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HYDROGENATION OF 1,4-NAPHTHOQUINONE AND 2-METHYL-1,4-NAPHTHOQUINONE WITH A COPPER CHROMITE CATALYST

P. A. ARGABRIGHT,[1a] H. D. RIDER[1a] and M. W. HANNA[1b]
Denver Research Center of the Marathon Oil Company Littleton, Colorado and
the Department of Chemistry, University of Colorado Boulder, Colorado

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Abstract—Hydrogenation of 1,4-naphthoquinone (I) using a copper chromite catalyst yields *trans*-1,4-dihydroxy-1,2,3,4-tetrahydronaphthalene (III), a new product. Similarly, 2-methyl-1,4-naphthoquinone (IV) gives two isomeric 1,4-dihydroxy-2-methyl-1,2,3,4-tetrahydronaphthalenes (VII and VIII) in which the hydroxyl groups are *trans*. At elevated temperatures quinone IV also produces two ac-2-methyl tetralols.

INTRODUCTION

THE reduction of 1,4-naphthoquinone (I) and its derivatives has been the subject of many investigations over the past seventy-five years. Among the chemical reduction methods[2a, b] are: tin–hydrochloric acid, stannous chloride–hydrogen chloride, phenylhydrazine (neat), sodium thiosulphate, triphenylmagnesium chloride, and hydrogen iodide–red phosphorus. All of these reagents reduce quinone I to 1,4-naphthohydroquinone (II). Catalytic reduction methods lead to different products depending on the catalyst and the severity of the reaction conditions. For example, quinone I can be hydrogenated to yield either hydroquinone II[3] or 1,4-dihydroxy 5,6,7,8-tetrahydronaphthalene.[4,5] The reduction of quinone I to 1,4-dihydroxy-1,2,3,4-tetrahydronaphthalene has not yet been demonstrated by chemical or catalytic methods. In addition, neither the *trans* nor the *cis* isomers of this diol have been previously reported.

We wish to report that naphthoquinones can be catalytically reduced to the corresponding diols using a copper chromite catalyst. Specifically, quinone I yields *trans*,-1,4-dihydroxy-1,2,3,4-tetrahydronaphthalene (III), and 2-methyl-1,4-naphthoquinone (IV) yields two isomeric 1,4-dihydroxy-2-methyl-1,2,3,4-tetrahydronaphthalenes. In addition, two *ac*-2-methyltetralols are formed in the latter reaction.

RESULTS AND DISCUSSION

1,4-*Naphthoquinone*. A number of catalysts, including platinum, palladium, rhodium, ruthenium, and copper chromite, were studied for the direct hydrogenation of I and IV. All of the catalysts were effective in promoting the hydrogenation of I, but, with the exception of copper chromite, hydrogenation was non-selective, leading to as many as seventeen products (palladium). Although hydrogenation was extensive with the non-selective metal catalysts, the presence of diol III or its *cis* isomer was

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[1a] Marathon Oil Company; [b] University of Colorado.

[2] See [a] N. Donaldson, *The Chemistry and Technology of Naphthalene Compounds* p. 384. E. Arnold, London (1958); [b] *Elseviers Encyclopedia of Organic Chemistry* Series III, Vol. 12B, p. 2770, New York (1952), for discussion and references.

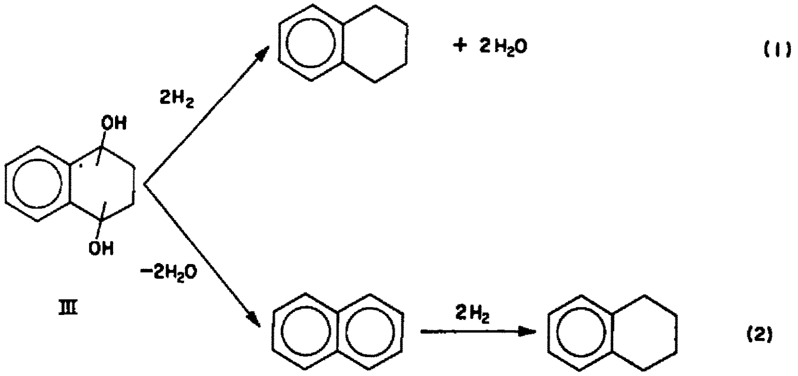
[3] B. R. Baker and G. H. Carlson, *J. Amer. Chem. Soc.* **64**, 2662 (1942).

[4] A. Skita and W. Rohrmann, *Ber. Dtsch. Chem. Ges.* **63B**, 0473 (1930).

[5] C. Cardani, *Gazz. Chim. Ital.* **82**, 155 (1952); *Chem. Abstr.* **47**, 7458 (1953).

not detected in the product mixture. When copper chromite was used as catalyst, however, quinone I was converted to diol III in good yield. A summary of the experimental results for the reduction of quinone I is given in Table 1.

As shown in Table 1, the selectivity as well as the reaction rate is quite temperature dependent (cf runs, 1, 3 and 5). It appears that 150° is optimum for facile reduction with high selectivity to III. Lowering the temperature to 125° markedly reduces the rate of hydrogenation. At higher temperatures (200°), the predominate product was tetralin. There was also an increase in α-tetralol formation at 200°. Tetralin may result from either direct hydrogenolysis of diol III (Eq. 1), or dehydration of diol III to form naphthalene which is subsequently hydrogenated (Eq. 2).



Hydrogenation of diol III at 200° using copper chromite gave tetralin in high yields. Under identical conditions, naphthalene was not reduced, however. These results indicate that diol III is a likely precursor to tetralin, but naphthalene is not an important intermediate in its formation. It appears that tetralin arises from hydrogenolysis of diol III or a similar intermediate. This conclusion is reasonable, in view of the ease with which benzyl alcohols and other benzylic derivatives undergo hydrogenolysis.[6]

Gas chromatographic analysis of the crude reaction mixtures obtained under the optimum conditions for formation of diol III indicated the presence of only one diol. Furthermore, no evidence for the presence of the *cis* isomer of diol III was found in the work-up of the reaction mixtures and product isolation. Thus, it would appear that diol III is the predominate, if not the exclusive, diol product from the hydrogenation of quinone I over copper chromite.

The foregoing conclusion is surprising in view of the fact that catalytic hydrogenations generally result in *cis* addition,[7] which, in this case, should give *cis*-1,4-dihydroxy-1,2,3,4-tetrahydronaphthalene. NMR evidence definitely shows that diol III is the *trans* isomer, however. It is well known that axial and equatorial protons in six membered ring systems usually exhibit different chemical shifts.[8] Furthermore, the

[6] For a good review on this subject, see W. H. Hartung and R. Simonoff, *Org. Reactions* 7, 267 (1953).

[7] For a brief discussion, see L. F. Fieser and M. Fieser, *Advanced Organic Chemistry* p. 180. Reinhold New York (1961).

[8] See, for example, L. W. Reeves and K. O. Strømme, *Canad. J. Chem.* **38**, 1241 (1960); R. N. Lemieux, R. K. Kullnig, H. J. Bernstein and W. G. Schneider, *J. Amer. Chem. Soc.* **80**, 6098 (1958).

TABLE 1. CATALYTIC HYDROGENATION OF 1,4-NAPHTHOQUINONE[a,b] (I)

Run no.	Catalyst[c,e]	Temp °C	H_2Pres Psi[d]	Time hr	Conv. of I, %	Yield,[e] %		
						III	α-Tetralol	Tetralin
1	$CuCr_2O_4$ (2·14)	150	3000	4	92·0	90·5	1·3	0·2
2	$CuCr_2O_4$ (2·14)	150	3000	2	82·7	78·8	3·9	Trace
3	$CuCr_2O_4$ (2·14)	125	3000	2	4·7	4·7	0	0
4	$CuCr_2O_4$ (1·07)	150	3000	4	40·5	39·1	1·4	Trace
5	$CuCr_2O_4$ (2·14)	200	3000	4	99·0	12·0[f]	8·2	76·2
6	$CuCr_2O_4$[g] (1·97)	150	3000	4	31·4	31·4	Trace	Trace
7	$CuCr_2O_4$[h] (1·80)	150	3000	4	80·0	77·6	1·5	0·9
8	$CuCr_2O_4$ (2·14)	150	1200	4	87·8	81·6[i]	Trace	Trace
9	$CuCr_2O_4$ (2·14)	150	1200	2	73·4	73·4	0	0
10[j]	$CuCr_2O_4$ (2·14)	150	3000	4	0	0	0	0
11	Pd–C[k] (8·6)	150	3000	4	—	17 Products[l]		
12	Rh–C[m] (8·6)	24	3000	2	—	8 Products[l]		
13	Ru–C[n] (8·6)	24–100[o]	3000	8	—	9 Products[l]		
14	Pt–C[p]	50–100	3000	5	—	II		

[a] Absolute ethanol employed as solvent in all runs.

[b] Conc. of I, 0·67 M.

[c] BaO stabilized lab. prep. (g/0·10 mole of I).

[d] Initial pressure at 24°.

[e] From gas chromatographic analyses of crude reaction mixture.

[f] Unidentified high boiling product, 12·6%, also formed.

[g] Catalyst recovered from run no. 5.

[h] Catalyst recovered from run no. 4.

[i] Unidentified high boiling product, 6·2%, also formed.

[j] Naphthohydroquinone used in place of I.

[k] 10% Pd on carbon.

[l] Product mixture contained tetralin, *cis*- and *trans*-decalins.

[m] 10% rhenium on carbon.

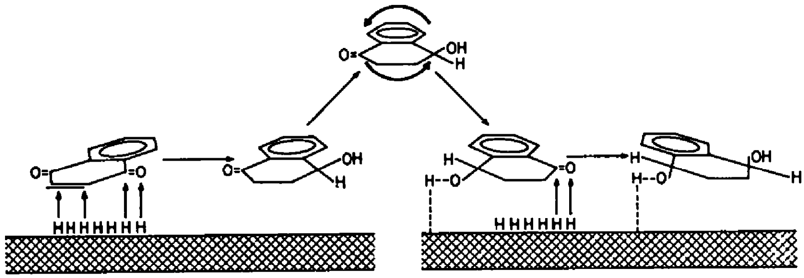
[n] 5% ruthenium on carbon.

[o] One hour at 24°; 6 hr at 50°; 1 hr at 100°.

[p] 10% platinum on carbon.

coupling constants between protons on six membered ring systems depend on the relative configurations of the two protons involved.[9] Thus, the axial–axial proton splitting (J_{aa}) is usually about 7–9 c/s while the axial–equatorial (J_{ae}) and equatorial–equatorial (J_{ee}) splittings are much smaller, usually 1–3 c/s. For diol III, approximately 0·2 M in acetic acid,[10a] the absorption due to the alpha protons was an incompletely resolved triplet at $5{\cdot}23 \pm 0{\cdot}02\ \tau$ with a width at one-half height ($\Delta\nu_{1/2}$) of 7–8 c/s. The presence of only one peak for the α-hydrogens in diol III indicates either that the two α-protons are in identical magnetic environments (both axial or both equatorial) or that the cyclohexene ring structure is "umklapping" rapidly enough so that only an average chemical shift is observed.[10b] This latter possibility is made highly unlikely, however, by the observation that only one α-proton peak with the same $\Delta\nu_{1/2}$ is observed in the diacetate and dibenzoate esters of diol III. This conclusion is further supported by the results for the 2-methyltetralin diols discussed below. The α-hydrogens must, therefore, be in equivalent magnetic environments. A decision can be made as to whether both are axial or both are equatorial by considering the value of $\Delta\nu_{1/2}$. There is now considerable evidence that the absorption peak of a single proton adjacent to a methylene group in a six membered ring will have a characteristic $\Delta\nu_{1/2}$ depending on whether the single proton is axial or equatorial.[11] If the single proton is equatorial, there will be one J_{ea} and one J_{ee} coupling giving rise to a partially resolved triplet with $\Delta\nu_{1/2}$ of 5–8 c/s. If the single proton is axial, there will be one J_{aa} and one J_{ae} coupling giving rise to a partially resolved quartet with $\Delta\nu_{1/2}$ of 12–18 c/s. The absorption from the α-protons of diol III fall in the former range and diol III is, thus, the *trans* isomer with both hydroxy groups axial.

A possible mechanism by which *trans* addition (overall) might take place on a catalyst surface is depicted by Eq. 3. Thus, in the first step, the quinone is adsorbed on the catalytic surface and one carbonyl group and the double bond is reduced to the corresponding alcohol. Next, the intermediate alcohol is desorbed and, subsequently,



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[9] J. A. Pople, W. G. Schneider and J. J. Bernstein, *High Resolution Nuclear Magnetic Resonance* Chap. 14. McGraw-Hill, New York (1959).

[10a] Acetic acid was used as a solvent to promote rapid exchange of the hydroxy protons. In the NMR spectrum of diol III in dimethyl sulphoxide, the hydroxy resonance and the alpha proton resonance overlap making analysis of the spin coupling constants of the alpha protons impossible. Exchange of the hydroxy protons was known to be slow in DMSO because of the observed spin coupling between the hydroxy and alpha protons.

[10b] The six membered ring in the tetralins is actually a cyclohexene ring so that the hydrogens in the 1 and 4 positions are pseudo-axial and equatorial. This, however, does not effect any of the discussions in this paper.

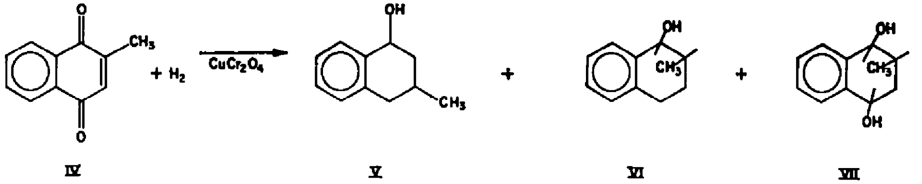
[11] A. Hassner and C. Heathcock, *J. Org. Chem.* **29**, 1350 (1964). See especially Ref. 26 and 27.

readsorbed preferentially with the hydroxyl group next to the catalyst. The driving force for adsorption in this manner would be due to the hydrogen bonding of the hydroxyl group with the oxide surface. Finally, while the intermediate is in this position, the remaining carbonyl group is reduced, leading to a *trans* diol. The fact that diol III is not formed when non-oxide catalysts are employed demonstrates the importance of the oxide surface in determining the stereochemistry of the product.

An alternate mechanism in which *cis* addition (overall) takes place leading to the *cis* product, which in turn isomerizes to the *trans* isomer (III), appears unattractive for the following reasons. At low conversions of I (run No. 3, Table 1), only the *trans* isomer (III) was detected. Under these mild conditions, it is unlikely that all of the *cis* isomer would be converted to III. Secondly, from inspection of the Dreiding stereomodels of the two isomers, their conformational similarity would not dictate the exclusion of the *cis* isomer at equilibrium.

Although hydroquinone II is a by-product in the reduction of quinone I over copper chromite, it is an unlikely intermediate in the formation of diol III since hydroquinone II does not yield diol III on hydrogenation over copper chromite (run No. 10, Table 1). It was for this reason that the reduction of the carbonyl group and the double bond was postulated to take place in the first step. If only the carbonyl group were reduced in the first step, the resulting intermediate would enolyze to hydroquinone II, and the reduction would stop.

2-*Methyl*-1,4-*naphthoquinone*. Hydrogenation of 2-methyl-1,4-naphthoquinone (IV) over copper chromite at 150° produces three hydroxylic products (Eq. 4) in an overall yield of 96·2%. The gas chromatographic area ratios of the products in the order of their increasing relative retention times are: 1·3 (V); 1 (VI); 1·6 (VII). The products were separated by elution chromatography and identified as *ac*-3-*methyl*-1-*tetralol* (V), ac-*trans*-2-methyl-1-tetralol (VI), and ac-*trans*-2-methyl-*trans*-4-hydroxy-1-tetralol (VII). Boyland and Manson[12] have prepared a diol in a 4% yield from the reduction of quinone IV with LAH. Comparison of the m.p. of their diol (182°) and its diacetate (115–117°) with the m.p. of diol VII (183·5–184°) and its acetate (116·5–118°) suggests that the two compounds are identical. No conclusions about the stereochemistry of diol VII were drawn by these workers. Tetralol VI has been prepared by reduction of 2-methyl-1-tetralone with sodium in alcohol[13] or LAH.[14] This compound was assigned the *trans* structure on the basis of the relative rates of thermal decomposition of the acetate and xanthate derivatives.[13] NMR analysis (see below) supports this assignment. To our knowledge, neither isomer of tetralol V has been reported.



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On lowering the reaction temperature to 125° and reducing the reaction time, the

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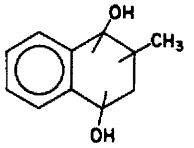
[12] E. Boyland and D. Manson, *J. Chem. Soc.* 1839 (1951).

[13] E. R. Alexander and A. Mudrak, *J. Amer. Chem. Soc.* **72**, 3194 (1950).

[14] G. Baddely, J. W. Rasburn and R. Rose, *J. Chem. Soc.* 3168 (1958).

reduction in Eq. 4 led to only two products in 54·3% yield. Unlike the 150° run, tetralols V and VI were not formed. The products were separated by elution chromatography and identified as isomeric ac-2-methyl-4-hydroxy-1-tetralols, one of which is VII. The other product was tentatively identified as *ac*-cis-2-*methyl*-trans-4-*hydroxy*-1-*tetralol* (VIII), which has not been reported in the literature. Since diol VIII is found at 125° but is absent at 150° (Table 2), it must readily undergo hydrogenolysis to give one or both of the tetralols V and VI. If the structure assigned to diol VIII above is correct, however, only tetralol V can result from hydrogenolysis of diol VIII. Tetralol VI would have to come from the hydrogenolysis of diol VII. At 175°, the only products detected by gas chromatography were tetralols V and VI arising from the complete hydrogenolysis of diols VII and VIII.



VIII

TABLE 2. CATALYTIC HYDROGENATION OF 2-METHYL-1,4-NAPHTHOQUINONE (IV) OVER COPPER CHROMITE[a]

Run no.	Temp °C	Time hr.	Conv. of IV,[b] %	% Yield[b] VII + VIII[c]	V	VI
16	100	4	12·4	12·4	0	0
17	125	2	54·3	54·3	0	0
18	150	4	96·2	39·4[d]	32·2	24·6
19	175	4	85·5	0	66·1	19·3

[a] Reactions carried out in absolute ethanol at 3000 psi H_2 press., using 2·14 g $CuCr_2O_4$/0·10 mole of IV.

[b] By gas chromatographic analysis of the crude reaction mixture.

[c] The isomeric diols VII and VIII were not separated by gas chromatography.

[d] The only diol present was VII.

The configurations of diols VII and VIII and tetralols V and VI were determined by NMR analysis. The NMR spectrum of diol VII contains two absorptions from the protons adjacent to the hydroxy groups. One absorption is a doublet centred at $5{\cdot}60 \pm 0{\cdot}02\ \tau$, with $J = 8$ c/s. The other is a broad unresolved band centred at $5{\cdot}10 \pm 0{\cdot}02\ \tau$ with $\Delta\nu_{1/2} = 18$ c/s. Keeping in mind the facts used above in the discussion of the configuration of diol III it must be true that:

1. The upfield doublet is from the proton in the 1 position.
2. The protons in the 1 and 2 position are both *axial.*
3. The proton in the 4 position has one axial-axial splitting and one axial–equatorial splitting.

These facts are consistent only with the structure that has both hydroxy groups and the methyl group *equatorial.*[15]

The NMR spectrum of diol VIII also contained two absorptions from the protons alpha to hydroxyl. The upfield absorption ($5{\cdot}48 \pm 0{\cdot}04\ \tau$) was a partially resolved doublet with $\Delta\nu_{1/2} = 4{\cdot}5$ c/s and the downfield absorption ($5{\cdot}22 \pm 0{\cdot}02\ \tau$) was again a broad multiplet with $\Delta\nu_{1/2} = 18$ c/s. The large value of $\Delta\nu_{1/2}$ for the 4-proton indicates that once again the 4-hydroxy group is equatorial. The relative positions of the 1-hydroxyl and 2-methyl groups cannot be determined with certainty, however, since only the configuration with both groups equatorial can be definitely ruled out. We have tentatively assigned this diol the ac-*cis*-2-methyl-*trans*-4-hydroxy-1-tetralol structure by analogy with the other two diols. This assignment is consistent with magnetic anisotropy considerations which predict that the 1-proton resonance should be shifted downfield and the 4-proton resonance should be shifted upfield when the position of the methyl group is changed from equatorial to axial.[16] Such shifts do occur between the appropriate resonances in diols VII and VIII. Conclusions based on magnetic anisotropy are always open to question, however.[17] In addition this structure is expected on the basis of the mechanism described in Eq. 3.

The NMR spectrum of tetralol V contains a triplet centred at $5{\cdot}12 \pm 0{\cdot}02\ \tau$ with relative intensities of approximately 1:2:1 and $J = 3{\cdot}2$ c/s. This tetralol is clearly 1-hydroxy-3-methyl tetralin and the 1-hydroxy group must be axial. The configuration of the 3-methyl group cannot be determined.

For tetralol VI, there is a doublet absorption centred at $5{\cdot}67 \pm 0{\cdot}02\ \tau$ with $J = 7$ c/s. This finding is only consistent with the 2-methyltetralol structure, and both the hydroxyl and methyl groups must be equatorial.

In summary, 1,4-naphthoquinone and 2-methyl 1,4-naphthoquinone are readily hydrogenated over a copper chromite catalyst to yield predominately, if not exclusively, the corresponding trans 1,4 glycols of 1,2,3,4-tetrahydronaphthalene. The surprising stereoselectivity to trans glycols may be rationalized in terms of a preferred adsorption of a monohydric intermediate on the metal oxide surface. Hydrogenolysis is the major side reaction which can be alleviated by avoiding high reaction temperatures.

EXPERIMENTAL[18]

Starting materials. These were obtained from commercial sources and used without further purification. Hydrogenation experiments using commercial and purified (steam distilled) 1,4-naphthoquinone gave comparable results.

1,4-*Naphthoquinone.* Matheson, Coleman and Bell, m.p. 124–125°.

2-*Methyl*-1,4-*naphthoquinone.* Matheson, Coleman and Bell, m.p. 104·6°.

1,4-*Naphthohydroquinone.* Eastman Organic Chemicals, practical grade.

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[15] A referee has given a possible explanation for why the hydroxyl groups are axial in diol III and equatorial in diol VII. For an equatorial hydroxyl group, there would be interaction with the peri hydrogen on the benzene ring. This interaction is not present if the hydroxyl group is axial. Some 1–3 interaction results from an axial hydroxyl, but this can be alleviated by a slight flattening of the ring. This flattening is interfered with if a 2-methyl group is present, forcing such compounds to assume the configuration in which the methyl group is equatorial and the hydroxyl group equatorial.

[16] H. M. McConnell, *J. Chem. Phys.* **27**, 226 (1957); J. I. Musher, *Ibid.* **35**, 1159 (1961).

[17] J. I. Musher, *J. Chem. Phys.* **37**, 192 (1962).

[18] All m.ps. were taken on a Fisher-Johns apparatus and are uncorrected. IR spectra were recorded on a Perkin-Elmer Model 21 spectrometer by the KBr disc technique; UV spectra were determined with a Cary Model 14 recording spectrometer using matched 1 cm cells; NMR spectra were obtained at 60 Mc with a Varian Model A-60 spectrometer. Microanalyses were performed by Galbraith Laboratories, Knoxville, Tennessee.

Catalysts. Unless otherwise indicated the copper chromite catalyst employed throughout this study was prepared according to the method of Lazier and Arnold.[19] The Pd (10% on carbon) and Pt (5% on carbon) were obtained from Eastman Organic Chemicals. The Ru (5% on carbon) and Rh (10% on carbon) were purchased from Englehard Industries.

Absolute EtOH was employed as the solvent for all of the hydrogenations.

Hydrogenation apparatus and method. The apparatus consisted of a 300 ml stainless steel rocking autoclave, equipped with a heater, rocking assembly which operated at a fixed 50 cycle/min, internal thermocouple, temp regulator and press. gauge. Prior to all hydrogenations, the system was degassed and brought to atm. press. with N_2. After introducing H_2 to the desired press., a period of 30 min was allowed to test for leaks.

In order to obtain reproducible results it is advisable to carry out at least two hydrogenations to condition the reactor surface.

Trans-1,4-dihydroxy-1,2,3,4-tetrahydronaphthalene (III). In a typical experiment, the reactor was charged with I (15·8 g; 0·10 mole) copper chromite (2·14 g), absolute EtOH (150 ml), pressurized to 3000 psi with H_2 and reacted at 150° for 4 hr. The maximum press. attained during the reaction was 3700 psi. The final press. at 24° was 2290 psi. The light purple reaction mixture was filtered through Hy-Flo Super Cell to remove the catalyst.

At this point, the filtrate was diluted with absolute EtOH to a known volume and a 4·0 ml aliquot removed. This sample was added to a known wt. of n-hexadecane (G.C. standard) and analysed by gas chromatography[20] to provide *in situ* conversion and yield data.

The filtrate was concentrated *in vacuo* to approximately 10% its original volume. The resulting dark residue was added to an equal volume of diethyl ether to precipitate 8·6 g (52% yield) of crude "diol III," m.p. 134–136°. Two recrystallizations from EtOH–petroleum ether gave colourless needles of pure III, m.p. 137·5–138°. (Found: C, 73·25; H, 7·42; OH (by acetylation), 20·0. Calc. for $C_{10}H_{12}O_2$: C, 73·17; H, 7·32; OH, 20·7.)

IR spectrum showed bands at 3280 cm^{-1} (H-bonded OH); 1042 cm^{-1} (alicyclic sec. OH); 760 cm^{-1} (1,2-disubstituted benzene). The absence of absorption in the region 1630–1685 cm^{-1} demonstrates the absence of carbonyl groups. 95% EtOH λ_{max} 261 mμ (log ε 2·44), 266 (2·36), 271 (2·25).[21]

The absence of phenolic OH, unsaturation and carbonyl groups was confirmed by negative tests with $FeCl_3$ and Br-water; cold dil. $KMnO_4$ and Br_2–CCl_4 at 25°;[22] 2,4-dinitrophenyl hydrazine. Compound III is stable in refluxing 5% NaOH but reacts rapidly in 5% HCl below 50° to give naphthalene.

The life of the copper chromite catalyst is dependent on the temp employed for hydrogenation. Thus, the catalyst recovered from a hydrogenation carried out at 200° is only 60% as active as the catalyst recovered from a hydrogenation performed at 150° (cf runs 6 and 7). On the other hand, the selectivities of the two catalysts are nearly the same.

Several experiments were carried out to compare commercially available copper chromite catalysts with that prepared by us. As shown in Table 3, the commercial catalysts are suitable for the reduction of I to III. The function of Ba in copper chromite catalysts is to inhibit[18] reduction of the catalyst surface. It is generally felt that reduced catalysts promote undesirable dehydrogenation reactions. From the data in Table 3, it appears that a slightly reduced catalyst (i.e., one which does not contain Ba) is as selective in the formation of III as the Ba stabilized catalysts.

trans-1,4-*Diacetoxy*-1,2,3,4-*tetrahydronaphthalene.* A solution of III (0·40 g; 2·4 mmoles), acetic anhydride (1·5 ml) in dry pyridine (4 ml) was heated at reflux for 8 min, cooled to room temp and poured over crushed ice. The resulting solid product, wt. 0·58 g (97% yield), was recrystallized from EtOH to give colourless needles of pure diacetate, m.p. 126°. (Found: C, 67·72; H, 6·46; O, 25·72; Sap. equiv., 120·3. Calc. for $C_{14}H_{16}O_4$: C, 67·75; H, 6·45; O, 25·82; Sap. equiv., 124·0.)

ac-trans-2-*Methyl*-trans-4-*hydroxy*-1-*tetralol* (VII). Compound IV (17·2 g; 0·1 mole) $CuCr_2O_4$

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[19] W. A. Lazier and H. R. Arnold, *Organic Syntheses* Coll. Vol. II; p. 142. J. Wiley, New York, N.Y. (1943).

[20] The crude reaction mixtures were analysed on a F and M Model 720 dual column gas chromatograph. A 6′ × ¼″ column, packed with SE-30 (20%) on Chromasorb W (60–80 mesh) programmed from 25° to 180° gave satisfactory results. Peak areas were obtained using a disc integrator and checked with a planimeter.

[21] The UV spectrum is identical to that of *o*-xylene, a structural model for III.

[22] Reacts on warming to liberate HBr presumably from oxidation of the CHOH groups.

(2·14 g) and absolute EtOH (150 ml) were placed in the reactor. The bomb was charged with 3000 psi of H_2 and brought to 150° for 4 hr. Maximum press. reached was 3600 psi. The final press. at 30° was 2250 psi. The light yellow solution was filtered through Hy-Flo filter cell (Johns-Manville) and diluted to a known volume. A sample was taken from this solution for GLC analysis.[19] The filtrate was concentrated *in vacuo* to about 10% of its original volume yielding a thick oil. Addition of an equal volume of diethyl ether and pet. ether (1 : 1) gave a white solid, m.p. 174–176°. This product was recrystallized from 95% EtOH and heptane to yield colourless platelets of VII, m.p. 183·5–184°. (Found: C, 73·98; H, 7·64; O, 17·94. Calc. for $C_{11}H_{14}O_2$: C, 74·20; H, 7·87; O, 17·97.)

TABLE 3. HYDROGENATION OF 1,4-NAPHTHOQUINONE (I) USING VARIOUS COPPER CHROMITE CATALYSTS[a]

Catalyst	Surface area m^2/g	% Bao	Conv. of I, %	Yield of III, %
Lab. prep.	18	11·8	92·0	90·5
Harshaw 0401	12	11·1	88·1	75·7
Harshaw 1800	37	0	98·5	92·2
Harshaw 1106-P[b]	47	10	75·8	30·8
Girdler 13	14	0	88·6	87·0

[a] Unless otherwise stated, reductions were carried out in absolute EtOH at 150° for 4 hr at 3000 psi.

[b] 1000 psi initial H_2 press.

ac-cis-2-*Methyl*-trans-4-*hydroxy*-1-*tetralol* (VIII). In a manner similar to the preparation of VII, quinone IV was hydrogenated over copper chromite at 125° for 2 hr. Precipitation of the concentrate with a mixture of pet. ether–ethyl ether afforded a white solid, m.p. 138–143°. Elution chromatography, using alumina (Fisher 80–200 mesh) and $CHCl_3$ as the elutant, provided two fractions. The first fraction was characterized as diol VII. The second fraction, after one recrystallization from EtOH–n-heptane solvent pair, gave VIII, m.p. 153·5–154°. (Found: C, 74·23; H, 7·80; O, 17·49. Calc. for $C_{11}H_{14}O_2$: C, 74·16; H, 7·87; O, 17·98.)

ac-trans-2-*Methyl*-trans-4-*hydroxy*-1-*tetralol diacetate* (IX). Compound VII (0·079 g 0·4 mmole), acetic anhydride (0·30 ml) and dry pyridine (0·79 ml) were heated in a steam bath (~94°) for 20 min. This solution was quenched over crushed ice and the solid filtered off to give 0·0865 g IX (75% yield), m.p. 117·5–118° from diethyl ether. (Found: C, 68·21; H, 6·69; O, 23·57. Calc. for $C_{15}H_{18}O_4$: C, 68·70; H, 6·87; O, 24·43.)

ac-3-*Methyl*-1-*tetralol* (V). The diethyl ether was blown off the filtrate derived from the final filtration, in the preparation of VII, to yield an oil. This oil was distilled (b.p. 61° at 0·2–0·3 mm Hg) and the fractions combined. Pet. ether (b.p. 20–40°) was then added to afford a white solid, collected by filtration and recrystallized from cyclohexane to yield colourless needles of V, m.p. 116·2–116·7°. (Found: C, 81·41; H, 8·47; O, 9·96. Calc, for $C_{11}H_{14}O$: C, 81·5; H, 8·64; O, 9·88.)

Compounds V and VII gave negative tests with Br_2–CCl_4 and $KMnO_4$ indicating the absence of non-aromatic double bonds.

ac-trans-2-*Methyl*-1-*tetralol* (VI). The filtrate recovered from the precipitation, in the isolation of V, was passed through an alumina column (Fisher, Adsorption Alumina, 80–200 mesh) using pet. ether and benzene as the elutant. This afforded a white crystalline solid, m.p. 68·5 to 70°. The product was recrystallized from cold pet. ether to give VI, m.p. 70·0°–70·8°. (Found: C, 80·60; H, 8·61; O, 10·16. Calc. for $C_{11}H_{14}O$: C, 81·5; H, 8·64; O, 9·88.) This solid was contaminated with diol VII as shown by gas chromatographic analysis.

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