the rate of homolysis of the carbon–cobalt bond is slow[13] 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 = dimethylglyoximato).[14]

$$\mathrm{Cl_4C + Co^{II}(dmgH)_2py \rightarrow ClCo^{III}(dmgH)_2py + Cl_3C\cdot} \qquad (1)$$

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 2[14] thus provides one of

$$\mathrm{Cl_3CSO_2Cl + Co^{II}(dmgH)_2py \rightarrow ClCo^{III}(dmgH)_2py + Cl_3C\cdot + SO_2} \qquad (2)$$

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 substitutents 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.

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(11) If we assume[12] 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 5×10^2 s^{-1}.

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(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) ^{13}C NMR δ 20.4, 30.7, 50.7, 53.2, 59.0, 96.9. Anal. Calcd for $C_6H_9Cl_3O_2S$; 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 substittued 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-trichlorononane-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. tamarensis*),[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 dinoflagellate[7] 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 HPLC[10] gave a crystalline compound (I) which was recrystallized with benzene to give colorless needles: mp 82–83 °C; IR (CCl$_4$) $\nu_{\max}$ 3590, 3350, 2930 cm^{-1}; $C_{10}H_{22}N_3O_3PS$ [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 $CHCl_3$ 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 μm 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.

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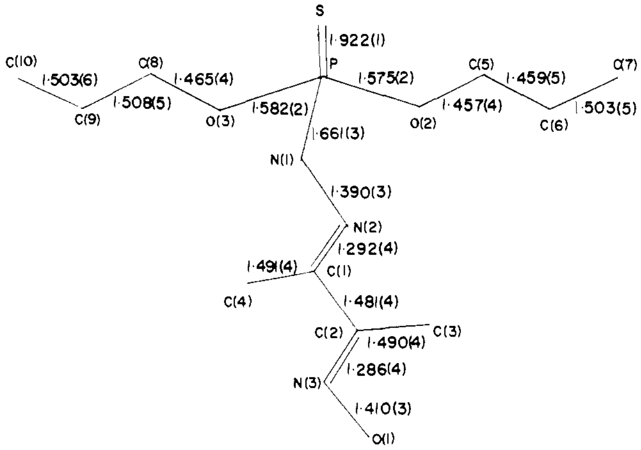

Figure 1. Molecular structure, atom numbering, and bond distances.

(24.4), 211 (42), 178.9 (17), 278 (19), 96.9 (39), 42 (100)] only the loss of an OH and one or two $CH_3—CH=CH_2$ groups could be recognized.[11]

X-ray analysis was carried out on crystals from benzene. Thin, plate-shaped crystals of the compound belong to the monoclinic space group $P2_1/c$, with $a = 11.255$ (4) Å, $b = 17.694$ (9) Å, $c = 8.214$ (2) Å, $\beta = 109.60$ (2)°, $V = 1541.0$ Å^3, $Z = 4$, at −135 (2) °C. Intensities of 3151 unique reflections with $2\theta < 150°$ were measured at −135 (2) °C on a Nonius CAD-4 automatic diffractometer, using Ni-filtered Cu K$\bar{\alpha}$ radiation and employing θ–2θ scan technique. Details of data collection procedures have been described in an earlier report.[13] Out of the total, 2436 reflections were considered observed on the basis that $I > 2\sigma(I)$. The data were corrected for Lorentz and polarization factors.

The structure was determined by a combination of direct methods, Patterson analyses, and difference Fourier syntheses. A preliminary partial structure (10 atoms) was obtained from a run of the direct method program MULTAN.[14] Least-squares refinement of this partial structure indicated that two of the atoms are much heavier than carbon. The presence of the heavier atoms was confirmed by a Patterson map. These two atoms were refined as oxygen atom with double occupancy. The remaining non-hydrogen atoms were located from a subsequent difference electron density map. The structure was refined isotropically to an R factor of 12.7%. In the next few steps, because the chemical composition was not known, all the atoms were identified on the basis of their electron density and isotropic temperature factors and by comparing molecular geometry with known structures. The structure was further refined with anisotropic thermal parameters. A difference Fourier map, evaluated at this stage, revealed all the hydrogen atoms. Some disorder was apparent along one of the propyl chains, and therefore the hydrogen atoms belonging to atoms C(5) and C(6) were not refined.

The final refinement converged to an R factor of 0.048 for 2436 observed reflections. All refinements were carried out by using a full-matrix least-squares routine.[15] The compound was thus identified as *O,O*-dipropyl (*E*)-2-(1-methyl-2-oxopropylidene)-phosphorohydrazidothioate (*E*)-oxime (Figure 1), $C_{10}H_{22}N_3O_3PS$. The final positional parameters of the non-hydrogen atoms are listed in Table I. The bond distances are given in Figure 1. Figure 2 shows a stereoview of the single molecule.

Table I. Positional Parameters ($\times 10^4$) of Non-Hydrogen Atoms. Standard Deviations of the Last Digits Are in Parentheses

atom	x	y	z
P	6270.1 (7)	3490.6 (4)	317 (1)
S	5268.6 (8)	3717.9 (5)	1745 (1)
O(1)	10585 (2)	688 (1)	−750 (4)
O(2)	7466 (2)	3996 (1)	538 (3)
O(3)	5581 (2)	3548 (1)	−1703 (3)
N(1)	6853 (2)	2621 (1)	684 (3)
N(2)	7747 (2)	2399 (1)	−47 (3)
N(3)	9572 (2)	824 (1)	−143 (4)
C(1)	8196 (3)	1725 (2)	326 (4)
C(2)	9211 (3)	1518 (2)	−362 (4)
C(3)	9814 (3)	2090 (2)	−1164 (5)
C(4)	7768 (3)	1177 (2)	1393 (5)
C(5)	7338 (4)	4815 (2)	442 (6)
C(6)	8486 (4)	5149 (2)	302 (6)
C(7)	8507 (5)	5998 (3)	318 (8)
C(8)	4294 (3)	3263 (2)	−2498 (5)
C(9)	3870 (3)	3454 (2)	−4396 (5)
C(10)	3799 (4)	4289 (3)	−4753 (6)

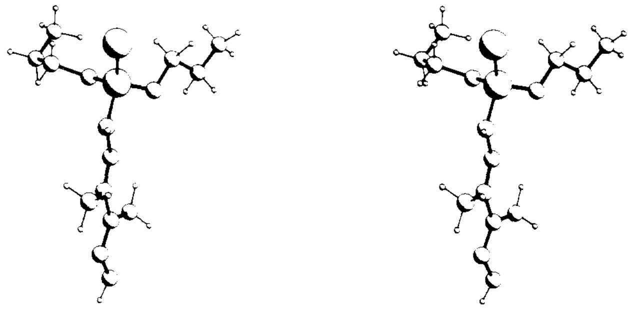

Figure 2. Stereoview of the single molecule.

The present structure is an example of a novel acyclic phosphorus compound. Excluding the two *O*-propyl groups, the remainder of the molecule lies approximately on a plane (root mean square deviation of 10 non-hydrogen atoms is 0.10 Å). The two propyl groups are not symmetrically oriented in the crystal structure; one propyl chain is extended, and the other is skewed. The distorted tetrahedral geometry around the phosphorus atom has features common to most four-coordinated organophosphorus compounds.[16-19] The P–N(1) distance of 1.661 (3) Å is significantly larger than that is generally found in similar systems,[16-18,20] indicating a rather weak p_π–d_π character for this bond. Atom N(1) shows a slight tetrahedral character (sum of angles at N(1) is 355.8°) and the S–P–N–H torsion angle is −13 (2)°. The P=S distance of 1.922 (1) Å is normal and comparable to that in many related structures.[16,20] The two P–O distances, 1.575 (1) and 1.582 (1) Å, compare well with the average value 1.59 ± 0.02 Å.[21] The 2-oxopropylidene oxime moiety is planar within experimental error (root mean square deviation is 0.08 Å). Even the hydroxyl hydrogen atom, trans to C(2), lies in the plane (deviation is 0.08 Å). The oxime groups of two symmetry related molecules are hydrogen bonded through O(1)–H···N(3) (2.796 Å) and H···N(3) (1.875 Å) as is observed in other oxime crystal structures.[22]

The 400-MHz ^{1}H NMR spectrum ($CDCl_3$)[12] of I [δ 0.9393 (6 H, t, $J = 7.45$ Hz), 1.6988 (4 H, m, $J = 7.06$ Hz), 1.9415 (3 H, s), 2.0483 (3 H, s), 3.2127 (1 H, br s), 3.9791, (2 H, m, $\omega_{1/2}$

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[11] the low- and high-resolution mass spectra were recorded at the Massachusetts Institute of Technology, Cambridge, MA 02139. The MS facility is supported by a grant (Principal Investigator, Professor K. Biemann) from the Biotechnology Research Branch, Division of Research Resources.

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= 12.62 Hz), 5.17 (1 H, br s) [8.391, s, in Me_2SO]] showed the presence of two methyl groups on vinylic carbon(s). The presence of two symmetrical *n*-propyl groups in structure I is supported by the decoupling experiments: irradiation at δ 1.69 collapsed the triplet at δ 0.9393 into a singlet, and absorptions centered at δ 3.971 and 4.026 were also collapsed to simple triplets ($J = 9.33$ and 9.40 Hz, respectively), which is expected in phosphorus compounds because of the three-bond coupling between hydrogen and phosphorus;[23] similarly, irradiation at 0.9393 caused the multiplet at δ 1.69 to collapse into a simple triplet ($J = 6.05$ Hz) while irradiation around δ 3.99 collapsed the multiplet at δ 1.69 into a simple quartet ($J = 6.30$ Hz). Structure I is also supported by the mass spectral fragmentation pattern (m/z 278 indicates the loss of a hydroxyl group while the peaks at m/z 253 and 211 indicate the loss of C_3H_6 and C_6H_{12} from the molecule). The presence of a thiophosphonate moiety in I is indicated by the MS fragment at m/z 96.951.

Although the presence of phosphorus-containing toxic metabolites has been reported,[1] this is the first report on the structure of a phosphorus-containing compound from *G. breve*. Compound I (tentatively named Gb-4) has an ichthyotoxicity of 0.9 ppm against *Lebistes reticulatus*. The crude extract of *G. breve* has at least five more toxic compounds including Brevetoxin B. Work on the structure elucidation of the other ichthyotoxic compounds is in progress.

Acknowledgment. This investigation was supported in part by PHS Grant No. CA 17562 (to D.v.d.H.), and by Robert A. Welch Foundation Grant No. E-745 (to M.A.). M.A. thanks Dr. A. J. Weinheimer for his help and suggestions, Kurt L. Loening, Chemical Abstract Service, for naming the compound, and Dr. S. M. Ray, Texas A&M University at Galveston, for the starter culture of *G. breve*.

Registry No. I, 82638-81-1.

Supplementary Material Available: Listings of bond angles, hydrogen atom parameters, anisotropic thermal parameters, and structure factors are available (14 pages). Ordering information is given on any current masthead page.

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Homogeneous Catalytic Hydrogenation. 1. Regiospecific Reductions of Polynuclear Aromatic and Polynuclear Heteroaromatic Nitrogen Compounds Catalyzed by Transition-Metal Carbonyl Hydrides

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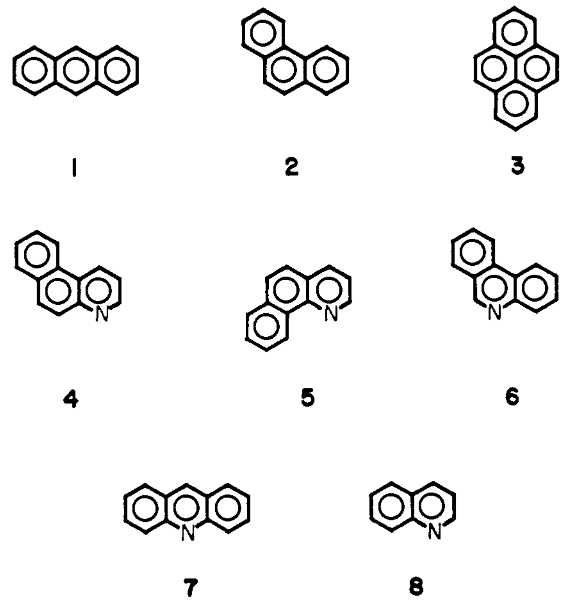
The various synthetic fuel products derived from coal or oil shale require additional hydroprocessing to minimize their nitrogen and sulfur content; therefore, the selective hydrogenation of polynuclear heteroaromatics becomes critical.[1] Thus, it is extremely important to have a basic understanding of which polynuclear aromatic and polynuclear heteroaromatic compounds are hydrogenated in these complex fossil fuel matrices.

Chart I. Model Synthetic Fuel Compounds Used in the Catalytic Hydrogenation with Transition-Metal Carbonyl Hydrides



Recently, Pettit and his co-workers[2-4] demonstrated, in an elegant manner, the use of carbon monoxide and water as an alternative reducing agent to that of hydrogen in the hydroformylation of olefins and the reduction of nitroarenes. These latter reactions were catalyzed by transition-metal carbonyl compounds ($M_x(CO)_y$) and thought to proceed via the formation of transition-metal carbonyl hydrides, (e.g., $H_2M_x(CO)_y$), by nucleophilic attack of water or base on coordinated carbon monoxide.[5] Other methods of generating transition-metal carbonyl hydrides from the corresponding carbonyls have used carbon monoxide and hydrogen and hydrogen alone as reagents.[6]

Therefore, we thought that the rather facile generation of transition-metal carbonyl hydrides under water gas shift (CO, H_2O, base) and synthesis gas (1:1 CO:H_2) conditions as well as strictly hydrogenation conditions (H_2 alone) made these reagents very attractive for the purpose of testing their regioselectivities in the reductions of polynuclear aromatics and polynuclear heteroaromatic nitrogen compounds. Additionally, it is well-known that homogeneous catalytic reductions proceed at lower temperatures and pressures and, in fact, give the higher regioselectivities we were seeking when compared to their heterogeneous counterparts.[7]

Chart I shows the polynuclear aromatic and polynuclear heteroaromatic nitrogen compounds, **1–8**, that we used as model synthetic fuel compounds for the above stated purposes.

We reacted a wide variety of transition-metal carbonyl compounds with compounds **1–3** under water gas shift (wgs) and synthesis gas (sg) conditions[8] and found that only $Fe(CO)_5$,

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