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Title: The Use of Selenium( IV) oxide to oxidize Aromatic
Methyl Groups

Abstract approved:
 Abstract:

In this series of experiments, the effect of selenium( IV) dioxide $\left(\mathrm{SeO}_{2}\right)$ on aromatic methyl group was investigated. The products obtained when 2-picoline, 4-picoline and 8-methyl quinoline were oxidized by selenium dioxide were 2-pyridine carboxylic acid, 4-pyridine carboxylic acid and 8-quinoline aldehyde, respectively. The yield corresponding to each product above is $50 \%, 77 \%$ and $49 \%$, respectively. Other compounds such as 2,6-lutidine, 2-methyl quinoline and 4methyl quinoline were also studied. The products were 2,6pyridine dicarboxylic acid, 2-quinoline aldehyde and 4quinoline aldehyde. Additionally, the compounds which did not react with $\mathrm{SeO}_{2}$ are toluene, 2-nitrotoluene, 4-nitrotoluene, 2,4-dinitrotoluene, 2-chlorotoluene, and 4-chlorotoluene. The mechanism for reactions involving selenium(IV) oxide is discussed in detail. The products were analyzed qualitively by using FTIR, NMR, and other physical and chemical methods.


# The Use of Selenium(IV) Oxide to Oxidize Aromatic Methyl Groups 

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## Introduction

Selenium dioxide is often used as an oxidant. Methyl or methylene groups $\alpha$ to a carbonyl can be oxidized with selenium dioxide to give, respectively, $\alpha$-keto aldehydes and $\alpha$ diketones.


Internal alkynes have been oxidized to $\alpha$-diketones by several oxidizing agents, including $\mathrm{SeO}_{2}$ with a small amount of $\mathrm{H}_{2} \mathrm{SO}_{4}$.


Treatment of double-bond compounds with selenium dioxide introduces an OH group into the allylic position.


Six-membered alicyclic rings can be aromatized in a number of ways. Aromatization is accomplished most easily if there are already one or two double bonds in the ring or if
the ring is fused to an aromatic ring.


Since the aromatic pyridine ring is very stable, generally, it is very difficult to oxidize. But in most cases, the alkyl group on the aromatic ring such as pyridine and quinoline can be oxidized fairly easily by other oxidant reagent. Some alkyl-substituted pyridine can be oxidized to corresponding carboxylic acid by $\mathrm{HNO}_{3}, \mathrm{KMnO}_{4}$, or $\mathrm{O}_{3}$ (1). In this series of experiments, our goals were to optimize the conditions for the reactions; simplify the isolation of products; improve the yields; and know the generality of the reactions.

The $\mathrm{SeO}_{2}$ is a non-metallic compound, in the form of a white crystalline solid. The Lewis structure of $\mathrm{SeO}_{2}$ is



in which there is comparatively high electron density around the higher electronegativity element, oxygen. The bond length is between that of a typical single bond and a double bond. Thus, the electron density around the selenium is lower than
that in an oxygen. $\mathrm{SeO}_{2}$ could be an electron accepter, or a Lewis acid, and the selenium is the center of this Lewis acid. The reactions involving $\mathrm{SeO}_{2}$ acting as oxidant would undergo Lewis acid-base reactions, which result in the se-o bond being broken followed by the element selenium produced.

## Experimental

## Reagents:

2-picoline, 4-picoline, 8-methyl quinoline, 2,6-lutidine, 2-methyl quinoline, 4-methyl quinoline, ethyl ether, methanol, silver nitrate, sodium hydroxide, ammonia, acetone (NMR grade), sodium bicarbonate ( $5 \mathrm{~g} / 100 \mathrm{ml}$ water), hydrochloric acid, copper(II) sulfate, pHydrion MIKRO 0 to 11 ( pH paper).

## Apparatus:

Heating mantle, hot plate, temperature controller, 25 ml round bottom flask (size 19/22), condenser (size 19/22), filter flask, vacuum pump, etc.

## Instrument:

FTIR, Bomen Michelson Series
NMR, Hitachi Perkin Elmer (High resolution 24-B)

## Procedure:

A. 8-methyl quinoline
0.5 g SeO 2 was mixed with 2.0 ml -methyl quinoline in a 25 ml round bottom flask, which was set in a heating mantle with temperature controller (See Figure 1 in the appendix). The mixture was heated in a refluxed manner for 5 hours at a temperature between $100{ }^{\circ} \mathrm{C}$ to $150{ }^{\circ} \mathrm{C}$. During the reaction, the color of the liquid changed little by little, from colorless
to yellowish-brown and then to dark brown. Finally, the original white "needle" solid, $\mathrm{SeO}_{2}$, changed to a black fine solid, selenium.

Next, the mixture was extracted with ethyl ether and the liquid was run through an alumina column. The ethyl ether eluant was set in the hood to evaporate the ether. A white crystalline solid was obtained. The solid left in the flask after ethyl ether extraction was a mixture of black solid and white crystals. The weight of the product was obtained by adding the weight value of the extracted portion together with the value of the solid mixture portion subtracted from the calculated weight of selenium.
B. 2-picoline
$0.5 \mathrm{~g} \mathrm{SeO}_{2}$ added to 2.0 ml 2 -picoline in a 25 ml round bottom flask (See Figure 1 in the appendix) was set in a heating mantle with a temperature controller. The mixture was heated for about 5 to 6 hours at a temperature below $120^{\circ} \mathrm{C}$. Finally, the color of the liquid changed from colorless to dark brown and a solid was formed.

Then the dark brown liquid was poured out of the flask. The solid mixture, which looked almost black, was taken out of the flask, weighed, and sublimated by using the equipment setup as in Figure 2 of the appendix. An off-white or slightly yellow platelet solid was collected from the test tube. The weight of the product was obtained by subtracting the calculated weight of selenium from the weight of the solid
mixture.
c. 4-picoline
0.5 g SeO 2 added to 2.0 ml 4 -picoline in a 25 ml round bottom flask (the same as in Figure 1) was set in a heating mantle with a temperature controller. The mixture was heated for about 5 to 6 hours at a temperature below $120{ }^{\circ} \mathrm{C}$. The color of the liquid changed from colorless yellow to dark red. The solid changed from white crystals, $\mathrm{SeO}_{2}$, to a black fine solid, Se, mixed with an orange-red color solid.

The liquid was then poured out and the solid was transferred to a filter flask to sublimate (Figure 2 in the appendix). An orange-colored solid was collected from the test tube. The weight of the product was obtained in the same manner as the one of 2-picoline.
D. 2,6-lutidine
$0.5 \mathrm{~g} \mathrm{SeO}_{2}$ was added with 1.5 ml colorless 2,6 -lutidine in a 25 ml round bottom flask (the same as in Figure 1) which was set in a heating mantle with temperature controller. The mixture was heated for about 10 hours at a temperature between $60-80{ }^{\circ} \mathrm{C}$. When the reaction was finished, a yellow liquid and a black fine solid were obtained. The liquid was transferred to an evaporating dish. Then a white "needle" solid was crystallized from the liquid.

## Results

A. 8-methyl quinoline

The weight of the product from the oxidation of 8 -methyl quinoline was 0.341 g . The percent yield was $49 \%$. Some pure solid was white crystal. Although contaminated by some impurities, most of the solid was slightly yellow. The melting point of the solid was $77-82{ }^{\circ} \mathrm{C}$. Tollens test (the procedure following reference 3) was positive. When sodium bicarbonate ( $\mathrm{NaHCO}_{3}$, 5 g per 100 ml water) was added drop-wise to the solid product, nothing happened. The solid didn't dissolve in $\mathrm{NaHCO}_{3}$ aqueous solution. Therefore, the product couldn't be carboxylic acid, but might be an aldehyde.

When analyzed with FTIR in nujol oil by using nujol oil as the reference, the sample showed the characteristic transmittance peaks at $2964.7-2864.4 \mathrm{~cm}^{-1}$, which was the $\mathrm{C}-\mathrm{H}$ stretch resonance peak in the aldehyde group (CHO), and 1701.7 $\mathrm{cm}^{-1}$, which was the $\mathrm{C}=0$ characteristic peak. There was no broad peak in the $2500-2800 \mathrm{~cm}^{-1}$ region where an $0-H$ stretch resonance peak in the carboxylic acid group ( COOH ) should be. See Figure 4.

When analyzed with NMR by using acetone (NMR grade) as solvent, the sample showed the multiple peaks at $7.0-9.0 \mathrm{ppm}$, which are aromatic protons on the pyridine, and a characteristic peak of -CHO at 11.55 ppm , which was a little further from which is supposed to be. See Figures 5 and 6 in
the appendix. The reason accounting for this is that the zero position (5\% TMS as the reference) shifted to the left.

The white "nesdee" product from o-methyl quinoline oxidized by Eeo, should be 8-guinoline aldehyde.

$$
\begin{equation*}
A_{6} N_{3}+M_{4} 0 H \longrightarrow M_{3}+4,04 \mid \tag{5}
\end{equation*}
$$

$$
\begin{equation*}
\mathrm{AgOH}+2 \mathrm{MH} \mathrm{OH} \longrightarrow-\mathrm{Ag}_{2}\left(\mathrm{YH}_{3}\right)_{2} \mathrm{OH}+2 \mathrm{H}_{2} \mathrm{O} \tag{5}
\end{equation*}
$$


B. 2-picoline

The raw product formed from the oxidation of 2-picoline finished was about g. g. Seraube the apparatus for sublimation was not very efficient, only about 30 ry was collected. the solid was white. Unifier the microscope, the product was a ting granulated solid. The melting point of the solid was 125-130 ${ }^{\circ} \mathrm{C}$. The product dissolved in water easily. mien the product vas adder? with Natron , a lot of bubbles appeared. When it was adder to en aqueous cusco, solution, a blue precipitate appeared.

When analyzed with FrIT in a Kex disk fRae disk as the reference), the product showed an intensive $c=0$ clamacteristio
peak at $1719.6 \mathrm{~cm}^{-1}$, a broad $0-\mathrm{H}$ (in COOH group) stretch peak at 2500-2800 $\mathrm{cm}^{-1}$, and a weaker $0-\mathrm{H}$ (in water) peak at 3391$3450 \mathrm{~cm}^{-1}$. See Figure 8. Therefore, the product was 2-pyridine carboxylic acid.


C. 4-picoline

The raw product formed from the oxidation of 4 -picoline finished was reddish orange in color. After sublimation, the product was orange, and looked like a fine powder. The weight of the impure product was 0.312 g . The yield was 77\%. Only about 25 mg of sublimated product was collected. When the melting point was checked, most of the product sublimated beginning at $260{ }^{\circ} \mathrm{C}$, and melted at $285-295{ }^{\circ} \mathrm{C}$. The pH of its aqueous solution was about 4 . When the product was mixed with $\mathrm{NaHCO} \mathrm{O}_{3}$ aqueous solution, bubbles appeared. When the product was added with aqueous $\mathrm{CuSO}_{4}$ solution, a blue precipitate was obtained.

The product was analyzed with FTIR using a KBr disk
(another $K B r$ disk was used as the reference). The product showed an intensive $C=0$ characteristic peak at $1722.2 \mathrm{~cm}^{-1}$, a medium broad $0-\mathrm{H}$ (in the COOH group) stretch peak at 2423.6$2374.6 \mathrm{~cm}^{-1}$, and an $0-\mathrm{H}$ (in water) peak at $3434.8 \mathrm{~cm}^{-1}$. See Figure 10. Thus, the reaction produced 4-pyridine carboxylic acid.



A comparison of the physical properties of the experimental results with the literature values is listed in Table $I$ in the appendix.
D. 2,6-lutidine

The raw product was a white needle solid, 0.15 g . The product dissolved in water easily, but dissolved in ethyl ether with difficulty. When the aqueous solution of the product was mixed with $\mathrm{NaHCO}_{3}$ solution, bubbles appeared. Its aqueous solution had a pH of about 4 .

The FTIR spectrum (Figure 13) showed several
characteristic peaks, including a sharp peak at $1717.3 \mathrm{~cm}^{-1}$ $(C=O)$, a broad peak at $2498 \mathrm{~cm}^{-1}(0-H$ in the $C O O H)$, and a peak at $3468.3 \mathrm{~cm}^{-1}(0-\mathrm{H}$ in water). All the results show that the product should be 2,6-pyridine dicarboxylic acid.

E. Others

Following the same procedure, 3-picoline, lepidine, quinaldine, and quinoline were also studied.
2.0 ml of 3 -picoline was heated with $0.5 \mathrm{~g} \mathrm{SeO}_{2}$ for 6 hours at a temperature just below $120{ }^{\circ} \mathrm{C}$. The FTIR spectrum (Figure 15) showed a sharp peak at $1722.4 \mathrm{~cm}^{-1}(\mathrm{C}=0)$, a broad peak at $2385.2 \mathrm{~cm}^{-1}(0-\mathrm{H}$ in the COOH$)$, and a peak at $3389.1 \mathrm{~cm}^{-}$ ${ }^{1}$ ( $\mathrm{O}-\mathrm{H}$ in water), which indicated that the product should be 3-pyridine carboxylic acid. The color of the liquid changed from colorless to yellow. The solid was black and there was no other kind of solid mixed in it. No product was obtained by using ethyl ether extraction and running through an alumina column.

The reaction of quinaldine (2-methyl quinoline) with $\mathrm{SeO}_{2}$ occurred between $100-120{ }^{\circ} \mathrm{C}$. The solid product was black.

Extracted by ethyl ether, a red liquid mixture with high viscosity was obtained, but the procedure failed to yield a pure product. No reaction occurred when a small portion of the liquid mixture was added with $\mathrm{NaHCO}_{3}$ aqueous solution. A pH test showed about 7. The product did not mix well with water. The spectrum (Figure 17) from the liquid mixture of 2 -methyl quinoline heated for 11 hours showed peaks at $3384 \mathrm{~cm}^{-1}(0-\mathrm{H}$ in water), 2923-3055 $\mathrm{cm}^{-1}(\mathrm{C}-\mathrm{H}), 1706.2 \mathrm{~cm}^{-1} \quad(\mathrm{C}=\mathrm{O})$. No peak occurred at the $2500-2800 \mathrm{~cm}^{-1}$ region ( $\mathrm{O}-\mathrm{H}$ in COOH ), which indicated that there was some 2 -quinoline aldehyde produced. 2.0 ml lepidine (4-methyl quinoline) was heated with 0.5 $g \mathrm{SeO}_{2}$ for 11 hours. Both the solid and liquid mixture were black and sticky. After the liquid mixture was extracted by ethyl ether and run through an aluminum oxide column, a brown liquid mixture with high viscosity was obtained. This mixture did not mix well with water, but mixed well with 6 M HCl . There was no reaction with $\mathrm{NaHCO}_{3}$. The spectrum of the liquid mixture from 4-methyl quinoline oxidized for 11 hours (Figure 19) showed peaks at $1713.3 \mathrm{~cm}^{-1}(\mathrm{C}=\mathrm{O}), 2870.3-3066.9 \mathrm{~cm}^{-1}(\mathrm{C}-\mathrm{H})$, and $3384.4 \mathrm{~cm}^{-1}(\mathrm{O}-\mathrm{H})$, which indicates that there was some 4quinoline aldehyde produced.

After the mixture of 2.0 ml quinoline with $0.5 \mathrm{~g} \mathrm{SeO}_{2}$ was heated for 17 hours at about $120^{\circ} \mathrm{C}$, the liquid was dark and reddish black, not too viscous. The solid was black. The spectra of the quinoline before and after heating with $\mathrm{SeO}_{2}$ were almost the same. See Figure 20 and 21 . Thus, the aromatic
rings on quinoline won't open when heated with $\mathrm{SeO}_{2}$.
F. Unsuccessful reactions whose the yield of the products were too small for the products to be collected

1. $0.500 \mathrm{~g} \mathrm{SeO}_{2}$ and 1.5 ml 2 -nitrotoluene were heated for about 14 hours at about $100^{\circ} \mathrm{C}$. Both black and white solid were obtained. A white "needle" solid was obtained which was studied by FTIR and the spectra was the same as the one of $\mathrm{SeO}_{2}$.
2. $0.500 \mathrm{~g} \mathrm{SeO}_{2}$ and 1.5 ml 2 -nitrotoluene with 7 ml water as solvent were heated for about 54 hours at about $100{ }^{\circ} \mathrm{C}$. No desired product was produced.
3. $0.500 \mathrm{~g} \mathrm{SeO}_{2}$ and $2.000 \mathrm{~g} \mathrm{4-nitrotoluene} \mathrm{(solid)} \mathrm{with}$ 5.5 ml benzene as solvent were heated for about 24 hours. No desired product was produced.
4. $0.500 \mathrm{~g} \mathrm{SeO}_{2}$ and 2.000 g 4-nitrotoluene with 5 ml pyridine as solvent were heated for about 24 hours. No desired product was obtained.
5. 0.500 g SeO 2 and $2.500 \mathrm{~g} 2,4$-dinitrotoluene with 6 ml benzene as solvent were heated for 48 hours. The spectrum of the solid product was extremely difficult to interpret, but did indicate that some kind of reaction had occurred.
6. $0.500 \mathrm{~g} \mathrm{SeO}_{2}$ and 5 ml pyridine were heated for about 15 hours. The spectra before and after pyridine was heated are the same.

## Discussion

The yield of product from 8-methyl quinoline, 2-picoline, and 4-picoline was fair, because some product was lost during either extraction or separation. Another reason for the low yield from 2-picoline and 4-picoline is that some products were not isolated in the liquid portion of the reaction mixture. The three reactions went to completion; no $\mathrm{SeO}_{2}$ was left.

When the Tollens test was done on the products from 2picoline and 4-picoline, which are carboxylic acids, positive results were obtained. The reason for this phenomenon is that the products are not pure enough.

The spectra of the product mixtures from 2-methyl quinoline and 4 -methyl quinoline show that some reactions occurred just like the suggested reaction equations in the introduction section. But the products were not obtained. The suggested reason is that the activation energies for the above three reactions are so high that the rates of the reactions are very slow. Moreover, the two compounds are both light and heat sensitive species. Even if there were no $\mathrm{SeO}_{2}$ added to them, the two compounds become darker and sticky. Thus, even though the spectra does show the desired information, only traces of the products were obtained.

The most successful reactions and their assumed stoichiometry are shown below.

$2+3 \mathrm{SeO}_{2} \longrightarrow 2+2 \mathrm{H}_{2} \mathrm{O}$


Other reactions are also possible.
$\mathrm{H}_{3} \mathrm{C}^{\mathrm{N}} \mathrm{CH}_{3}+3 \mathrm{SeO}_{2} \longrightarrow \mathrm{HOOC-N}$

$+\mathrm{SeO}_{2} \longrightarrow \mathrm{OHC}+\mathrm{Se}_{3}+\mathrm{HeO}_{2}$


The postulated mechanism of one of the typical methyl quinoline oxidation reactions, the 8 -methyl quinoline oxidation reaction, is shown below.

Scheme 1:




The postulated mechanism of one of the typical methyl pyridine oxidation reactions, the 2 -picoline oxidation reaction, is shown below.

Scheme 2:
Step 1:




Step 2:
$\mathrm{H}_{2} \mathrm{O}+\Theta \mathrm{Se}_{0}^{0}$



Step 3:




The postulated mechanism of the 4 -picoline oxidation reaction is shown below.

Scheme 3:
Step 1:



Step 2:



## Step 3:



Step 4:



When water was added to the mixture of $\mathrm{SeO}_{2}$ and 4picoline ( $0.500 \mathrm{~g} \mathrm{SeO}_{2}, 0.5 \mathrm{ml} \mathrm{H} \mathrm{O}$, and $1.0 \mathrm{ml} \mathrm{4-picoline)}$, reaction occurred at a lower temperature than without water, which is around $75{ }^{\circ} \mathrm{C}$. The solid mixture was separated by decanting the liquid and then sublimating. The melting point of the sublimated solid was $319{ }^{\circ} \mathrm{C}$, which is almost the same as the one obtained following the same procedure without water. The FTIR spectrum of the sublimated solid obtained by water dissolving $\mathrm{SeO}_{2}$ first was very similar to the one without water (Figure 11). Since the temperature for the one with water is lower than the one without water, 4-pyridine carboxylic acid was obtained more easily when water was added than it was obtained when no water was added. Thus, water assists the reactions.

Furthermore, there is no reaction when toluene was heated with $\mathrm{SeO}_{2}$. The only difference between the methyl pyridine and toluene is that the pyridine ring contains a nitrogen, while the benzene ring does not. Thus, the lone pair of electrons of nitrogen on the ring may play a very important role in these reactions. One important function of the lone pair of electrons on the nitrogen atom is a Lewis base center which can take part in the reaction like those suggested in the mechanism. Especially when a methyl group is on the para and ortho positions, the resonance forms showed that nitrogenselenium bond formation or carbocation formation would be more important in 2-picoline and 4-picoline than in 3-picoline.

The resonance forms of carbanions:

1. 2-picoline

2. 4-picoline

3. 3-picoline




## Conclusion

The products from 2-picoline, 4-picoline and 8-methyl quinoline oxidized by selenium dioxide were 2-pyridine carboxylic acid, 4-pyridine carboxylic acid, and 8-quinoline aldehyde, respectively, and the percentage yields were $50 \%$, 76.8\%, and 49.1\%, respectively. 2,6-pyridine carboxylic acid was also the product when $2,6-1$ utidine was oxidized by $\mathrm{SeO}_{2}$, and 3-pyridine carboxylic acid was the product from 3picoline. Aldehydes were the products from lepidine and quinaldine oxidation reactions.

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## Appendix

Table I: The comparison of the physical properties of the experimental results with the literature values

|  | color, state |  | m.p. ( ${ }^{\circ} \mathrm{C}$ ) |  | b.p. ( ${ }^{\circ} \mathrm{C}$ ) |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | lit | exp | lit | exp | lit | exp |
| 8-quinoline <br> aldehyde |  | white <br> crys |  | 77-82 |  |  |
| 2-pyridine carboxylic acid | nd (w <br> al) | white granu | 136.7 | $\begin{aligned} & 126- \\ & 130 \end{aligned}$ | sub | sub |
| 4-pyridine carboxylic acid | plat <br> elet | orang <br> plat | 319 | $\begin{aligned} & 285- \\ & 295 \end{aligned}$ | sub <br> 260 <br> 15 va | sub <br> 260 <br> va |

Note for the shorthands:
m.p. $=$ melting point
b.p. = boiling point
lit $=$ literature
$\exp =$ experimental
crys $=$ crystals
nd $=$ needle
$\mathrm{w}=\mathrm{white}$
granu $=$ granulate
plat $=$ platelet
al $=$ alcohol
sub $=$ sublimation
va $=$ vacuum

Figure 1: The equipment setup for experiments


Figure 2: The equipment setup for sublimation


Transmittance


Figure 3: 8-methyl quinoline before reaction Reference: air

Scan: 16


Figure 4: Solid From 8-methyl quinoline product mixture after ether extraction

Reference: nujol
Scan: 16


Figure 5: Solid from 8-methyl quinoline oxidized mixture after ether extraction (I)

Reference: TMS (5\%) H1 level: normal
Sovlent: acetone (NMR grade) Gain: x1

Amplitude: 10
Sweep time: 150/sec
Filter Hz: normal
X axis: normal


Figure 6: Solid from 8-methyl quinoline oxidized mixture
after ehter extraction (II)
Reference: TMS (5\%) Solvent: acetone (NMR grade)
Amplitude: 10 H1 level: normal Gain: x1
Filter Hz : normal
Sweep time: 150/sec
X axis: x 10
Date: Jan 30, 1992
















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