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AROMATIZATION OF CYCLOHEXENES AND CYCLOHEXADIENES WITH SELENIUM DIOXIDE-TRIMETHYLSILYL POLYPHOSPHATE

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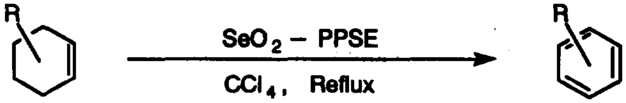
Summary: Selenium dioxide is depolymerized and activated by trimethylsilyl polyphosphate in carbon tetrachloride. The reagent effectively aromatizes substituted cyclohexenes and cyclohexadienes under mild reaction conditions.

Six-membered alicyclic compounds can be aromatized through a sequence of dehydrogenation reactions. The presence of one or more double bonds in the ring or a fusion to an aromatic ring facilitates the aromatization.[1] Hydrogenation catalysts such as platinum, palladium, and nickel along with elemental sulfur and selenium were used for this purpose. The use of these aromatizing agents in the synthesis of more complicated structures is limited by the harsh reaction conditions, and consequent impracticality of controlling the extent of dehydrogenation. Quinones such as DDQ and choranil are much milder than the elemental reagents and are widely used for the aromatization of cyclohexenes, especially for those fused to an aromatic ring.[2]

Although selenium dioxide[3] has been used for some dehydrogenation reactions, the application was limited to the compounds like 1,2-diarylethanes and 1,4-diketones which yield conjugated diarylethenes and 2,3-unsaturated 1,4-diketones.[4] An aromatization of simple alicyclic compounds to benzene or other polycyclic aromatic compounds has not been reported in the literature.

We now wish to report that selenium dioxide mixed with trimethylsilyl polyphosphate (PPSE)[4] in carbon tetrachloride is an excellent aromatizing reagent for cyclohexenes. The reagent effectively aromatizes many substituted cyclohexenes and produces the corresponding benzene derivatives in high yields. The reaction conditions are much milder than those required by the dehydrogenation not only with the elemental dehydrogenating agents but also with quinones like chloranil and DDQ.



The procedure for the aromatization of cyclohexene to benzene is representative. PPSE can be prepared through the addition of phosphorus pentoxide (2 g) to hexamethyldisiloxane (5 mL) in carbon tetrachloride (15 mL) according to the known procedure.[5] Added selenium dioxide (1.2 g) was partially dissolved by the PPSE solution.[6] Cyclohexene (5 mmol) was then added and the resulting reaction mixture was heated to reflux. After 20 hours, the reaction

Table I. Aromatization of Cyclohexenes and Related Compounds with SeO_2-PPSE in Refluxing Carbon Tetrachloride[a]

Entry	Substrate	Ratio SeO_2:Substrate	Reaction Time (hr)	Product	% Yield[b]
1	Cyclohexene	2.2	22	benzene	95
2	1-methylcyclohexene	2.2	26	toluene	96
3	3-methylcyclohexene	2.2	26	toluene	96
4	1-phenylcyclohexene	2.2	15	biphenyl	99
5	1,3-dimethylcyclohexene	2.2	20	*m*-xylene	97
6	cyclohexene-1-carbonitrile	2.2	20	benzonitrile	90
7	cyclohexene-1-carboxylic acid	2.2	18	benzoic acid	80
8	1-chlorocyclohexene	2.3	20	chlorobenzene	91
9	1,3-cyclohexadiene	1.4	18	benzene	99
10	α-terpinene	1.5	20	*p*-cymene	100
11	γ-terpinene	1.4	21	*p*-cymene	99
12	1,2-dihydronaphthalene	1.4	20	naphthalene	89
13	1,2,3,4-tetrahydronaphthalene	2.5	30		0[c]
14	9,10-dihydrophenanthrene	1.5	48		0[c]

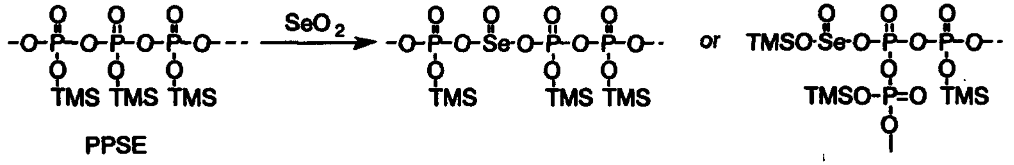
a. 1.2 equivalents of SeO_2 and 10 mmol of PPSE solution in CCl_4 were employed for each degree of unsaturation introduced. b. Yields were determined by GC using an internal standard method. Reaction conditions were not optimized. c. No reaction. The starting material was recovered quantitatively.

mixture was poured into saturated sodium carbonate solution and the organic layer was separated. Toluene was added as an internal standard, and the mixture was analyzed by a 20 meter HP1 capillary column on a HP 5880A Gas Chromatograph. Benzene was produced in better than 95% yield.

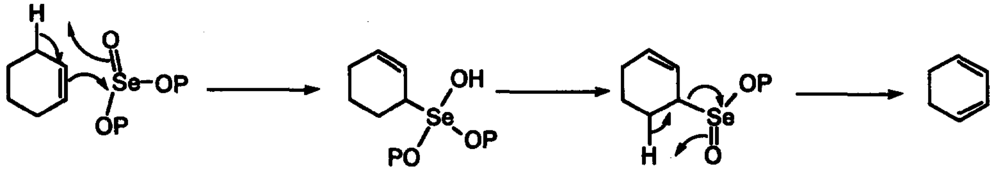
Other substituted cyclohexenes and cyclohexadienes were aromatized in excellent yields under similar reaction conditions. The results are summarized in Table I. Both 1-methylcyclohexene and 3-methylcyclohexene produced toluene in near quantitative yields (entry 2 and 3). 1-Phenylcyclohexene was similarly aromatized to biphenyl (entry 4). 1,3-Dimethylcyclohexenes were converted into *m*-xylene (entry 5). Halogen, cyano, and carboxyl groups survived under the reaction conditions.[7] Cyclohexenes bearing these substituents yielded the corresponding benzene derivatives in good yields (entry 6-8).

Cyclohexadienes and substituted cyclohexadienes also aromatized in excellent yields. The reaction requires only one half the reagent needed for cyclohexenes. 1,3-Cyclohexadiene was easily aromatized to benzene (entry 9), while α- and γ-terpinene produced *p*-cymene in good yields (entry 10 and 11). Neither rearrangement of the carbon skeleton nor any oxidation of the side chain was observed at all.[8]

The aromatization obviously took place through sequential introduction of the double bonds in conjugation with the existing one. Cyclohexene was not converted to benzene after days of refluxing with either selenium dioxide or PPSE alone in carbon tetrachloride. The aromatization took place only when selenium dioxide and PPSE were combined. Selenium dioxide must have been activated by PPSE to be an effective aromatizing reagent. Based on our earlier findings,[9] the activation is believed to be a depolymerization linear polymer of the selenium dioxide (selenous anhydride). Monomeric selenium dioxide is believed to be inserted into the silicon-oxygen or phosphorus-oxygen bonds of trimethylsilyl polyphosphate, forming at least one mixed anhydride unit.[9] The activated selenium dioxide (mixed anhydride with PPSE) seems to serve as an active aromatization reagent.



The dehydrogenation by the present selenium reagent is believed to proceed through several steps. The initial step is the ene reaction of cyclohexene with the activated selenium reagent like selenenic acid does in aqueous media.[3] Dehydration follows to produce 2-cyclohexeneselenite as an intermediate. The intermediate selenite undergoes selenoxide type elimination to complete the dehydrogenation. Although further investigation on the mechanism needs to be done, selenoxide type elimination route is preferred at the present time. Similar selenoxide type syn elimination was claimed in the dehydrogenation of ketones to the corresponding conjugated enones.[10] An allylic oxidation of cyclohexene to 2-cyclohexenol followed by simple β-elimination seems less probable. On reaction with selenium dioxide-PPSE,[11] 2-cyclohexenol and 1,2,3,4-tetrahydro-1-naphthol undergo aromatization very slowly and produced benzene and naphthalene in much poorer yields than did cyclohexene and 1,2-dihydronaphthalene.



P = polyphosphoric acid residue

Most of the cyclohexenes and cyclohexadienes tested were aromatized effectively by selenium dioxide-PPSE in boiling carbon tetrachloride. Not only the yields of the aromatized compounds are higher, but also the reaction conditions are milder compared with the other known reagents . The reaction is characteristic in that cyclohexanes fused to an aromatic ring were not aromatized. Unlike 1,2-dihydronaphthalene (entry 11), 1,2,3,4-tetrahydronaphthalene and 9,10-dihydrophenanthrene were recovered unreacted after prolonged reaction with the reagent (entry 12, 13).[12] Further study on the application of this reagent is in progress.

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Note and References

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2. For dehydrogenation reactions using quinones, see (a) Jackman, L. M., *Adv. Org. Chem.*, **1960**, *2*, 239. (b) Turner, A. B. *Synthetic Reagents* (Pizey, J. Ed.), Ellis Horwood: Chichester, 1977; Vol. 3, p. 193.
3. For reviews on selenium dioxide oxidation, see (a) Rabjohn, N. *Org. React.*, **1976**, *24*, 261. (b) Nicolaou, K. C.; Petasis, N. A. *Selenium in Natural Products Synthesis*; CIS, Inc.: Philadelphia, 1984; pp. 5-65.
4. Astin, S.; Moulds, de V.; Reiley, H. L. *J. Chem. Soc.*, **1935**, 901. (b) Schaefer, J. P. *J. Am. Chem. Soc.* **1962**, *84*, 713.
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6. SeO_2 was found to be inserted into Si-X bond of halotrimethylsilanes producing selenoxy halides, but not into the Si-O bond of trimethylsilyl acetate, trifluoroacetate, and hexamethyldisiloxane.
7. 3-Cyclohexene-1-carboxaldehyde was converted to produce benzaldehyde.
8. On prolonged heating at 320°C, toluene was oxidized sluggishly by selenium dioxide to produce benzaldehyde and benzoic acid in poor yields. See Sultanov, A. S.; Rodinov, V. M.; Shemyakin, M. M. *J. Gen. Chem. USSR*, **1946**, *16*, 2072, (*CA* **1948**, *42*, 880i)
9. Lee, J. G.; Kang, K. K. *J. Org. Chem.*, **1988**, *53*, 3634. Chromic anhydride also has a linear polymeric structure and reacts with TMSCl to form chromyl chloride. See Lee, J. G.; Ha, D. S. *Bull. Korean Chem. Soc.*, **1991**, *12*, 149, and references cited therein.
10. Selenoxide type syn elimination was postulated for the oxidation of ketones to α,β-unsaturated carbonyl compounds. (a) Sharpless, K. B.; Gorden, K. M. *J. Am. Chem. Soc.*, **1976**, *98*, 300 (b) Umbreit, M. A.; Sharpless, K. B. *J. Am. Chem. Soc.*, **1977**, *99*, 5526. (c) Reference 4b.
11. PPSE is a powerful dehydrating agent for oximes and amides. Alcohols are converted to alkyl iodides by PPSE-NaI, see Ref. 4c.
12. The failure of aromatization of these compounds is probably due to the absence of the olefinic double bond which is essential for the initial ene reaction.

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