined Extended Hückel Hamiltonian used in our band structure computations does in fact contain some sort of electrostatic contribution which of course is never evaluated explicitly.

Intramolecular Homolytic Displacement of Cobaloxime(II) from Saturated Carbon. A Novel Synthesis of (Trichloroethyl)cyclopentanes and -sulfolanes

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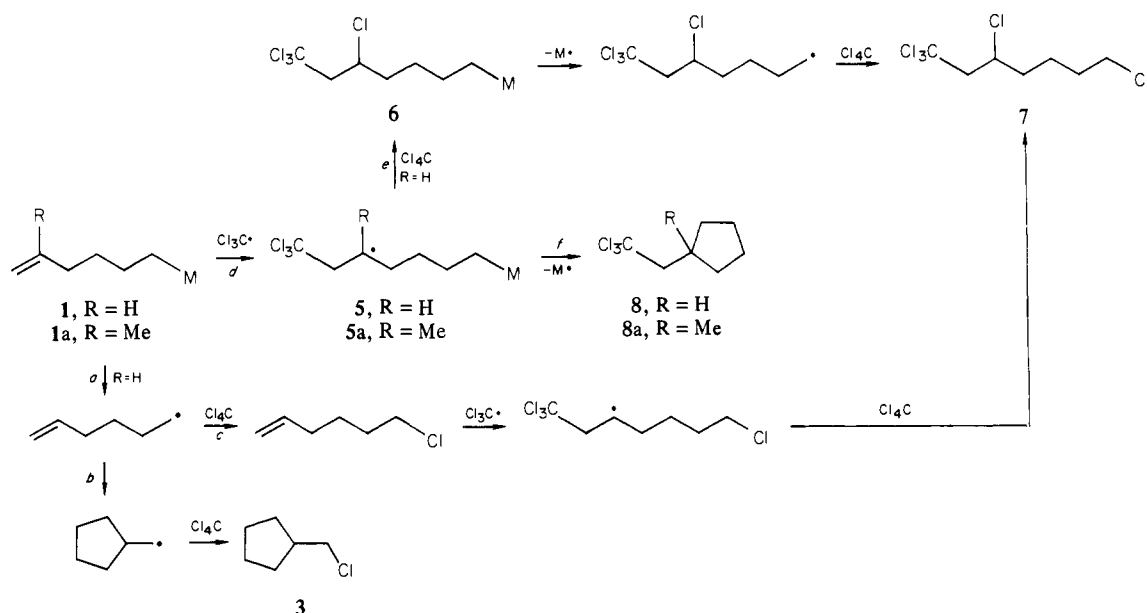
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Bimolecular homolytic displacement at saturated carbon has been characterized only in a very few cases.¹ Two definitive examples are the stereospecific ring opening of 1,1-dichlorocyclopropane by attack of a chlorine atom at C-2² and, in the gas phase, the displacement of the *tert*-butyl radical by attack of a

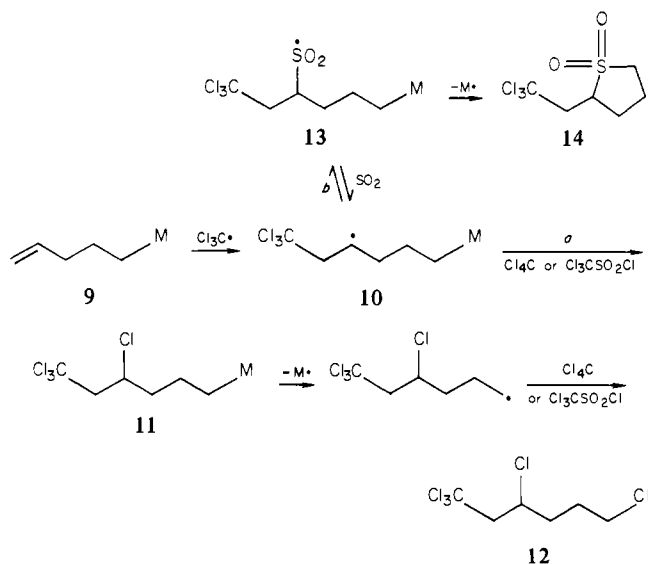
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(2) Incremona, J. H.; Upton, C. J. *J. Am. Chem. Soc.* **1972**, *94*, 301.

Scheme I^a^a M = Co(dmgH)₂py.

trifluoromethyl radical at a peripheral carbon of neopentane.³ Ring closure to cyclopropane by loss of an iodine atom from a 3-iodopropyl radical has also been detected,⁴ and though cyclopentanes are formed in very low yield in some free-radical reactions of 1,5-diiodopentanes,⁵ an attempt to induce an S_Hi reaction of the 5-bromopentyl radical was unsuccessful.⁶ We have recently shown in the reactions of polyhalogenomethyl and sulfonyl radical precursors with a variety of alkenylcobaloxime(III) complexes⁷ that the paramagnetic cobaloxime(II) complex is a potential leaving group for homolytic displacement reactions. We now report two related reactions that show that, under favorable conditions in which a five-membered ring may result, an intramolecular homolytic (S_Hi) displacement of cobaloxime(II) can take place through the attack of carbon- or sulfur-centered radicals at the α carbon of an alkyl chain of an organocobaloxime(III) complex. These reactions are the first examples of homolytic displacement by attack of a remote radical at a saturated carbon of an alkyl chain and provide a novel synthetic route to five-membered rings.

Thus, the main product of photolysis of hex-5-enylbis(dimethylglyoximate)(pyridine)cobalt(III) (**1**, 10⁻¹ mol dm⁻³)⁸ with a 10-fold excess of carbon tetrachloride (**2**) in methylene chloride at 0–10 °C, using tungsten illumination in all-glass apparatus, is (chloromethyl)cyclopentane (**3**), formed by photolysis of the carbon-cobalt bond (Scheme I, path a)⁹ rearrangement of the

Scheme II^a^a M = Co(dmgH)₂py.

hex-5-enyl radical (branch b)¹⁰ and abstraction of a chlorine atom from **2** by the cyclopentylmethyl radical. When the same reaction is carried out in the presence of a large excess of **2** or of trichloromethanesulfonyl chloride (**4**), not only does the rate at which the hex-5-enyl radical abstracts a chlorine atom from **2** or from **4** (Scheme I, branch c) become larger than the rate at which that radical rearranges but the radical chain addition of the elements of carbon tetrachloride to the double bond of the alkenylcobaloxime (Scheme I, path d, branch e) becomes important, giving the tetrachloroheptylcobaloxime(III) **6** and, subsequently through further reaction, the pentachloroheptane **7**.

However, when the reaction of **1** is carried out *thermally* by using only a limited excess (2–10-fold) of **2**, at 80–100 °C in the dark for 1 h, the main product (ca. 85%) is the (trichloroethyl)cyclopentane **8**.¹¹ Clearly, under these conditions, where

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(8) All the compounds described here have been characterised by NMR spectroscopy and elemental analysis or accurate molecular mass measurement.
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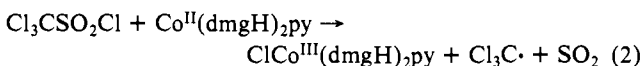
(10) The hex-5-enyl radical cyclizes with a rate constant of ca. 1 × 10⁵ s⁻¹ at ambient temperature. Beckwith, A. L. J.; Ingold, K. U. "Rearrangements in Ground and Excited States"; De Mayo, P., Ed.; Academic Press: New York, 1980; Chapter 4, p 1.

the rate of homolysis of the carbon-cobalt bond is slow¹³ and where the rate of the bimolecular reaction of the intermediate **5** with **2** is reduced, the intramolecular homolytic displacement of cobaloxime(II) (Scheme I, branch f) from **5** becomes the dominant pathway. Trichloromethyl radicals, necessary for promoting the reaction, are regenerated by the reaction of the displaced cobaloxime(II) complex with **2** (eq 1, dmGH = dimethylglyoximate).¹⁴



Thus reaction 1 and Scheme I, path d and branch f, form the propagation steps of a reasonably efficient chain reaction. Surprisingly, in the corresponding thermal reaction of the (5-methylhex-5-enyl)cobaloxime(III) (**1a**) in **2** as solvent, the (trichloroethyl)methylcyclopentane **8a** is the sole organic product, suggesting that a tertiary carbon radical as in **5a** attacks the α carbon in preference to abstracting a chlorine atom from the solvent.

In the corresponding thermal reaction of the pent-4-enylcobaloxime(III) (**9**, 0.1 mol dm⁻³) with **2** and in the photochemical reaction of **9** with an excess of **2** or of **4** in methylene chloride at 0–10 °C, the main product is the pentachlorohexane **12**, formed as in Scheme II, branch a. When this reaction is interrupted before completion, the (tetrachlorohexyl)cobaloxime(III) **11** can be isolated and characterized. However, in the corresponding photochemical reaction of **9** with 1 equiv of **4** in methylene chloride and in the thermal reaction of **9** with **4** in methylene chloride saturated with sulfur dioxide, in a sealed tube at 100 °C for 1 h, the main product is the (trichloroethyl)sulfolane **14** (isolated in 87% and 72% yield, respectively).¹⁵ In these cases, where the rate of chlorine atom abstraction by the radical **10** (Scheme II, branch a) is low, the initially formed radical **10** can capture sulfur dioxide (Scheme II, branch b).¹⁶ The sulfonyl radical **13** can then undergo an efficient intramolecular homolytic displacement, similar to that shown in Scheme I, to give **14**. Regeneration of the trichloromethyl radical through eq 2¹⁴ thus provides one of



the propagation steps required for the chain reaction and at the same time liberates the sulfur dioxide necessary for branch b.

The formation of substituted (trichloroethyl)sulfolanes also takes place with a variety of mono- and disubstituted pent-4-enylcobaloximes, provided those substituents are in positions 1–4. Further experiments on the stereochemistry of such processes are in hand.

Registry No. 1, 42568-40-1; **1a**, 82639-73-4; **2**, 56-23-5; **3**, 13988-39-1; **4**, 2547-61-7; **6**, 82639-74-5; **7**, 59261-00-6; **8**, 82639-75-6; **8a**, 82639-76-7; **9**, 36630-47-4; **11**, 82648-56-4; **12**, 82639-77-8; **14**, 82639-78-9.

(11) If we assume¹² that the rate of chlorine abstraction from **2** by the radical **5** at 100 °C has a rate coefficient of at least 50 M⁻¹ s⁻¹, then the first-order rate coefficient for the intramolecular homolytic displacement, assuming a ratio of 10:1 for the formation of **8** and **6**, respectively, in 1 mol dm⁻³ carbon tetrachloride, must be at least 5 × 10² s⁻¹.

(12) Ingold, K. U. In "Free Radicals", Kochi, J. K., Ed.; Wiley-Interscience: New York, 1973; Vol. 1, Chapter 2.

(13) The rate of homolysis of primary alkylcobaloxime(III) complexes at 100 °C is very much less than the rate of photolysis under the conditions used in the other experiments.

(14) The formation of trichloromethyl radicals and of chlorocobaloxime(III) in the reaction of **2** with cobaloxime(II) has a rate coefficient of ca. 1 L mol⁻¹ s⁻¹ at 25 °C: Espenson, J. H., personal communication; that for cobaloxime(II) with **4** is even larger.

(15) ¹³C NMR δ 20.4, 30.7, 50.7, 53.2, 59.0, 96.9. Anal. Calcd for C₆H₉Cl₃O₂S; C, 28.65; H, 3.6; S, 12.75. Found: C, 28.45; H, 3.65; S, 12.9.

(16) In the reaction of simple alkylcobaloxime(III) complexes with 1 equiv of **4**, the main product is the alkanesulfonyl chloride, formed by homolysis of the carbon-cobalt bond, capture of sulfur dioxide by the alkyl radical, and chlorine abstraction by the sulfonyl radical so formed. Capture of sulfur dioxide by substituted trichloropropyl radicals such as **10** is slightly less favored because of the effect of the neighboring trichloromethyl group but does readily occur. For example, some 1,1,1-trichloroethane-2-sulfonyl chloride is formed in the reaction of oct-1-ene with **4** catalyzed by radicals formed on photolysis of secondary alkylcobaloximes at ca. 0 °C.

Gymnodinium breve Toxins. 1. Isolation and X-ray Structure of *O,O*-Dipropyl (*E*)-2-(1-Methyl-2-oxopropylidene)phosphorohydrazidothioate (*E*)-Oxime from the Red Tide Dinoflagellate *Gymnodinium breve*

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The dinoflagellate *Gymnodinium breve* (*Ptychodiscus brevis*) has been implicated in the production of toxic red tides along the Gulf coast of Florida.^{1,2} In contrast to other toxic red tide producing microorganisms (*Gonyaulax catenella* and *G. tamaricensis*),^{3,4} which produce water-soluble saxitoxin and its hydroxy derivatives, toxins produced by *G. breve* are lipoidal in nature. In this respect *G. breve* toxins resemble ciguatoxin, which has recently been shown to be produced by the benthic dinoflagellate *Gambierdiscus toxicus*.⁵ Although a number of attempts have been made to determine the chemical nature of *G. breve* toxins, only very recently the structure of one of its toxic metabolites (Brevetoxin B) has been determined by X-ray crystallography.⁶

In this communication we report the isolation and X-ray crystal structure of an ichthyotoxic metabolite of *G. breve*. The dinoflagellate⁷ was cultured in 15-L solution bottles (10-L volume) in NH-15 medium.⁸ The cells were exposed to a 24-h light period, 500 foot-candles. The cells were harvested at the peak of the growth period by direct extraction with chloroform.⁹ The residue from the chloroform extract was successively extracted with hexane, benzene, and chloroform. The chloroform-soluble fraction after repeated HPLC¹⁰ gave a crystalline compound (I) which was recrystallized with benzene to give colorless needles: mp 82–83 °C; IR (CCl₄) ν_{max} 3590, 3350, 2930 cm⁻¹; C₁₀H₂₂N₂O₃PS [by high-resolution mass spectrometry (calcd. 295.1119, found 295.1135) and by X-ray analysis]. From the mass spectral fragmentation pattern of I [*m/z* 295.1 (44), 278.1 (19), 253.0

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(7) A starter culture of the dinoflagellate *G. breve* was obtained from Dr. S. M. Ray of the Moody College of Marine Science and Maritime Resources, Texas A&M University, Galveston, TX. The cells were cultured in NH-15 medium at 24 ± 1 °C and were exposed to a 24-h light period for 21 days. In order to determine the origin of the isolated compounds, we used three 40-L batches of the NH-15 medium as controls (medium without inoculum) which were allowed to incubate along with the cultures for 21 days. The controls were processed exactly the same way as the inoculated medium. No trace of the isolated compounds was found in the controls.

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(9) The dinoflagellate *Gymnodinium breve* is an example of the so-called naked dinoflagellates and has a fragile cell wall. Attempts to separate the cells by centrifugation resulted in the lysis of cells. A simple procedure for harvesting the cells, used in this study, was developed in Dr. Y. Shimizu's laboratory. The procedure involves placing 35 mL of CHCl₃ in centrifuge tubes of the KSB continuous-flow system, before starting the centrifugation. This method will extract chloroform solubles from the culture medium and cells very efficiently but has an upper limit of 75 L of culture medium before requiring a fresh quantity of chloroform.

(10) A 5 μ m silica gel column (0.5 × 30 cm) was used for HPLC. The eluting solvent was benzene:ethyl acetate (1:1 v/v), and a 280-nm UV detector was used to monitor the eluting solutes. The column pressure was 750 psi at a flow rate of 2.0 mL/min.