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Silver(I) Oxide Catalyzed Oxidation of *o*-Allyl- and *o*-(1-Propenyl)phenols

Meera R. Iyer and Girish K. Trivedi
Department of Chemistry, Indian Institute of Technology, Powai, Bombay 400076, India
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The oxidation behavior of *o*-alkenylphenols towards a one-electron transfer agent, silver(I) oxide, was studied. Oxidation of an *o*-(1-alkenyl)phenol yields a dimeric product via the intermediacy of a quinonemethide radical. However, in the case of an *o*-(2-alkenyl)phenol where the γ-carbon bears substituents, a 2*H*-chromene is the product. During the course of this study, carpanone, a naturally-occurring lignan, was synthesized.

o-Quinonemethides have known been to be unstable intermediates in many chemical and biochemical reactions of phenols. The oxidative cyclization of *o*-allyl- and *o*-(1-propenyl)phenols by enzymatic dehydrogenation in biological systems and by chemical oxidation proceeds via intermediate quinonemethides.[1] The quinonemethides are believed to play an important role in the biosynthesis of lignans. Interest in the chemistry of these phenols stems from the fact that quinonemethides formed by oxidation of the same are the precursors of naturally-occurring physiologically active molecules.

Carpanone (**1**), is a lignan obtained from the light petroleum extracts of the carpano tree, a *Cinnamomum* species of the family *Lauraceae*.[2] Any synthetic strategy must involve the generation of five continuous asymmetric centers with the correct relative stereochemistry. The earlier reported syntheses of carpanone involve palladium(II) chloride,[3] a two-electron oxidant and (*N,N′*-disalicylidene ethylenediaminato)cobalt(II) as the catalysts. Though one-electron oxidants are known to oxidize phenolic compounds, there are very few reports[5,6] wherein silver(I) oxide, a single-electron-transfer agent has been used in the synthesis of naturally-occurring substances. Our previous work dealt with the oxidation of allylphenols with a two-electron oxidant, palladium (II) chloride.[7,8] In continuation with the same, the oxidation of *o*-allyl- and *o*-(1-propenyl)phenols were carried out using a one-electron oxidant, silver(I) oxide. During the course of this study, the synthesis of carpanone (**1**) was achieved from the *o*-(1-proponyl)phenol (**5**).

Results and Discussion

2-Allyl-4,5-(methylenedioxy)phenol (**2**) and 2-(*trans*-1-propenyl)-4,5-(methylenedioxy) phenol (**5**) were subjected to oxidative reactions with silver(I) oxide in dichloromethane. Whereas the product from the reaction of **2** could not be isolated, the phenol **5** gave a crystalline solid, mp 194—195 °C; UV spectrum (MeOH) λ_{max} 243, 262, 298 nm; IR spectrum (nujol) 1670 cm^{-1}; MS m/z 354 (M$^+$). The ^{1}H NMR spectral data are sumarized in Table 1. On comparison with the reported data for **1**,[2] the product was identified as the natural carpanone **1**.

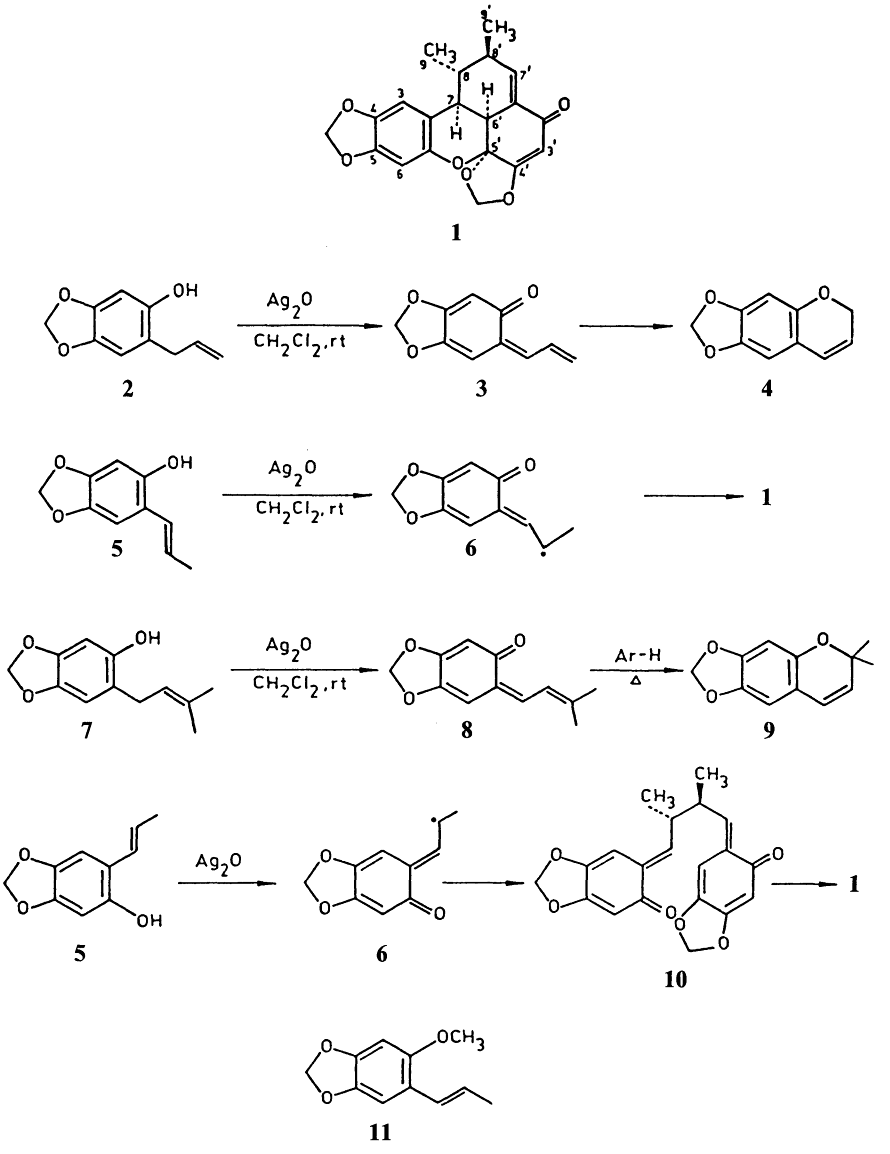
Table 1. ^{1}H NMR Values for Carpanone **1**[a)]

Proton	δ/ppm	J/Hz
9′-CH$_3$	0.71(d) [0.70]	7.62(8′,9′)
9-CH$_3$	1.14(d) [1.13]	7.71(8,9)
H-8′	2.22(m) [2.21]	7.40(6′,7)
H-8	2.51(m) [2.52]	5.00(7′,8′)
H-6′	3.18(m) [3.17]	2.40(6′,7′)
H-7	3.28(m) [3.27]	2.40(6′,8′)
4′,5′-O-CH$_2$-O	5.64, 5.67(d) [5.62, 5.66]	2.10(7,8)
H-3′	5.69(s) [5.68]	1.00(7,8′)
4,5-O-CH$_2$-O	5.88, 5.90(d) [5.88]	1.00(7′,8)
H-3	6.33(s) [6.32]	1.00(8,8′)
H-6	6.80(s) [6.81]	
H-7′	7.02(m) [7.01]	

a) Values in parentheses indicate the chemical shifts for the naturally-occurrig carpanone.[2]

The mechanism of formation of carpanone envisages the formation of the *o*-quinonemethide radical **6**. Two units of this radical then combine to yield the intermediate bis(*o*-quinonemethide) **10**. This is subsequently followed by an intramolecular cycloaddition reaction to yield **1**. The biogenesis of carpanone may involve the demethylation of the methoxyl group and oxidative dimerization of carpacin **11**, a trioxygenated 1-propenylbenzene that occurs in the carpano tree.

It is noteworthy that the intermediate involved in the reaction of phenol **5** is the quinonemethide radical **6** whereas that taking part in the reaction of **2** is the propenylidene cyclohexadienone **3**. The intermediate **3** cyclizes to 2*H*-chromene **4**. 2*H*-Chromenes such as **4**, unsubstituted at C-2 are unstable and hence, the product from the reaction of phenol **2** could not be isolated. In order to strengthen this proposition, the oxidation of 2-



Scheme 1.

(3-methyl-2-butenyl)-4,5-(methylenedioxy)phenol **7** was studied. On reaction with silver(I) oxide in dichloromethane, it gave the bright red *o*-quinonemethide **8** which on refluxing in benzene subsequently yielded 2,2-dimethyl-6,7-(methylenedioxy)-2*H*-chromene (**9**). It is, therefore, evident that the preferred mode of reaction of quinonemethides of type **3** and **8** is cyclization and that of the quinonemethide radical **6** is dimerization.

Conclusion

The oxidative behavior of *o*-allyl- and *o*-(1-propenyl) phenols towards silver(I) oxide, a one-electron oxidant has been studied. The position of the double bond with respect to the phenyl moiety determines the nature of the intermediate and hence, the subsequent mode of reaction. Cyclization is the favored mode of reaction when the double bond is at the β-carbon of the pendant group, while dimerization results when the double bond is at the α-carbon in the substrate molecule. Furthermore, the synthesis of carpanone, a naturally-occurring lignan has been achieved.

Experimental

Melting points are uncorrected. The UV spectra were recorded on a Shimadzu UV-vis 260 spectrophotometer. The IR spectra were run on a Perkin-Elmer model 681 spectrophotometer. ^{1}H NMR spectra, COSY, and spin decoupling experiments were carried out with a Varian VXR-300S spectrometer. The mass spectra were taken on a Shimadzu QP-1000 spectrometer.

Oxidation of 2-(*trans*-1-Propenyl)-4,5-(methylenedioxy)phenol (5). A solution of **5** (0.150 g, 0.84 mmol) in dry dichloromethane (10 mL) was stirred at room temperature. Silver(I) oxide (0.389 g, 1.68 mmol) was added to the stirred solution, which was followed by a color change from colorless to dark yellow. After 30 min, the solution was filtered through a pad of celite. Evaporation of the solvent followed by column chromatography over silica gel (elution with petroleum ether–ethyl acetate, 94:6) gave 0.072 g (48%) of **1**, mp 194—195 °C; IR (nujol) 1670, 1610, 1500, 1480, 1370, 1210, 1030 cm^{-1}. ^{1}H NMR see Table 1, MS *m*/*z* 354 (M$^+$), 177 (100). Anal. Calcd for $C_{20}H_{18}O_6$: C, 67.79; H, 5.08%. Found: C, 67.61; H, 4.86%.

2-(3-Methyl-2-butenyl)-4,5-(methylenedioxy)phenol (7). An aqueous solution of 3,4-(methylenedioxy)phenol (1.0 g, 7.2 mmol) was stirred at 70 °C. Formic acid (1.0 mL) and 2-methyl-3-buten-2-ol (0.62 g, 7.2 mmol) were added to stirred solution. The reaction was continued for a period of 6 h. The resulting solution was poured in water and extracted with ether. The ethereal solution was washed with $NaHCO_3$ solution, water and dried (Na_2SO_4). Chromatography of the residue over silica gel gave 0.45 g (45% yield) of **7**. IR ($CHCl_3$) 3450, 1630, 1600, 1480, 1210, 840 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ=1.70 (s, CMe$_2$, 6H), 3.20 (d, Ar–CH$_2$, 2H), 4.65 (s, OH, 1H), 5.10 (t, C=CH, 1H), 5.90 (s, O–CH$_2$–O, 2H), 6.30 (s, Ar–H, 1H), 6.50 (s, Ar–H, 1H).

Oxidation of 2-(3-Methyl-2-butenyl)-4,5-(methylenedioxy)-phenol (7). A solution of **7** (0.200 g, 0.970 mmol) in dry dichloromethane (10 mL) was stirred at room temperature. To this was added silver(I) oxide (0.450 g, 1.94 mmol) and the mixture was stirred for 1 h. The solution was filtered through a celite pad. Removal of solvent furnished a red solid: UV (MeOH) λ_{max} 339, 432 nm. IR (Nujol) no OH. The solid was taken in 10 mL benzene and refluxed for 2 h. Evaporation of the solvent followed by silica-gel chromatgraphy gave 0.160 g (80% yield) of **9**. IR ($CHCl_3$) 1610, 1490, 1370, 1280, 1210, 1120 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ=1.40 (s, C–Me$_2$, 6H), 5.48—5.50 (d, *J*=10 Hz, H-3, 1H), 5.85 (s, O–CH$_2$, 2H), 6.19—6.21 (d, *J*=10 Hz, H-4, 1H), 6.38 (s, Ar–H, 1H), 6.49 (s, Ar–H, 1H); MS *m*/*z* 204 (M$^+$), 189 (100).

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