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.

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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.

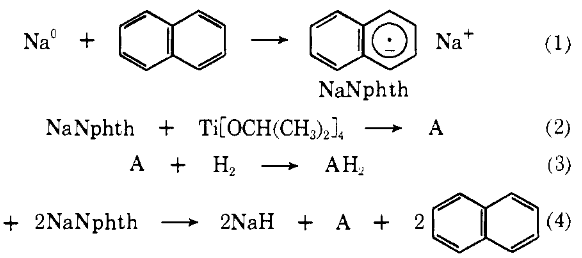
Hydrolysis of a typical reaction product mixture gave 1.9 moles of gas per mole of hydrogen absorbed. That the gas evolved was hydrogen was demonstrated by its utility in the quantitative conversion of maleic acid to succinic acid in the presence of PtO_2.

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]



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[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.