

SELENIUM CATALYZED GENERATION OF DIIMIDE FROM HYDRAZINE.

SELENIUM AS A NOVEL OXIDIZING REAGENT

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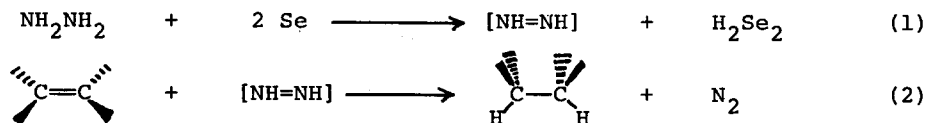
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Since the work of van Tamelen and Corey in 1961, diimide¹ has been used successfully as a reducing agent for stereospecific cis-hydrogenation of multiple bonds of olefins, acetylenes, and azo compounds. The stereospecificity has been interpreted in terms of a cyclic transition state², which seems to imply a cis (syn) structure of diimide³, functioning as a reducing agent for the multiple bond. In practice, a large excess (at least two fold) amount of diimide precursors with respect to multiple bond to be reduced was necessarily required in order to compensate for loss of the trans (anti) diimide and the concurrent disproportionation of the diimide⁴. At the step for the generation of diimide from hydrazine, hydrogen peroxide (with traces of cupric ion)⁵, hexacyanoferrate(III)⁶, iodine⁷, potassium periodate⁸, have been used for dehydrogenation of hydrazine.

Now we wish to report that elemental selenium acts as a unique oxidizing reagent⁹ for hydrazine to generate diimide. The stereospecific cis-addition of hydrogen from diimide generated by the selenium oxidation of hydrazine was confirmed by the facts that 1,2-dimethylcyclohexene and diphenylacetylene gave cis-1,2-dimethylcyclohexane and cis-stilbene, respectively; cis-stilbene was further reduced to bibenzyl with excess diimide.

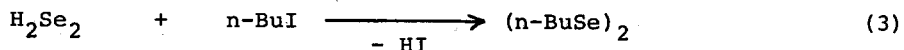
In a typical reaction, the reduction of styrene was undertaken. Under carefully deoxygenated reaction system, styrene (100 μmol) was dissolved in EtOH (0.2 ml) containing amorphous selenium (200 μmol) and cumene (100 μmol)

as an internal standard, and then anhydrous hydrazine in absolute EtOH (1 mmol/2 ml) was added under nitrogen (or helium) at 0°C. The glpc analysis of the product after 25 hr showed the formation of ethylbenzene (82 μmol). For the completion of the reduction of styrene (100 μmol), 1.3 mol equivalent hydrazine was required in total. This stoichiometric reduction is shown as in Reactions (1) and (2).

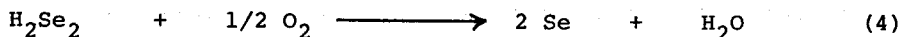


The observed high efficiency of selenium as an oxidizing reagent is noteworthy, since the minimum and ideal ratio of hydrazine to olefin is 1.0 assuming quantitative conversion of hydrazine to cis-diimide¹⁰ (no trans isomer formation or complete trans to cis isomerization) and quantitative reduction by cis-diimide without any loss of diimide by disproportionation.

In the oxidation step, selenium seems to be reduced to hydrogen diselenide, as suggested by the following reaction. The reaction of amorphous selenium (10 mmol) in the presence of n-butyl iodide (20 mmol) with hydrazine (20 mmol) in CH₃CN under nitrogen at 0°C with vigorous stirring afforded di-n-butyl diselenide (74% based on selenium) as a major product, together with trace amounts of di-n-butylselenide and alkylated hydrazines [Reaction (3)].



We found also that hydrogen diselenide formed in the present reaction was readily oxidized with oxygen to give water and regenerate amorphous selenium [Reaction (4)].



By taking advantage of this observation, the unique selenium catalyzed hydrogenation of olefins with diimide from hydrazine and oxygen was successfully performed. For instance, amorphous selenium (100 μmol), styrene (1000 μmol), and slight excess of hydrazine (1700 μmol) in EtOH (0.4 ml) were reacted at 25°C in the presence of cumene (100 μmol) as an internal standard. The amount

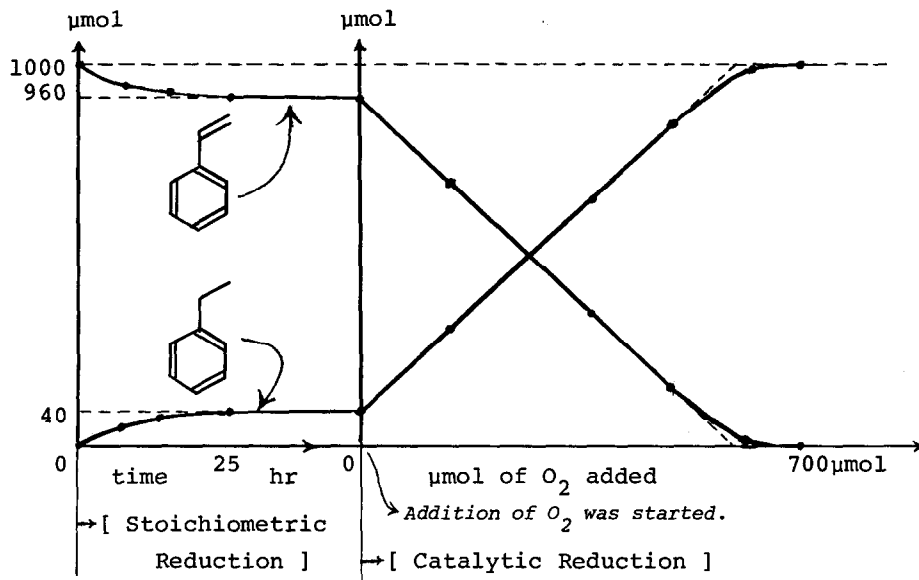
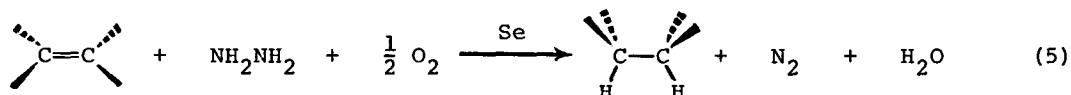
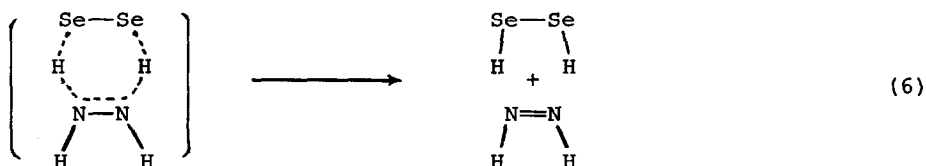


Figure. Selenium Catalyzed Hydrogenation of Styrene with Hydrazine.

of ethylbenzene formed after 25 hr was found to be 40 μmol (80 % yield based on selenium according to equations 1 and 2) and not to increase on the prolonged reaction time; and then oxygen was added to the reaction mixture to perform the catalytic reduction. Plots of ethylbenzene and styrene during the catalytic reaction showed that styrene was quantitatively converted to ethylbenzene as indicated in the Figure. By the combination of equations 1, 2, and 4, we have concluded the novel selenium catalyzed stereospecific reduction of double bond to be described as in reaction 5.



At present we are inclined to propose that the unique oxidation of hydrazine with selenium would involve such an interaction between them that might enable the predominant formation of cis-diimide¹¹ as shown [reaction (6)].



REFEREDCES AND NOTES

- 1) For reviews on the chemistry of diimide, see S. Hünig, H. R. Muller, and W. Thier, *Angew. Chem. intern. Ed.*, 4, 271(1965); C. E. Miller, *J. Chem. Education*, 42, 245(1965); W. C. Baird, Jr., B. Franzus, and J. H. Surridge, *J. Amer. Chem. Soc.*, 89, 401(1967); G. Nagendrappa and D. Devaprabhakara, *Tetrahedron Lett.*, 1970, 4243; H.O. House, "Modern Synthetic Reactions", W. A. Benjamin Inc., 1972, pp. 248.
- 2) R. B. Woodward and R. Hoffmann, *Angew. Chem. intern. Ed.*, 8, 781(1969).
- 3) A predominant generation of cis-diimide would be possible only by such a reaction that the concerted two bond fission from the same side of the precursor, as would be expected in the cases of diimide generation from anthracene-9,10-diimine [E. J. Corey and W. L. Mock, *J. Amer. Chem. Soc.*, 84, 685 (1962)], and cyclopentadiene adduct of diimide [J. C. Mackenzie, A. Rodgman, and G. F. Wright, *J. Org. Chem.*, 17, 1666(1952)].
- 4) For instance, the kinetics of the reduction with hydrazine as the source of diimide showed that exactly two moles of hydrazine were required to reduce one double bond. Consequently, cis- and trans-diimide seemed to be formed almost in equal amounts. See F. Aylward and M. Sawistowska, *Chem. Ind.*, 484(1962).
- 5) E. J. Corey, M. L. Mock, and D. J. Pasto, *Tetrahedron Lett.*, 1961, 347.
- 6) S. Hünig, H. R. Muller, and W. Thier, *Tetrahedron Lett.*, 1961, 353.
- 7) H. Nozaki, Y. Simokawa, T. Mori, and R. Noyori, *Can. J. Chem.*, 44, 2921(1966).
- 8) D. J. Cram and J. S. Bradshaw, *J. Amer. Chem. Soc.*, 85, 1108(1963).
- 9) For the use of selenium as an oxidizing reagent, see N. Sonoda, T. Yasuhara, K. Kondo, T. Ikeda, and S. Tsutsumi, *J. Amer. Chem. Soc.*, 93, 6344(1971); K. Kondo, N. Sonoda, and S. Tsutsumi, *Tetrahedron Lett.*, 1971, 4885; idem, *J. C. S. Chem. Commun.*, 307(1972); K. Kondo, N. Sonoda, and H. Sakurai, *Tetrahedron Lett.*, 1974, 803; idem, *Bull. Chem. Soc. Japan*, 48, 108(1975).
- 10) Trans-diimide was calculated to be more stable than cis- by 7.5 kcal/mol, and the difference of the energy corresponds to an equilibrium constant of $K = [\text{trans}]/[\text{cis}] = 2.7 \times 10^5$ at 25°C, if there should be an interconversion [L. J. Schaad and H. B. Kinser, *J. Physical Chem.*, 73, 1901(1969)]. Diimide generated by a microwave discharge of hydrazine was determined to be entirely trans (no trace of cis, by IR and UV) [A. Trombetti, *J. C. S. (A)*, 1086(1971)]. Pure diimide isolated at liquid nitrogen temperature from the thermolysis of alkali metal tosylhydrazides, $\text{Tos}(M)\text{N}_2\text{H}_2$ ($M = \text{Li}, \text{Na}, \text{and K}$) was all trans [N. Wiberg, G. Fischer, and H. Bachhuber, *Chem. Ber.*, 107, 1456(1974); idem, *Angew. Chem. intern. Ed.*, 11, 829(1972).
- 11) The selective formation of cis-diimide in the present selenium catalysed reaction would be conclusively rationalized if two isomers were not equilibrated under the reaction conditions.