allows the effective asymmetric reagent to be cycled, eliminating the need for a new resolution step with each asymmetric synthesis. Extensive studies of these seemingly versatile ylides as well as the properties of optically active products of the type reported here continue in our laboratories.[12,12a]

effect of the conversion of I to VI is to interchange the position of a substituent on sulfur and the free electron pair. Note that the configuration label remains *R* throughout the series although the sulfur atom of the sulfinamide and sulfoxide has the opposite chirality.

(12) M. E. Munk and J. L. Horvath, Jr., have recently resolved a sulfonium salt suitable for the generation of an optically active methylide (private communication, Professor Munk, Arizona State University).

(12a) NOTE ADDED IN PROOF. D. Darwish and R. L. Tomilson [*J. Am. Chem. Soc.* **90**, 5938 (1968)] have recently reported on the preparation and racemization of an optically active sulfonium ylide.

(13) (a) Alfred P. Sloan Research Fellow, 1965–1968; (b) National Science Foundation Graduate Trainee, 1967–1968.

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The Titanium–Naphthalene-Catalyzed Synthesis of Sodium Hydride from the Elements at Room Temperature and Atmospheric Pressure

Sir:

Recent endeavors in this laboratory have been concerned with effecting normally difficult reductions, *e.g.*, molecular nitrogen to ammonia,[1-3] under mild conditions by employing selected transition metal coordinating species along with suitable electron sources. An issue of this program is the high-yield room-temperature–atmospheric pressure synthesis of sodium hydride from molecular hydrogen and metallic sodium, described herein. Traditionally an uncatalyzed reaction requiring several hundred degree temperatures,[4] such ready and complete combination of these elements can be achieved in a matter of minutes by addition of catalytic amounts of titanium tetraisopropoxide and naphthalene to the reaction medium.

The general procedure involves vigorously stirring a mixture of sodium chunks and naphthalene in dry THF (80–100 ml) at room temperature under 1 atm of hydrogen (passed through a P_2O_5 drying tower and then a solution of sodium benzophenone ketyl in tetraglyme) while adding dropwise a solution of $(i\text{-PrO})_4Ti$ in tetrahydrofuran (THF) (10^{-1} to 10^{-4} *M*) fast enough to maintain a maximum rate of hydrogen absorption. The total amount of $(i\text{-PrO})_4Ti$ used was 0.1–1 mole % of the sodium. The gas volume changes were measured with a gas buret system connected to the reaction flask. As the reaction neared completion, the dark green mixture took on a brown coloration and finally reached a red-brown to brown color, depending upon the relative amounts of reactants used. The amount of hydrogen absorbed corresponded to 90–100% of that required for sodium hydride formation.

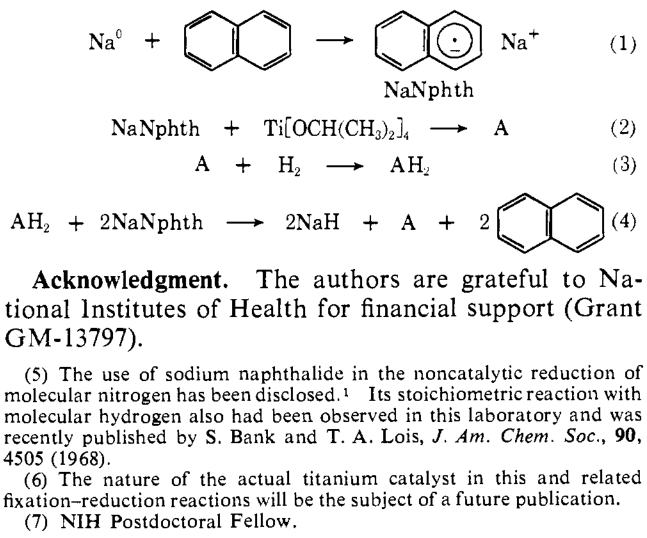
Hydrolysis of a typical reaction product mixture gave 1.9 moles of gas per mole of hydrogen absorbed. That the gas evolved was hydrogen was demonstrated by its utility in the quantitative conversion of maleic acid to succinic acid in the presence of PtO_2.

The role of $(i\text{-PrO})_4Ti$ was demonstrated by stirring a room-temperature THF solution of sodium naphthalide (50 mmoles) under hydrogen and observing only very slow hydrogen absorption.[5] Upon commencement of addition of 0.1 mole % $(i\text{-PrO})_4Ti$, the absorption rate increased sharply and the reaction was complete in 47 min.

Naphthalene is a required catalytic constituent of the reaction. No hydrogen absorption was observed during 25 min by a mixture of sodium dispersion (50 mg-atoms) in THF and $(i\text{-PrO})_4Ti$ (0.1 g-atom % of sodium). Upon addition of naphthalene (5 mole % based on sodium) and further amounts (0.2 mole % based on sodium) of $(i\text{-PrO})_4Ti$, hydrogen absorption commenced and was complete in 29 hr. In a similar run on a slightly larger scale (65 mg-atoms of sodium) the naphthalene was present in 20 mole % (based on sodium), and the reaction was over in 3 hr. The naphthalene can be recovered quantitatively from a hydrolyzed reaction mixture.

To demonstrate that the product is indeed sodium hydride, the flask content at the end of a reaction was centrifuged, providing a gray substance contaminated with small quantities of a white solid. A sample of gray material was hydrolyzed to give the theoretical (based on sodium hydride) amount of hydrogen and 89% of the theoretical amount of sodium hydroxide. Two samples each containing some white material gave a ratio of H_2:NaOH = 0.98 and 0.95, respectively.

Although the entire catalytic sequence cannot be delineated unequivocally at this time, the phenomena featured in eq 1–4 seem likely (A = lower valent titanium species).[2,6]



Acknowledgment. The authors are grateful to National Institutes of Health for financial support (Grant GM-13797).

(1) E. E. van Tamelen, G. Boche, S. W. Ela, and R. B. Fechter, *J. Am. Chem. Soc.*, **89**, 5707 (1967).

(2) E. E. van Tamelen, G. Boche, and R. Greeley, *ibid.*, **90**, 1677 (1968).

(3) E. E. van Tamelen and B. Åkermark, *ibid.*, **90**, 4492 (1968).

(4) G. W. Matson and T. P. Whaley, *Inorg. Syn.*, **5**, 10 (1957).

(5) The use of sodium naphthalide in the noncatalytic reduction of molecular nitrogen has been disclosed.[1] Its stoichiometric reaction with molecular hydrogen also had been observed in this laboratory and was recently published by S. Bank and T. A. Lois, *J. Am. Chem. Soc.*, **90**, 4505 (1968).

(6) The nature of the actual titanium catalyst in this and related fixation–reduction reactions will be the subject of a future publication.

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The Molecular Structure of a Thiocarbonyl Oxide[1]

Sir:

Although numerous compounds with the thiocarbonyl oxide grouping have been prepared, generally

(1) Abstracted from the Ph.D. Thesis of G. A. Wolfe, University of Arizona, 1968.

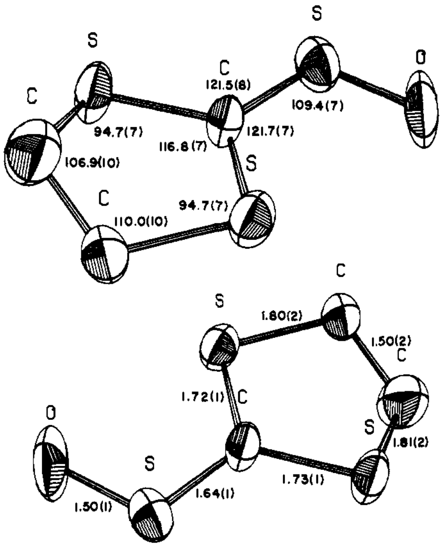

Figure 1. An ORTEP plot of the two molecules in a unit cell, looking approximately down *b*. Bond distances are in ångströms, bond angles in degrees, and thermal ellipsoids enclose 50% probability.

by oxidation of the corresponding thiocarbonyl compound, the only evidence regarding the geometry of this grouping appears to be that obtained by King and Durst,[2] who obtained two interconvertible forms of oxythiobenzoyl chloride and presumed them to be *cis,trans* isomers. We wish to report the results of a crystal structure analysis on ethylene trithiocarbonate oxide[3] which provides the first experimental values for bond parameters in a substance with the thiocarbonyl oxide grouping.

The crystals were grown from ethanol–pentane solution, mounted quickly, and sprayed immediately with Teflon to retard the otherwise very rapid oxidation. Pertinent crystal data are: space group $P\bar{1}$; $a = 7.20$ (1), $b = 5.41$ (1), and $c = 8.16$ (1) Å; $\alpha = 102.7°$ (3), $\beta = 100.0°$ (3), and $\gamma = 73.3°$ (3); $Z = 2$. The intensities of 770 independent reflections were estimated visually from Cu Kα photographs around all three axes. The three sulfur atoms were located from the three-dimensional Patterson map, and the first Fourier map revealed the carbons and oxygen. Refinement, first isotropic and then anisotropic, gave an *R* of 12.7.

Bond distances and angles are shown in Figure 1 on an ORTEP plot showing the contents of a unit cell. The C–S–O angle of 109.4° (7) is consistent with the use of (a) atomic orbitals by this sulfur, with the expected 90° angle expanded by 19° due to electrostatic repulsion between the oxygen and adjacent ring sulfur, or (b) sp^2 hybridization by the sulfur, with the optimum 120° angle contracted by 11° due to electrostatic repulsion between the oxygen and the unshared pair on sulfur. The hybridization of this sulfur is probably similar to that in sulfur dioxide, whose O–S–O angle of 119.0–119.5° (5)[4,5] suggests sp^2 hybridization with 1° distortion but can be rationalized in terms of atomic orbitals with 29° distortion.

The oxygen is 0.25 Å out of the plane formed by the three sulfurs and the carbon among them, presumably due to repulsion between the oxygen and the adjacent ring sulfur. The nonplanarity observed in the ring is expected since it relieves eclipsing of the two methylene groups.

The sulfur–oxygen bond length of 1.495 (11) Å compares with values of 1.4321 (5) Å for SO_2[4] and 1.47 (3) Å for dimethyl sulfoxide.[6] The amount of double bond character in the exocyclic carbon–sulfur bond can be estimated from its observed length to be 90%.[7]

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The Te_4^{2+} Cation

Sir:

Very recently Bjerrum and Smith[1] have shown that in Te–$TeCl_4$ melts with a mole ratio of 7 or greater a tellurium species with the formal oxidation state of $+1/2$ is formed. They formulate this species as the polymeric cation Te_{2n}^{n+} which they believe to be the Te_4^{2+} cation. We recently reported that selenium can be oxidized to the Se_8^{2+} and Se_4^{2+} cations in solution in various highly acidic media, *e.g.*, H_2SO_4, $H_2S_2O_7$, and HSO_3F.[2] We have been investigating the colored solutions that are formed by sulfur and tellurium in these same media, and we now report our evidence for the formation of the Te_4^{2+} cation.

Tellurium dissolves slowly in cold sulfuric acid or fluorosulfuric acid to produce a red solution. With oleum the reaction is more rapid, and on warming the red oleum solution a color change to orange and finally to yellow occurs. A yellow-orange color is also produced on adding persulfate to the red sulfuric acid solution or peroxydisulfuryl difluoride to the fluorosulfuric acid solution. In the reaction of tellurium with the pure solvents, sulfur dioxide is produced in all three cases. The colored tellurium species are, therefore, positive oxidation states of tellurium, the yellow species being a higher oxidation state than the red.

The absorption spectra of tellurium in fluorosulfuric acid under different conditions show clearly the existence of two distinct species. In Figure 1, curve A was obtained from the reaction of tellurium with pure fluorosulfuric acid after removal of the sulfur dioxide produced in the reaction. This red species has an intense absorption maximum at 510 mμ and a shoulder between 400 and 450 mμ. This spectrum is almost identical with that reported by Bjerrum and Smith[1] for their Te_{2n}^{n+} species and is quite similar to that previously reported

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[1] N. J. Bjerrum and G. P. Smith, *J. Amer. Chem. Soc.*, 90, 4472 (1968).

[2] J. Barr, R. J. Gillespie, R. Kapoor, and K. C. Malhotra, *Can. J. Chem.*, **46**, 149 (1968).