Studies in dehydrogenation of 6-methoxy-1-tetralone. Structure of a novel product formed with tetrachloro-1,2-benzoquinone

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Dehydrogenation of 6-methoxy-1-tetralone (**1**) using palladium–carbon (30%), palladium black, and quinones has been studied with a view to preparing 6-methoxy-1-naphthol (**3**). A novel addition product formed, during dehydrogenation of **1** with tetrachloro-1,2-benzoquinone, has been proved to be 2,2-(tetrachloro-*o*-phenylenedioxy)-3,4-dehydro-6-methoxy-1-tetralone (**5**). Bromination of **1** followed by dehydrobromination gave the naphthol **3** in excellent yield.

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In continuation of our effort (1) to prepare 6-methoxy-1-naphthol (**3**), which was required in connection with a projected synthesis of oxasteroids, in fairly good amount from 6-methoxy-1-tetralone (**1**), we undertook a detailed study of dehydrogenation of **1** with various dehydrogenating agents. This was necessary as the methods reported in the literature (2–4) for the preparation of **3** were not satisfactory and the yields reported were low. As reported earlier (1), our attempt to prepare **3** by treating **1** with potassium *t*-butoxide in *t*-butanol in an atmosphere of oxygen[1] failed to give **3**, but gave 2-hydroxy-6-methoxy-1,4-naphthaquinone (**2**) in very good yield. Subsequently, this was shown to be a simple and general method of preparation of 2-hydroxy-1,4-quinones (1, 6).

Initially, we studied the dehydrogenation of tetralone **1** using 30% palladized carbon around 280–300 °C for 2–3 h in an atmosphere of carbon dioxide and the naphthol **3** was obtained in 50–60% yield; however, on a larger scale, the yield was poor. The yields were also poor when palladium black in xylene or naphthalene was used (7). Hence, an alternative method has to be developed.

Quinones, such as chloranil (8), 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) (9) have been used for introducing double bonds in conjugation with a ketone or an α,β-unsaturated ketone. Initially, we tried the dehydrogenation of tetralone **1** with chloranil (10), but there was no formation of the naphthol **3**. When the more powerful dehydrogenating agent, tetrachloro-1,2-benzoquinone (**4**) (11) (1 mole) was used in xylene or benzene, again no naphthol **3**[2] was formed, but a greenish-yellow crystalline solid, m.p. 191–192 °C, could be isolated in 20% yield. When the above reaction was repeated using two moles of **4** for one mole of **1**, the yield of the solid could be increased to 30%. The solid showed λ_{max} at 220 (ε 53 500), 258 (ε 30 515), and 330 mμ (ε 9615) in the ultraviolet (u.v.) spectrum and ν_{max} at 1686 (conjugated C=O), 1597, 1572, 1497 (aromatic), 1250, 1215, 1163, 1149, 1131, 1070, 1025, and 909 cm^{-1} (probably due to 1,3-dioxole) (12) in the infrared (i.r.) spectrum. It showed positive test for the presence of chlorine and the elemental analyses corresponded to a molecular formula $C_{17}H_8O_4Cl_4$. The presence of three intense molecular ion peaks at *m/e* 416 (^{35}Cl), 418, and 420 in 3:4:2 ratio in the mass spectrum clearly indicated the presence of four chlorine atoms (13) besides confirming the above molecular formula. The solid, on pyrolysis at 200 °C at 1 mm, gave tetrachlorocatechol and a tar which could not be purified. The formation of tetrachlorocatechol proved beyond doubt that the aforementioned solid must be an addition product of tetralone **1** with the quinone **4**.[3]

The nuclear magnetic resonance (n.m.r.) spectrum of this "adduct"[4] showed the following signals; a sharp singlet with three proton intensity at δ 3.9 ($ArOCH_3$), a doublet with one proton

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[1] N. A. J. Rogers and co-workers (5) have converted a Δ^2-cyclohexenone derivative to the corresponding phenol by the same reaction.

[2] Thin-layer chromatography was used for identification using an authentic sample of **3** as the reference compound.

[3] Our experience (14) with this quinone **4** in the dehydrogenation of abietic acid was helpful in arriving at the structure of this "adduct".

[4] This term has been used only for the sake of convenience while referring to it in the discussion though it is not a true adduct of **1** and **4**.

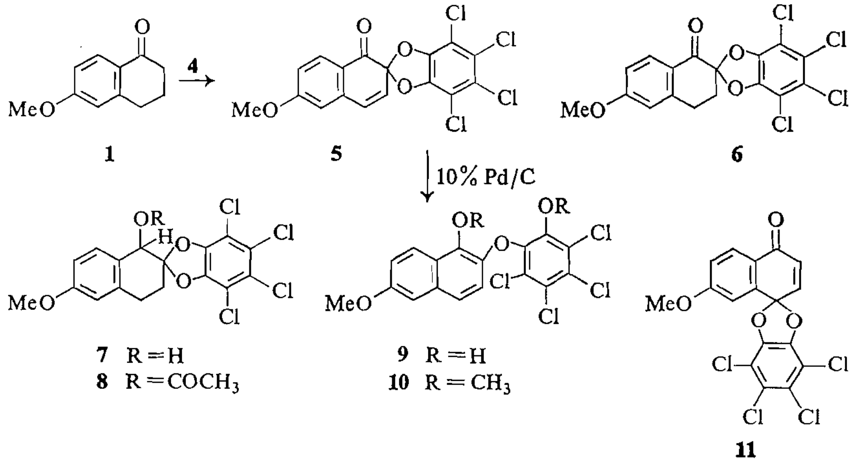

Chart I

intensity at δ 8.05 ($J = 8.5$ c.p.s.) (aromatic proton in *peri* position to the carbonyl group), a multiplet centered at δ 6.78 with two proton intensity (aromatic protons in *ortho* position to the methoxy group), a multiplet centered at δ 6.86 with one proton intensity (Ar—*CH*=CH—), and a doublet at δ 6.3 ($J = 10$ c.p.s.) with one proton intensity (Ar—CH=*CH*—). The above data indicated that the two carbonyl oxygen atoms of quinone moiety must be attached to a single carbon atom of tetralone **1** and the δ values of the two olefinic protons indicated the conjugation of the double bond with the phenyl ring. Therefore, the structure of the solid could be as represented in **5**.

Further proof in favor of structure **5** was arrived at as follows. The "adduct" **5**, on hydrogenation with 10% palladinized carbon in ethyl acetate, absorbed one mole of hydrogen and gave a mixture of a phenolic product, m.p. 188–189 °C (80%) and a ketone m.p. 208–209 °C (20%). When the hydrogenation was carried out with a little excess of catalyst, the aforementioned phenolic product was again formed in 80% yield, but none of the above ketone was obtained. Instead, an alcohol, m.p. 216–217 °C was obtained in 15–20% yield. The ketone exhibited λ_{max} at 217 (ε 51 860) and 306 mμ (ε 18 290) in the u.v. spectrum and in the i.r. spectrum it showed peaks at 1694 (conjugated C=O), 1607, 1493 cm^{-1} (aromatic). The elemental analyses corresponded to a molecular formula $C_{17}H_{10}O_4Cl_4$, which was supported by the presence of an intense molecular ion at *m*/*e* 418 (^{35}Cl) accompanied by peaks at *m*/*e* 420 and 422 in 3:4:2 ratio. In the n.m.r. spectrum of the ketone, signals due to the two olefinic protons found in the spectrum of "the adduct" **5**, disappeared; instead, two sets of triplets appeared around δ 3.22 and 2.68 due to the presence of two methylene groups adjacent to each other. The signal in the down field region (δ 3.22) could be assigned to the benzylic methylene. Further, the signals due to the following protons were also noticed in the above spectrum; a singlet at δ 3.87 (ArOCH$_3$), a doublet at δ 8.05 ($J = 9$ c.p.s.) (aromatic proton in *peri* position to the carbonyl), and a multiplet centered at δ 6.75 (2 aromatic protons on either side of the methoxyl group). These data indicated that this ketone must be the dihydro "adduct" **6**.

Unambiguous evidence for the structure of the "adduct" was obtained from the spectral data of the aforementioned alcohol, and its acetate which was prepared by treating the former with acetic anhydride in excess of pyridine. The i.r. spectrum of the alcohol showed peaks at 3610 (OH), and 1605 and 1497 cm^{-1} (aromatic) and it analyzed for $C_{17}H_{12}O_4Cl_4$. The acetate showed peaks in the i.r. spectrum at 1754 (acetate) 1613, 1587 (sh), and 1504 cm^{-1} (aromatic) and analyzed for $C_{19}H_{14}O_5Cl_4$. These data suggested structures **7** and **8** for the alcohol and its acetate respectively. If the structures **7** and **8** are correct for the alcohol and its acetate, the methine proton, attached to the carbon atom carrying the hydroxyl group in **7** and the acetate in **8**, should appear as a singlet in the n.m.r. spectrum as there are no protons to couple at the adjacent carbon atom. In fact, the

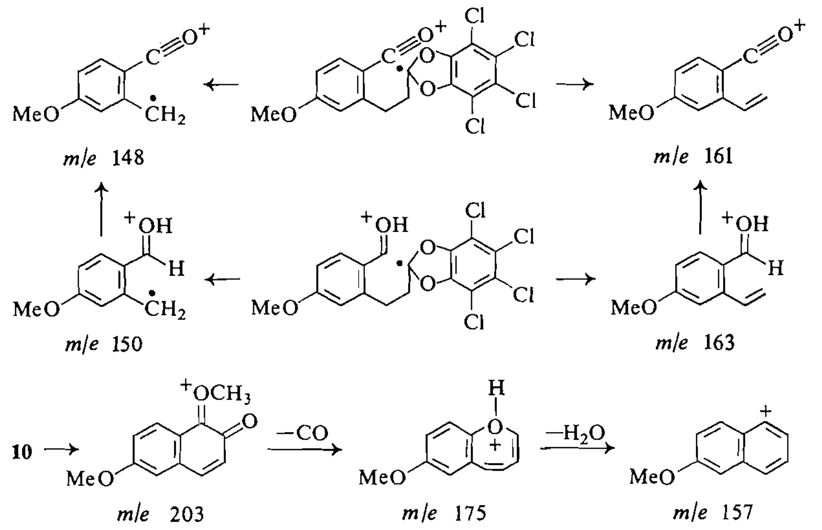

CHART II

n.m.r. spectrum[5] of the alcohol showed a singlet at δ 4.84 for the above methine proton (O*H* at δ 3.55, disappeared on shaking with D_2O), while that of the acetate, as expected, showed the signal for the methine proton in the downfield region at δ 6.2. These data clearly support the structures **7** and **8** for the alcohol and the acetate respectively. Since the alcohol **7** is obtained from the "adduct" by hydrogenation, the structure of the "adduct" should be **5** rather than **11**.

Additional support for the structure of the "adduct" could be obtained from the mass spectral fragmentation of these compounds (15) (Chart II). The presence of ions, at *m/e* 148 and 161 in **6**, at *m/e* 148, 150, 161, and 163 in **7**, and at *m/e* 157, 175, and 203 in **10**, clearly indicated that the tetrachloro-*o*-phenylenedioxy moiety, present in the "adduct", must be attached to the carbon atom α to the keto group as in **5** and not to the benzylic carbon atom as in **11**. Thus, all these data indicated that the "adduct" must be 2,2-(tetrachloro-*o*-phenylenedioxy)-3,4-dehydro-6-methoxy-1-tetralone (**5**).

The formation of the phenolic product in major amount during hydrogenation of the "adduct" **5** is an interesting observation. In the u.v. spectrum, this phenol showed λ_{max} at 220 (ε 42 840), 246 (ε 27 720), 286 (ε 2574), and 316 mμ (ε 4325) and in the presence of alkali it exhibited λ_{max} at 258 (ε 27 720) and 318 mμ (ε 6845). In the i.r. spectrum, it showed peaks at 3570 (free OH), 3460 (bonded OH), 1608, 1558, and 1515 cm^{-1} (aromatic) and analyzed for $C_{17}H_{10}O_4Cl_4$. The phenol could be methylated with dimethyl sulfate in the presence of anhydrous potassium carbonate in acetone to the corresponding methyl ether which analyzed for a molecular formula $C_{19}H_{14}O_4Cl_4$ which was again confirmed by the presence of intense molecular ion peaks at *m/e* 446 (^{35}Cl), 448 and 450 in 3:4:2 ratio in its mass spectrum. The n.m.r. spectrum of the methyl ether showed complete absence of methylene and methine protons, but showed three sharp singlets of three proton intensity at δ 4.11, 3.9, and 3.77 corresponding to three methoxyl groups attached to aromatic system. It also showed signals due to five aromatic protons, one of which appeared at δ 8.05 as a doublet (J = 9 c.p.s.) due to the proton at the *peri* position (with respect to methoxyl), which is deshielded by the methoxyl group (16). These data suggested structure **10** for the phenolic methyl ether and **9** for the parent phenol. The formation of the phenol **9** in major amount indicated that the hydrogenolysis of the "adduct" **5** took place preferably at the ketal function.

The "adduct" **5** is formed probably by the initial addition of the quinone **4** followed by dehydrogenation by another mole of quinone.

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[5] Because of the poor solubility of **7** and **8** even in DMSO-d_6, good spectra could not be obtained.

If the dehydrogenation process is the first step then the naphthol **3** would have been formed.[6]

Finally, we tried to prepare the naphthol **3** by bromination of tetralone **1** followed by dehydrobromination. Bromination of tetralone **1**, carried out under normal conditions, viz., in acetic acid or carbon tetrachloride, gave a mixture of two products as shown by thin-layer chromatography. However, when the above reaction was carried out in ether containing a trace of hydrogen chloride (17), 2-bromo-6-methoxy-1-tetralone (**1***a*) was obtained exclusively in an excellent yield. The α-bromo ketone **1***a* was dehydrobrominated by refluxing in dimethyl formamide (DMF) with either calcium carbonate or a mixture of lithium bromide and lithium carbonate. With the latter reagent, the yield of 6-methoxy-1-naphthol (**3**) was as high as 80% and this method was finally chosen for large scale preparation.

Experimental

All melting points are uncorrected. The u.v. spectra were determined in ethanol on a Beckman DU spectrophotometer. The i.r. spectra were recorded in Nujol with a Perkin–Elmer model 137B infracord spectrophotometer. The n.m.r. spectra were taken in $CDCl_3$ (except those of 7 and **8** which were recorded in DMSO-d_6), at 60 Mc.p.s. using TMS as internal standard. The mass spectra were determined in an Atlas CH-4 spectrometer. The microanalyses were carried out by the CIBA research center, Bombay, India.

Dehydrogenation of 6-Methoxy-1-tetralone (1)

(a) With 30% Palladized Carbon

A mixture of 1.76 g of 6-methoxy-1-tetralone (18) and 0.88 g of 30% Pd/C was heated around 280–300 °C while a steady stream of dry carbon dioxide was passed through the system. When the evolution of hydrogen ceased (2 h), the mixture was cooled and repeatedly extracted with ether. The ether extract was washed with dilute sodium hydroxide; the alkali extract acidified with ice cold dilute hydrochloric acid to give the naphthol **3** as a gum which was again extracted with ether. Removal of solvent, after washing with water, afforded 1.05 g of crude naphthol **3** which was purified by passing through an alumina column followed by crystallization from 90% *n*-hexane/benzene to give 0.88 g of crystalline 6-methoxy-1-naphthol (**3**), m.p. 85 °C (lit. 85 °C (4)).

In a large scale experiment, the combined ether extract, obtained after washing with dilute alkali, was washed with water, the solvent removed, and the residue distilled under reduced pressure to afford 2-methoxynaphthalene, naphthalene, and the starting material.

(b) With Palladium Black

A mixture of 1.0 g of tetralone **1** and 0.2 g of palladium black (19) in 30 ml of xylene was refluxed for 24 h and after the removal of solvent *in vacuo*, the residue was extracted with ether and worked up as before to give 0.15 g of naphthol **3**.

(c) With Tetrachloro-1,2-benzoquinone (4) (11, 20)

A mixture of 1.76 g (0.01 *M*) of tetralone **1** and 5.92 g (0.02 *M*) of **4** in 40 ml of benzene was refluxed for 8 h. The solvent was removed *in vacuo* and the resulting gummy product was chromatographed over neutral alumina (120 g). Elution with pure *n*-hexane, and then with 90% *n*-hexane/benzene afforded the "adduct" **5** which was crystallized from benzene/hexane mixture as shining greenish-yellow crystals; yield 1.2 g, m.p. 191–192 °C (decomposed).

Anal. Calcd. for $C_{17}H_8O_4Cl_4$: C, 48.8; H, 1.91; Cl, 33.97. Found: C, 48.76; H, 2.04; Cl, 33.66.

Hydrogenation of the "Adduct" 5

(*a*) A solution of 1.00 g of the "adduct" **5** in 50 ml of dry ethyl acetate was hydrogenated in the presence of 10% palladized carbon. After 2–3 h, the solution had absorbed one mole of hydrogen and the greenish-yellow color had disappeared. After filtration of the catalyst, the solvent was removed and the residue was taken up in ether and washed with dilute sodium hydroxide solution followed by water. On concentration of the ether solution, the ketone **6** began crystallizing out, yield 0.18 g, m.p. 208–209 °C.

Anal. Calcd. for $C_{17}H_{10}O_4Cl_4$: C, 48.57; H, 2.40; Cl, 33.81. Found: C, 49.04; H, 2.84; Cl, 33.28.

The above alkali extract was acidified with dilute hydrochloric acid and the separated product was extracted with ether. The ether extract was washed with water and the removal of solvent gave a gummy product which on crystallization from chloroform/hexane furnished 0.7 g of the phenol **9**, m.p. 188–189 °C;

Anal. Calcd. for $C_{17}H_{10}O_4Cl_4$: C, 48.57; H, 2.40; Cl, 33.81. Found: C, 48.07; H, 2.81; Cl, 33.38.

Methyl ether **10**, m.p. 108–109 °C (from ethanol).

Anal. Calcd. for $C_{19}H_{14}O_4Cl_4$: C, 50.89; H, 3.08; Cl, 31.69. Found: C, 50.61; H, 3.42; Cl, 31.30.

(*b*) The above hydrogenation was repeated with 1.00 g of "adduct" **5** in the presence of 0.4 g of 10% palladium carbon for 4–5 h. The product was worked up as before. From the alkali extract, 0.75 g of phenol **9** was obtained. The neutral fraction, on crystallization from chloroform–hexane, gave 0.21 g of alcohol **7**, m.p. 216–217 °C.

Anal. Calcd. for $C_{17}H_{12}O_4Cl_4$: C, 48.58; H, 2.84; Cl, 33.65. Found: C, 49.11; H, 3.26; Cl, 33.20.

Acetyl derivative **7**, m.p. 238–240 °C (80% benzene/hexane).

Anal. Calcd. for $C_{19}H_{14}O_5Cl_4$: C, 49.35; H, 3.02; Cl, 30.60. Found: C, 49.81; H, 3.38; Cl, 30.40.

Bromination of 6-Methoxy-1-tetralone (1)

A solution of 6.4 g of analar bromine in 20 ml of carbon tetrachloride containing a few ml of dry ether was added dropwise (each drop was added only after the previous drop was completely decolorized) to a stirred solution of 7 g of tetralone **1** in 200 ml dry ether. The ether contained 2 ml of ethereal hydrogen chloride and was maintained at 0–5 °C throughout the addition. After

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[6] *Note added in proof:*—Recent experiments have conclusively proved that the "adduct" is formed via the napthol **3**.

the complete addition of bromine, the reaction mixture was stirred for another 0.25 h and then water was added followed by ether. The ether layer was separated and washed with water. Removal of solvent afforded 10.1 g of gummy 2-bromo-6-methoxy-1-tetralone (**1***a*) and this material was used as such for the subsequent step. For analysis, a small amount of the above product was crystallized from *n*-hexane, m.p. 83 °C.

Anal. Calcd. for $C_{11}H_{11}O_2Br$: C, 51.80; H, 4.32; Br, 31.34. Found: C, 51.62; H, 4.35; Br, 31.30.

6-Methoxy-1-naphthol (3)

A solution of 10.1 g of the above α-bromoketone (**1***a*) in 200 ml of dimethyl formamide containing a mixture of 8 g of lithium bromide and 6 g of lithium carbonate was refluxed for 3 h in an atmosphere of nitrogen. The solvent was removed *in vacuo* and the residue treated with ice cold water followed by cold dilute hydrochloric acid. The separated gummy product was extracted with ether and washed with 10% sodium hydroxide solution. The alkali extract was acidified and again extracted with ether. Removal of ether afforded 5.85 g of crude naphthol **3** which was chromatographed over silica gel (120 g). Elution with *n*-hexane followed by 25% benzene/*n*-hexane mixture gave 4.95 g of 6-methoxy-1-naphthol (**3**), m.p. 85 °C (lit. 85 °C (4)).

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