

The Ring Opening of Aromatic *O*-Heterocycles by Sodium in Pyridine

JARL GRIPENBERG and TAPIO HASE

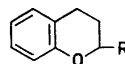
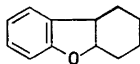
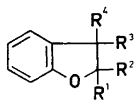
Department of Chemistry, Institute of Technology, Helsinki, Finland

A number of 2,3-dihydrobenzofuran derivatives have been treated with sodium in pyridine, giving *o*-vinylphenol derivatives. Some other related compounds have also been tested by this reagent. The NMR-spectra of the 2,3-dihydrobenzofuran derivatives are discussed.

Prey^{1,2} introduced the use of sodium in pyridine as a reagent for the cleavage of aromatic ethers. We have now studied this reaction, with respect to its use for the opening of the heterocyclic ring in 2,3-dihydrobenzofuran and chroman derivatives.

Such a ring cleavage of 2,3-dihydrobenzofuran derivatives has been brought about by sodium or potassium in liquid ammonia, whereas the chroman-ring is much more resistant to opening, except when it carries an aromatic substituent in the 2-position.^{3,4} The ring opening is accompanied by hydrogenation, giving *o*-alkylsubstituted phenols. By using sodium amide instead of sodium Hurd and Oliver,⁴ however, obtained *o*-propenylphenol from 2-methyl-2,3-dihydrobenzofuran (2). In view of the fact that Prey and Pieh² obtained *o*-ethinylphenol from benzofuran with sodium in pyridine it appeared possible that ring-cleavage, without reduction, of 2,3-dihydrobenzofuran and chroman derivatives could also be achieved by this reagent.

The following compounds were tested with the sodium/pyridine-reagent: 2,3-dihydrobenzofuran (1), 2-methyl- (2), 2-benzyl- (3), 3-methyl- (4), 2,2-dimethyl- (5), and 3,3-dimethyl-2,3-dihydrobenzofuran (6), 1,2,3,4,4a,9b-



- | | | | | | |
|---|---|---|--|---|--------------|
| 1 | $R^1 = R^2 = R^3 = R^4 = H$ | 7 | | 8 | $R = H$ |
| 2 | $R^1 = CH_3; R^2 = R^3 = R^4 = H$ | | | 9 | $R = C_6H_5$ |
| 3 | $R^1 = C_6H_5CH_2; R^2 = R^3 = R^4 = H$ | | | | |
| 4 | $R^3 = CH_3; R^1 = R^2 = R^4 = H$ | | | | |
| 5 | $R^1 = R^2 = CH_3; R^3 = R^4 = H$ | | | | |
| 6 | $R^3 = R^4 = CH_3; R^1 = R^2 = H$ | | | | |

hexahydrodibenzofuran (7), chroman (8), and flavan (9). For comparison benzofuran (studied already by Prey and Pieh²), dibenzofuran, and 1,2,3,4-tetrahydrodibenzofuran were also tested.

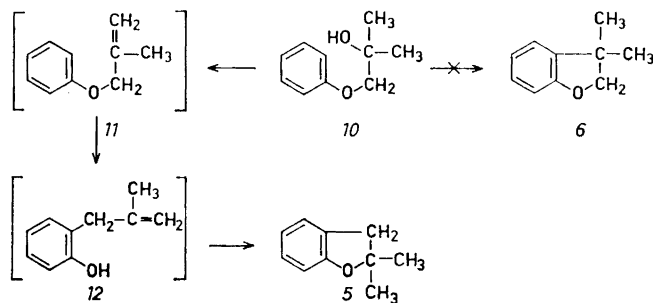
Of these compounds all except 4 and 6 are well established and were prepared by methods given in the literature, as indicated in the experimental part.

Niederl and Storch⁵ have reported the preparation of 3-methyl- and 3-benzyl-2,3-dihydrobenzofuran from the condensation of allyl alcohol and cinnamyl alcohol, respectively, with phenol and the cresols in the presence of conc. sulphuric acid. However, repetition of the condensation of phenol with allyl alcohol and cinnamyl alcohol as described by Niederl and Storch⁵ gave definitely 2-methyl- and 2-benzyl-2,3-dihydrobenzofuran, respectively. It is thus very probable that all the compounds described by Niederl and Storch⁵ are the corresponding 2-substituted 2,3-dihydrobenzofurans and not the 3-substituted as alleged by them. This is also supported by the fact that an attempt to prepare 3,3-dimethyl-2,3-dihydrobenzofuran (6) from phenol and β -methylallyl alcohol in the same way, gave 2,2-dimethyl-2,3-dihydrobenzofuran (5).

3-Methyl-2,3-dihydrobenzofuran (4) was synthesised by treatment of *o*-isopropenylphenyl acetate with hydrobromic acid in the presence of benzoyl peroxide, followed by hydrolysis with alkali, a method analogous to that used by Hurd and Hoffman⁶ for the synthesis of chroman from *o*-allylphenol.

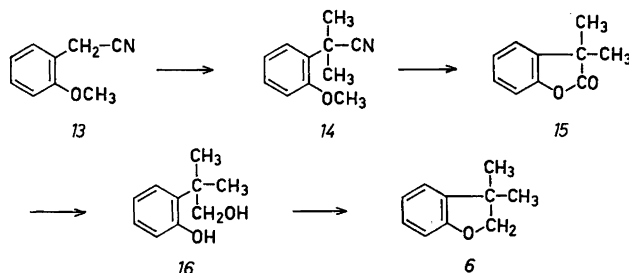
3,3-Dimethyl-2,3-dihydrobenzofuran (6) has been reported as the product from solvolysis of *o*-methoxyneophyl *p*-toluenesulphonate,⁷ but no proof of its structure was given; and the reaction did not appear very attractive as a preparative method.

In an attempt to synthesise 6 by the method of Rindfusz,⁸ 2-methyl-1-phenoxy-2-propanol (10) was treated with zinc chloride. The product of the reaction was, however, 5. The reaction can be visualized as occurring through the intermediates 11 and 12.



6 was finally prepared by the following sequence of reactions (see p. 1563).

An attempt to convert 15 directly into 6 by the method of Pettit and Piatak⁹ failed. The ring closure of 16 into 6 was, however, easily achieved by the method of Guss and Jules.¹⁰ The physical properties of 6 were in good agreement with those given by Heck *et al.*⁷



The structure of the methyl substituted 2,3-dihydrobenzofurans was confirmed by their NMR-spectra. The chemical shifts of the hydrogen atoms of the dihydrofuran ring and the attached methyl groups are given in Table 1. All compounds have in addition complex absorption at τ 2.8–3.5 due to the aromatic hydrogen atoms.

Table 1.

	2-H	3-H	2-Me	3-Me
1	5.60 (t)	6.93 (t)	—	—
2	5.20 (m)	6.85 } (m)	8.63 (d)	—
		7.33 }		
4	5.42 } (m)	6.56 (m)	—	8.73 (d)
	6.02 }			
5 ^a	—	7.11 (s)	8.60 (s)	—
6	5.88 (s)	—	—	8.70 (s)

^a Shulgin and Baker¹¹ report 7.12 and 8.62

In 2,3-dihydrobenzofuran (1) the four hydrogen atoms at the carbon atoms 2 and 3 form an A_2X_2 -system in which $J_{AX} = J_{AX'} = 8.5$ cps, thus forming two triplets.¹² In 2-methyl- and 3-methyl-2,3-dihydrobenzofuran the three hydrogen atoms of the dihydrofuran ring form an ABX-system, in which the X-part is further split by the hydrogen atoms of the methyl groups. This part of the spectra is reproduced in Figs. 1 and 2, respectively. Analysis of the AB-part according to the graphical method given by Bible¹³ gave the following parameters for the two systems:

	$\Delta\nu$ AB	J_{AB}	J_{AX}	J_{BX}
2-Methyl-2,3-dihydrobenzofuran (2)	29	15.4	8.6	7.6 cps
3-Methyl-2,3-dihydrobenzofuran (4)	36	8.4	8.8	7.2 cps

In Figs. 1 and 2 are also included the theoretical spectra¹⁴ obtained by using these parameters and for the secondary splitting of the X-part the values 6.4 cps for 2 and 6.6 for 3, obtained from the splitting of the methyl signals. In the case of 3 the spectrum is not strictly of an ABX-type because of the small difference between the X-part and one of the hydrogens of the AB-part, but approaches an ABC-type. This is also evident from the rather great deviation of the intensities from the theoretical values.

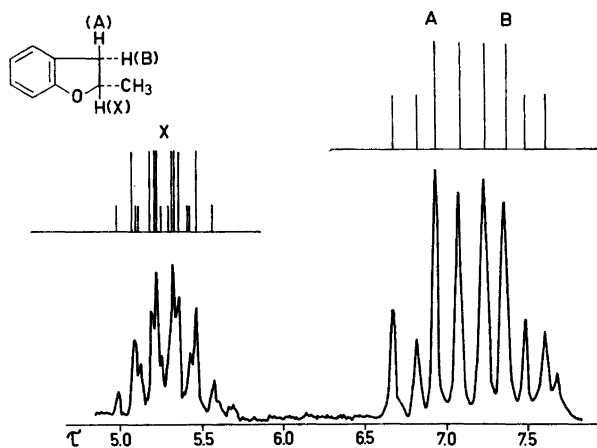


Fig. 1. Part of the NMR-spectrum of 2-methyl-2,3-dihydrobenzofuran.

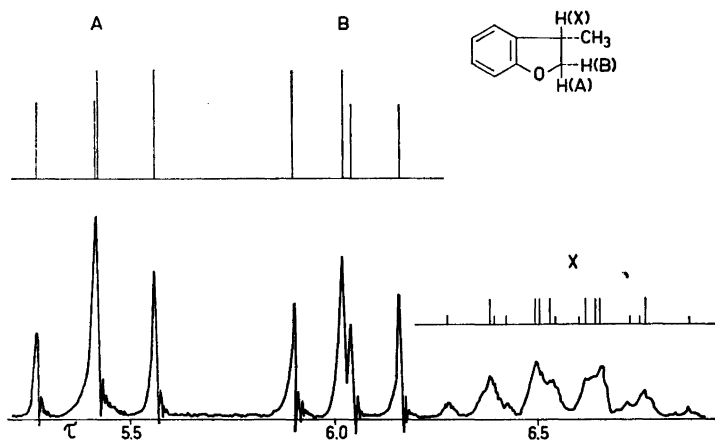


Fig. 2. Part of the NMR-spectrum of 3-methyl-2,3-dihydrobenzofuran.

All the values, both with regard to the chemical shifts and coupling constants, are in good agreement with values reported for similarly substituted 2,3-dihydrobenzofuran-systems,¹⁵⁻²¹ except that there appears to be no value reported in the literature for the geminal coupling constant of the pair of hydrogen atoms at position 2. The much lower absolute value of this geminal coupling constant than the constant for the 3-hydrogen atoms is, however, in agreement with the coupling constant found for a CH_2 -group adjacent to an oxygen atom in other oxygen-cyclic systems.²²⁻²⁴

The result of the treatment of the compounds with the sodium/pyridine-reagent is contained in Table 2.

Table 2.

Cyclic ether	Resulting phenol	Yield %	Unreacted starting material
2,3-Dihydrobenzofuran (1)	<i>o</i> -Vinylphenol	41	—
2-Methyl-2,3-dihydrobenzofuran (2)	<i>o</i> -Propenylphenol	53	—
2-Benzyl-2,3-dihydrobenzofuran (3)	<i>o</i> -(3-Phenylpropenyl)-phenol	69	—
3-Methyl-2,3-dihydrobenzofuran (4)	<i>o</i> -Isopropenylphenol	47	—
2,2-Dimethyl-2,3-dihydrobenzofuran (5)	<i>o</i> -Isobutenylphenol	92	—
3,3-Dimethyl-2,3-dihydrobenzofuran (6)	—	—	90
1,2,3,4,4a,9b-Hexahydrodibenzofuran (7)	<i>o</i> -(1-Cyclohexenyl)-phenol	14	69
Chroman (8)	<i>o</i> -Propenylphenol	10	63
Flavan (9)	<i>o</i> -(3-Phenylpropyl)-phenol	71	—
Benzofuran	<i>o</i> -Ethinylphenol	83	—
Dibenzofuran	<i>o</i> -Hydroxybiphenyl	9	6
1,2,3,4-Tetrahydrodibenzofuran	Not identified	3	64

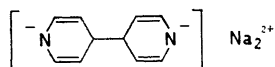
The products obtained were identified by comparison with authentic samples obtained as described in the experimental part. Only the phenol formed from 2-benzyl-2,3-dihydrobenzofuran (3) caused some trouble. The phenol was a liquid with UV-maxima at 252 $m\mu$ ($\log \epsilon$ 4.00), 283 $m\mu$ ($\log \epsilon$ 3.45) and 313 $m\mu$ ($\log \epsilon$ 3.51). The expected product of the reaction would be *o*-(3-phenylpropenyl)phenol. This compound has been described by Bokadia *et al.*²⁵ They reported that the substance has an UV-maximum at 254 $m\mu$ ($\log \epsilon$ 4.43). However, compounds with the *o*-vinylphenol-chromophore usually have two maxima at 240–255 $m\mu$ ($\log \epsilon$ 3.8–4.1) and at 280–305 $m\mu$ ($\log \epsilon$ 3.3–3.7), respectively (this work and Refs. 26–28). The product we obtain in a repetition of the procedure of Bokadia *et al.*²⁵ was evidently a mixture from which no pure compound could be obtained, but its UV-spectrum (with no significant absorption above 270 $m\mu$), as well as its IR-spectrum were very close to those of *o*-cinnamylphenol. It thus appears somewhat doubtful, whether Bokadia *et al.*²⁵ ever have had *o*-(3-phenylpropenyl)phenol in their hands. An attempt was also made to obtain *o*-(3-phenylpropenyl)phenol by alkali-isomerization of *o*-cinnamylphenol, but this procedure gave a product which was very similar to that obtained by the procedure of Bokadia *et al.* Although we thus have been unable to procure an authentic sample of *o*-(3-phenylpropenyl)phenol, we believe that our product from the treatment of 3 with sodium and pyridine is this compound, in view of its UV-spectrum, which corresponds well with that of other *o*-vinylphenols; also its formation is in agreement with this structure.

From an inspection of the results reported in Table 2 it is evident that the sodium/pyridine-reagent opens the heterocyclic ring in 2,3-dihydrobenzofuran derivatives giving the corresponding *o*-vinylphenol derivatives, with the exception of 3,3-dimethyl-2,3-dihydrobenzofuran (6), which of course cannot give an unsaturated phenol. Somewhat surprising is the much lower yield with 7 than with the alkyl substituted 2,3-dihydrobenzofuran derivatives.

The chroman ring on the other hand is opened much more difficultly, except when it has a phenyl group in the 2-position. However, in this case the reaction product is the corresponding saturated phenol.

With benzofuran the result is the same as that reported by Prey and Pieh.² Dibenzofuran and 1,2,3,4-tetrahydrodibenzofuran, in which a ring opening without reduction cannot occur, gave only very low yields of phenols.

According to Emmert²⁹ the compound formed when sodium reacts with pyridine is to be formulated as the disodium salt of tetrahydro- γ , γ -bipyridyl (17) (contaminated with some of the corresponding α,α -derivative).



17

Opening of the dihydrofuran ring with β -elimination under the influence of this base, as proposed by Hurd and Oliver⁴ would thus appear as a reasonable mechanism for the reaction. The possibility that metallic sodium is the actual reagent could, however, not be completely ruled out — since a certain amount of sodium was always present in the reaction mixture.

In order to decide between these two alternatives an experiment was carried out with 2 under otherwise identical conditions, but using such a great excess of pyridine that no sodium was present. However, the result was not quite conclusive in that *o*-propenylphenol was formed, but in a yield of only 10 %, whereas 80 % unreacted starting material was recovered. Although it is thus evident that the reaction does occur in the absence of metallic sodium, the much lower yield remains to be explained.

It appears possible that the method described above might have some merits in the structure determination of compounds containing the 2,3-dihydrobenzofuran moiety. Its use in the degradation of lignin can also be foreseen.

EXPERIMENTAL

The UV-spectra were measured for ethanol solutions on a Beckman DK-2 instrument. The IR-spectra were recorded on a Perkin-Elmer 125 instrument for molecular films (liquid compounds) or KBr-discs (crystalline compounds). Spectral data for known compounds are included only when they have not been reported before or differ significantly from those given in the literature. NMR-spectra were obtained from carbon tetrachloride solutions on a Varian A-60 instrument using tetramethylsilane as internal standard. The microanalyses have been performed by Dr. A. Bernhardt, Mülheim, Germany.

Preparation of starting materials

2,3-Dihydrobenzofuran (1) was prepared by the method of Chatelus and Cagniant,³⁰ b.p. 82–83°/19 mm.

2-Methyl-2,3-dihydrobenzofuran (2) was prepared by the method of Entel *et al.*,³¹ b.p. 85°/19 mm. UV-spectrum: λ_{\max} 225sh(3.64), 278(3.37), 281.5(3.37), 287.5(3.26) $m\mu$ (log ϵ); λ_{\min} 243(2.59), 286.5(3.28) $m\mu$ (log ϵ). This compound was also obtained, in a yield of 11 %, when phenol was treated with allyl alcohol as described by Niederl and Storch.⁵

2-Benzyl-2,3-dihydrobenzofuran (3) was prepared by the method of Stoermer *et al.*,³² b.p. 141–142°/0.6 mm. UV-spectrum: λ_{\max} 248(4.20), 268.5(3.43), 270sh(3.43), 273(3.42), 276.5(3.55), 283.5(3.57), 310sh(2.09) $m\mu$ (log ϵ); λ_{\min} 228(3.77), 266(3.42), 272(3.41), 273.5(3.41), 280.5(3.15) $m\mu$ (log ϵ). Main IR-maxima: 1452, 1252, 957, 754, 707 cm^{-1} . The same compound was formed, in a yield of 16 %, when phenol was treated with cinnamyl alcohol according to Niederl and Storch.⁵

3-Methyl-2,3-dihydrobenzofuran (4), Gaseous hydrobromic acid was introduced for 45 min into a solution of *o*-isopropenylphenyl acetate (10 g) and benzoyl peroxide (1 g) in carbon tetrachloride kept at 0°. The solvent was removed and the residue was dissolved in ether. The ethereal solution was washed twice with dilute sodium hydroxide, the ether evaporated and the residue refluxed with a solution of potassium hydroxide (2 g) in dilute (2:1) ethanol (75 ml). The mixture was extracted with ether, and the residue remaining after evaporation of the ether was distilled under vacuum, b.p. 86–87°/16 mm. Yield 5 g (66 %). (Found: C 80.67; H 7.26. $C_9H_{10}O$ requires C 80.51; H 7.46). UV-spectrum: λ_{\max} 226sh(3.65), 276(3.41), 282(3.43), 287sh(3.26) $m\mu$ (log ϵ); λ_{\min} 239(3.29), 279.5(3.38) $m\mu$ (log ϵ). Main IR-maxima: 2956, 1595, 1480, 1461, 1452, 1226, 966, 835, 749 cm^{-1} .

2,2-Dimethyl-2,3-dihydrobenzofuran (5). This was prepared by the method of Shulgin and Baker;¹¹ b.p. 79–81°/14 mm. UV-spectrum: λ_{\max} 226sh(3.70), 251sh(2.95), 272sh(3.33), 280(3.46), 283sh(3.45), 287sh(3.38) $m\mu$ (log ϵ); λ_{\min} 242.5(2.85) $m\mu$ (log ϵ). Main IR-maxima: 2972, 1590, 1477, 1458, 1368, 1259, 1221, 1138, 872, 753 cm^{-1} . The same compound was formed, in a yield of 10 %, when phenol was treated with β -methylallyl alcohol according to Niederl and Storch.⁵ It was also formed when 2-methyl-1-phenoxy-2-propanol (see below) was heated with zinc chloride (*cf.* Ref. 8). The yield in this case was 21 %.

2-Methyl-1-phenoxy-2-propanol (10). Phenol was refluxed with an equivalent amount of 1-chloro-2-methyl-2-propanol in 10 % sodium hydroxide solution for 3 h. The mixture was extracted with ether and the residue from the ethereal solution was distilled under vacuum, b.p. 115–116°/13 mm (Lit.³³ b.p. 125–125.5/20 mm). Yield 71 %. (Found: C 72.07; H 8.60. $C_{10}H_{14}O_2$ requires C 72.26; H 8.49). Main IR-maxima: 3405, 2971, 2922, 1596, 1583, 1496, 1489, 1463, 1453, 1384, 1362, 1298, 1285, 1240, 1225, 1169, 1150, 1074, 1042, 918, 752, 691 cm^{-1} .

*2-Methyl-2-(*o*-methoxyphenyl)propionitrile (14)*. *o*-Methoxyphenylacetoneitrile (66 g) dissolved in dry ether (300 ml) was slowly added to a stirred and cooled suspension of sodium amide (36 g) in dry ether (300 ml). Methyl iodide (130 g) dissolved in dry ether (300 ml) was then added and the mixture refluxed for 6 h. Water: methanol (1:1) (250 ml) and thereafter water (250 ml) were carefully added and the ether layer separated. This was washed with sodium hydrogen sulphite, sodium carbonate, and water and dried. The residue was distilled under vacuum, b.p. 121–122°/0.3 mm. Yield 33 g (42 %). (Found: C 75.31; H 7.61; N 8.02. $C_{11}H_{13}NO$ requires C 75.40; H 7.48; N 7.99). Main IR-maxima: 2980, 2939, 2233, 1599, 1490, 1459, 1451, 1434, 1289, 1248, 1089, 1024, 751 cm^{-1} .

3,3-Dimethyl-2,3-dihydrobenzofuran-2-one (15). 2-Methyl-2-(*o*-methoxyphenyl) propionitrile (31.5 g) was dissolved in acetic acid (100 ml) and 63 % hydrobromic acid (100 ml) was added and the mixture refluxed for 17 h. Water (200 ml) was then added and the product taken up in ether. After washing with sodium hydroxide and water, the ether was removed and the residue distilled under vacuum, b.p. 101–102°/2 mm. Yield 23.8 g (82 %). (Found: C 74.32; H 6.41. $C_{10}H_{10}O_2$ requires C 74.05; H 6.22). UV-spectrum: λ_{\max} 225sh(2.59), 262sh(2.01), 269(2.13), 276(2.10), 322(1.95) $m\mu$ (log ϵ); λ_{\min} 250(1.76), 273(1.98), 292(1.86) $m\mu$ (log ϵ). Main IR-maxima: 2971, 1802, 1618, 1478, 1463, 1458, 1289, 1230, 1185, 1118, 1103, 1032, 935, 875, 753 cm^{-1} . NMR-spectrum: τ 2.85(4 H) unresolved multiplet, 8.55(6 H) singlet.

2-Methyl-2-(o-hydroxyphenyl)propanol (16). 3,3-Dimethyl-2,3-dihydrobenzofuran-2-one (21 g) dissolved in ether was added while stirring to a suspension of lithium aluminium hydride (1.5 g) in ether. After refluxing for 1 h dilute hydrochloric acid (50 ml) and then water (400 ml) were carefully added. Evaporation of the ether from the ethereal layer and recrystallisation of the residue from dilute ethanol gave 19.8 g (92 %) of 2-methyl-2-(o-hydroxyphenyl)propanol, m.p. 90–91°. (Found: C 72.20; H 8.41. $C_{10}H_{14}O_2$ requires C 72.26; H 8.49). Main IR-maxima: 3540, 3420, 1446, 1228, 1026, 1010, 760 cm^{-1} .

3,3-Dimethyl-2,3-dihydrobenzofuran (6). 2-Methyl-2-(o-hydroxyphenyl) propanol (19.2 g), phthalic anhydride (33 g), and pyridine (35 ml) were dissolved in dioxane (200 ml). The mixture was kept at room temperature for 48 h, after which ether (450 ml) was added. The solution was washed with dilute hydrochloric acid and water and then extracted with 4 portions (200 ml) of 4 % sodium hydrogen carbonate. The combined extracts together with the precipitate, that formed during the extraction, were refluxed for 1 h after addition of 5 % sodium hydroxide (250 ml). To the cooled solution was added sodium hydroxide (50 g) and the solution extracted with ether. Removal of the ether and distillation of the residue under vacuum gave 3,3-dimethyl-2,3-dihydrobenzofuran (14.4 g; 84 %) of b.p. 94°/27 mm. (Found: C 81.24; H 8.12. $C_{10}H_{14}O$ requires C 81.04; H 8.16). UV-spectrum: λ_{max} 224(3.71), 279(3.50), 285(3.43) $m\mu$ (log ϵ); λ_{min} 220(3.70), 243(2.03), 284(3.42) $m\mu$ (log ϵ). Main IR-maxima: 2959, 1609, 1597, 1478, 1451, 1282, 1240, 1189, 1012, 983, 828, 749, 741 cm^{-1} .

1,2,3,4,4a,9b-Hexahydrodibenzofuran (7) was prepared by the method of Viktorova *et al.*,³⁴ b.p. 125–127°/14 mm. UV-spectrum: λ_{max} 267sh(3.15), 274(3.32), 279.5(3.35), 285sh(3.20) $m\mu$ (log ϵ); λ_{min} 244(2.42), 276(3.31) $m\mu$ (log ϵ). Main IR-maxima: 2941, 1593, 1489, 1470, 1454, 1237, 1224, 1049, 945, 749, 693 cm^{-1} .

Chroman (8). This compound was prepared both according to Maitte³⁵ and according to Hurd and Hoffman,⁶ both methods giving approximately equal results. B.p. 97–98°/19 mm. UV-spectrum: λ_{max} 273sh(3.37), 277(3.39), 283(3.33) $m\mu$ (log ϵ); λ_{min} 244(2.41), 284(3.27) $m\mu$ (log ϵ). Main IR-maxima: 1493, 1274, 1236, 1074, 764 cm^{-1} .

Flavan (9) was prepared by the method of Hultzsch,³⁶ b.p. 144–147°/0.5 mm, m.p. 45°. UV-spectrum: λ_{max} 227sh(3.82), 245sh(3.52), 274(3.21), 282.5(3.18) $m\mu$ (log ϵ); λ_{min} 271(3.19), 280(3.09) $m\mu$ (log ϵ). Main IR-maxima: 1493, 1457, 1240, 764, 710 cm^{-1} .

1,2,3,4-Tetrahydrobenzofuran was prepared by the method of of Ebel.³⁷ b.p. 147–148°/16 mm. UV-spectrum: λ_{max} 248sh(4.13), 251.5(4.17), 258sh(4.10), 272sh(3.67), 278.5(3.91), 285.5(3.67) $m\mu$ (log ϵ); λ_{min} 230(3.60), 275(3.61), 282.5(3.35) $m\mu$ (log ϵ). Main IR-maxima: 2929, 1453, 1300, 1279, 1260, 1226, 1194, 1126, 881, 747 cm^{-1} .

General procedure for the reaction with sodium/pyridine

About 10–20 mmoles of the appropriate compound were dissolved in dry pyridine (10 ml). Sodium (3 g) was introduced and the mixture was refluxed for 4 h in a stream of nitrogen. After cooling more pyridine (20 ml) and thereafter pyridine:water (3:1) (50 ml) were added. The solution was extracted with light petroleum (b.p. 40–60°) (3 × 50 ml). After acidification with dilute sulphuric acid it was extracted with ether (2 × 50 ml) and the ether solution extracted with Claisen-alkali (2 × 50 ml). The light petroleum and ether extracts were combined, washed with dilute sulphuric acid and water and dried. Evaporation of the solvent and distillation of the residue gave unreacted starting material. The Claisen-alkali-extract was acidified and extracted with ether (3 × 50 ml). From the ether extract the phenol was obtained by distillation in vacuum and identified by a comparison of its IR-spectrum with that of authentic samples, except in the case of 2-benzyl-2,3-dihydrobenzofuran.

o-(3-Phenylpropenyl)phenol. The pheno obtained from 2-benzyl-2,3-dihydrobenzofuran (3) as described above could not be successfully distilled, but was purified by chromatography on aluminium oxide using benzene:light petroleum (2:1) as eluent. UV-spectrum: λ_{max} 252(4.00), 256sh(3.99), 264sh(3.85), 268sh(3.66), 283(3.45), 294sh(3.49), 313(3.51), 318sh(3.26) $m\mu$ (log ϵ); λ_{min} 235(3.83), 276.5(3.41), 288(3.43) $m\mu$ (log ϵ).

Preparation of reference phenols

o-Vinylphenol was prepared by the method of Fries and Fickewirth,³⁸ b.p. 106°/18 mm. UV-spectrum: λ_{\max} 245(3.85), 249sh(3.85), 274sh(3.23), 283(3.33), 294sh(3.42), 303(3.46), 318sh(3.14) $m\mu$ (log ϵ); λ_{\min} 233.5(3.70), 268.5(3.13), 286.5(3.32) $m\mu$ (log ϵ). Main IR-maxima: 3520, 3410, 1621, 1598, 1577, 1492, 1485, 1479, 1446, 1338, 1322, 1290, 1227, 1179, 1091, 995, 912, 840, 760, 749 cm^{-1} .

o-Isopropenylphenol was prepared by the method of Wiberg and Rowland,³⁹ b.p. 90–92°/18 mm. UV-spectrum: λ_{\max} 237sh(3.59), 280(3.36), 305sh(2.98) $m\mu$ (log ϵ); λ_{\min} 262(3.05) $m\mu$ (log ϵ). Main IR-maxima: 3500, 3370, 1581, 1483, 1440, 1231, 1188, 833, 750 cm^{-1} .

o-Isobutenylphenol was prepared according to Bartz *et al.*,⁴⁰ b.p. 98°/20 mm. Main IR-maxima: 3500, 3430, 1485, 1452, 1449, 1219, 1174, 754 cm^{-1} .

o-(3-Phenylpropyl)phenol. *o*-Cinnamylphenol was hydrogenated with a Raney-nickel catalyst at 75° and 90 atm. for 4 h. Yield of product 12%, b.p. 141°/0.5 mm (Lit.¹⁴ b.p. 133–135°/0.3 mm). UV-spectrum: λ_{\max} 228sh(3.54), 268sh(3.18), 274(3.25), 283sh(3.19) $m\mu$ (log ϵ); λ_{\min} 245(2.82) $m\mu$ (log ϵ). Main IR-maxima: 3535, 3400, 2923, 1490, 1450, 750, 699 cm^{-1} .

o-(1-Cyclohexenyl)phenol. 2-Cyclohexenyl phenyl ether⁴² (37 g) was refluxed for 5 h in *N,N*-dimethylaniline (37 g). Extraction with Claisen-alkali gave *o*-(2-cyclohexenyl)phenol (23.5 g), b.p. 95–105°/0.5 mm. This was treated with potassium hydroxide according to Viktorova *et al.*³⁴ giving *o*-(1-cyclohexenyl)phenol, b.p. 93–96°/0.6 mm. The distillate solidified and was recrystallised from light petroleum, m.p. 36°. Viktorova *et al.*³⁴ give b.p. 139–145°/17 mm; m.p. 89–91° for their product. The difference in m.p. is regarded as due to dimorphism. UV-spectrum: λ_{\max} 239sh(3.76), 275sh(3.39), 281(3.45) $m\mu$ (log ϵ); λ_{\min} 263(3.14) $m\mu$ (log ϵ). Main IR-maxima: 3505, 2930, 2850, 1482, 1443, 1277, 1219, 1187, 1150, 815, 751 cm^{-1} . NMR-spectrum: τ 2.8–3.3 (4 H) complex absorption, 4.2 (1 H) broad, 4.70 (1 H) singlet, 7.75 (4 H) unresolved multiplet, 8.22 (4 H) unresolved multiplet.

This investigation has been supported by a grant from the *Finnish Research Council for Technical Sciences* (Valtion Teknillis-Tieteellinen Toimikunta). One of the authors (T.H.) also wishes to thank the governors of *Alfred Kordelinin säätiö* and *Emil Aaltosen säätiö* for supporting grants, as well as the Head of the Institute of Technology for a grant from the funds for younger scientists appropriated to this Institute.

REFERENCES

1. Prey, V. *Ber.* **76** (1943) 156.
2. Prey, V. and Pieh, G. *Monatsh.* **80** (1949) 790.
3. Freudenberg, K., Lautsch, W. and Piazzolo, G. *Ber.* **74** (1941) 1879.
4. Hurd, C. D. and Oliver, G. L. *J. Am. Chem. Soc.* **81** (1959) 2795.
5. Niederl, J. B. and Storch, E. A. *J. Am. Chem. Soc.* **55** (1933) 4549.
6. Hurd, C. D. and Hoffman, W. A. *J. Org. Chem.* **5** (1940) 212.
7. Heck, R., Corse, J., Grunwald, E. and Winstein, S. *J. Am. Chem. Soc.* **79** (1957) 3278.
8. Rindfusz, R. E. *J. Am. Chem. Soc.* **41** (1919) 665.
9. Pettit, G. R. and Piatak, D. M. *J. Org. Chem.* **27** (1962) 2127.
10. Guss, C. O. and Jules, L. H. *J. Am. Chem. Soc.* **72** (1950) 3462.
11. Shulgin, A. T. and Baker, A. W. *J. Org. Chem.* **28** (1963) 2468.
12. Jackman, L. M. *Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry*, Pergamon 1959, p. 93.
13. Bible, Jr., R. H. *Interpretation of NMR Spectra*, Plenum Press 1965, p. 89.
14. Pople, J. A., Schneider, W. G. and Bernstein, H. J. *High Resolution Nuclear Magnetic Resonance*, McGraw 1959, p. 134.
15. Goodwin, S., Shoolery, J. N. and Johnson, L. F. *J. Am. Chem. Soc.* **81** (1959) 3065.
16. Kun, K. A. and Cassidy, H. G. *J. Org. Chem.* **27** (1962) 841.
17. Ludwig, C. H., Nist, B. J. and McCarthy, J. L. *J. Am. Chem. Soc.* **86** (1964) 1186.
18. Romo, J. and Joseph-Nathan, P. *Tetrahedron* **20** (1964) 2331.

19. Binsch, G., Huisgen, R. and König, H. *Chem. Ber.* **98** (1965) 2893.
20. Krauch, K. H., Farid, S. and Schenck, G. O. *Chem. Ber.* **98** (1965) 3102.
21. Marini Bettolo, G. B., Casanovi, C. G. and Galeffi, C. *Tetrahedron Letters* **1965** 4857.
22. Grombie, L. and Lown, J. W. *J. Chem. Soc.* **1962** 775.
23. Fraser, R. R., Lemieux, R. U. and Stevens, J. D. *J. Am. Chem. Soc.* **83** (1961) 3901.
24. Pople, J. A. and Bothner-By, A. A. *J. Chem. Phys.* **42** (1965) 1339.
25. Bokadia, M. M., Brown, B. R., Cobern, D., Roberts, A. and Somerfield, G. A. *J. Chem. Soc.* **1962** 1658.
26. Gaertner, R. *J. Am. Chem. Soc.* **73** (1951) 4400.
27. Hurd, C. D. and Dowbenko, R. *J. Am. Chem. Soc.* **82** (1960) 3662.
28. Bader, A. R. *J. Am. Chem. Soc.* **78** (1956) 1709.
29. Emmert, B. *Ber.* **50** (1917) 31.
30. Chatelus, G. and Cagniant, P. *Compt. Rend.* **224** (1947) 1777.
31. Entel, J., Ruof, C. H. and Howard, H. C. *J. Am. Chem. Soc.* **73** (1951) 2365.
32. Stoermer, R., Chydenius, C. W. and Schirm, E. *Ber.* **75** (1924) 72.
33. Petrov, A. A. and Pritula, E. N. *Zh. Prikl. Khim.* **28** (1955) 4003.
34. Viktorova, E. A., Shuikin, N. I. and Polyanskaya, E. J. *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk* **1960** 2048.
35. Maitte, P. *Ann. Chim. (Paris)* [12] **9** (1954) 433.
36. Hultzsch, K. *J. prakt. Chem.* [2] **158** (1941) 275.
37. Ebel, F. *Helv. Chim. Acta* **12** (1929) 3.
38. Fries, K. and Fickewirth, G. *Ber.* **41** (1908) 367.
39. Wiberg, K. B. and Rowland, B. I. *J. Am. Chem. Soc.* **77** (1955) 2206.
40. Bartz, Q. R., Miller, R. F. and Adams, R. *J. Am. Chem. Soc.* **57** (1935) 371.
41. Mozingo, R. and Adkins, H. *J. Am. Chem. Soc.* **60** (1938) 669.
42. Cornforth, J. W., Hughes, G. K. and Lions, F. J. *Proc. Roy. Soc. N. S. Wales* **71** (1938) 323; *Chem. Abstr.* **33** (1939) 148.

Received March 3, 1966.