# CHLORINATION OF PHENOL AND SOME ALKYL- AND ARYL-SUBSTITUTED PHENOLS IN ACETIC ACID FORMATION OF UNSATURATED CHLORINATED CYCLOHEXANONE DERIVATIVES

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Abstract—Exhaustive chlorination of phenol and some substituted phenols in acetic acid yielded chlorinated cyclohexenone derivatives. 3,5-Dimethylphenol gave a chlorinated cyclohexadienone. The structures of these compounds were elucidated mainly by IR, UV and NMR spectroscopy. A simple reaction mechanism is proposed.

#### INTRODUCTION

EXHAUSTIVE chlorination of phenolic substances was extensively investigated between 1880 and 1910 and reviewed in Houben-Weyl.<sup>1</sup> In recent literature, Müller and Linde<sup>2</sup> described the chlorination of 2,5- and 3,5-dimethylphenol; Burgstahler *et al.*,<sup>3</sup> and Moye and Sternhell<sup>4</sup> described the alkaline chlorination of phenol, resulting in ring contraction to 5-membered rings probably by a Favorskii type rearrangement and Denivelle and Fort<sup>5-10</sup> studied the chlorination of pentachlorophenol under various conditions as well as the isomerization of the final products. Their IR and UV data on the two isomeric substances presented in Table 1 have been used in the structural analysis of products in the present investigation in which phenol, 2,6-dimethyl-, 2,6-dimethyl- and 3,5-dimethyl-phenol were chlorinated. The products from 2,6-dimethyl- and 2,6-diphenylphenol are new, while in our opinion the structures assigned to the products from phenol and 2,5-dimethylphenol are incorrect.



# **RESULTS AND DISCUSSION**

# A. IR and UV spectra of chlorinated cyclohexane derivatives

The IR and UV data for the two isomeric cyclohexenone derivatives 1a and 1b (cf. Table 1) have been applied to our cyclohexenone derivatives. The substantial UV absorption of the non-conjugated structure 1a at 236 mµ can be explained by the non-planarity of the  $\beta$ , $\gamma$ -cyclohexanone ring which causes some overlap of the non-bonding p-orbital of the O atoms with the  $\pi$ -orbitals of the double bond, resulting in a bathochromic shift.<sup>11, 12</sup> With regard to the IR data, it is well known that in ketones  $\alpha$ -Cl atoms cause an upward shift of the carbonyl frequency. In  $\alpha$ -halogenated cyclohexanones Eliel gives a shift of 25  $\pm$  7 cm<sup>-1</sup> for an equatorial chlorine and 6  $\pm$  4 cm<sup>-1</sup> for an axial chlorine.<sup>13</sup> Thus, the carbonyl frequencies can be estimated by adding these increments<sup>+</sup> to the frequencies of the reference compounds cyclohexanone (1712 cm<sup>-114</sup>) and  $\Delta$ -2,3-cyclohexanone (1680 cm<sup>-115</sup>). The results, 1774 cm<sup>-1</sup> for 1a and 1736 cm<sup>-1</sup> for 1b (the increment of the unsaturated chlorine in 1b was taken equal to that of an equatorial atom), are in good agreement with the experimental values (cf. Table 1).

## B. Structure analysis of chlorinated phenol derivatives

Phenol. The chlorinations were carried out at 25° and 90°. The first product formed, 2,4,6-trichlorophenol, was slowly converted to other products. At a reaction temperature of 25° a slighly impure product 2 was obtained which was suitable for spectroscopic analysis. The IR carbonyl absorption at  $1780 \text{ cm}^{-1}$  is at exactly the same frequency as found by Denivelle and Fort for 1a. Therefore it seems justified to assume that in compound 2 two Cl atoms are both in  $\alpha$ -position. As explained a calculated frequency of 1778 cm<sup>-1</sup> is obtained on a value of 1716 cm<sup>-1</sup> for the carbonyl band of cyclohexanone as measured on our own apparatus. Structure 1b was ruled out on account of the low wavelength UV absorption maximum at 209 mµ (cf. Table 1 and 2). The NMR spectrum reveals the presence of 2 different and weakly coupled protons (cf. Table 3), the chemical shifts and coupling constants of which are in accord with structure 2. Further evidence comes from the position of the C-C double bond absorption in the IR spectrum. Compounds 2, 5, and 6 which have monochlorinated double bonds, all show absorptions at higher frequencies (ca. 1645  $\text{cm}^{-1}$  cf. Table 2) than the products 3 and 4 having dichlorinated double bonds (ca. 1620 cm<sup>-1</sup>). This is in accord with the observation of Jones and Sandorfy that ethylenic Cl atoms tend to lower the double bond stretching frequency.<sup>17</sup>

The chlorination of phenol at 90° yielded a crystalline product 3, which differs from 2 in having only one hydrogen atom, as shown by elemental analysis (cf. Table 4) and quantitative proton determination by NMR (cf. Table 3). The NMR also shows it to be a chloromethine proton. The IR spectrum shows the presence of a double bond and a non-conjugated carbonyl group, which is corroborated by the UV spectrum. The calculated carbonyl frequency of 1778 cm<sup>-1</sup> (two equatorial and two axial Cl atoms) compares well with the experimental value of 1776 cm<sup>-1</sup>. Therefore, structure 3

<sup>&</sup>lt;sup>†</sup> In cyclohexene derivatives the bonds at the C atoms adjacent to those of the double bond are somewhat differently disposed than in cyclohexane and therefore called pseudoaxial and pseudoequatorial.<sup>16</sup> The deviations of the increments due to a pseudoaxial or pseudoequatorial chlorine are thought to be small in comparison to the variations in the increments themselves. For convenience the prefix "pseudo" will be omitted.

has been assigned to this compound, although a structure with the chloromethine hydrogen in axial position on one of the  $\alpha$ -C atoms can not be excluded (calculated carbonyl frequency in this case 1772 cm<sup>-1</sup>).

2,6-Dimethylphenol. The chlorination at room temperature in acetic acid or carbon tetrachloride or nitromethane gave a crystalline product with composition  $C_8H_7Cl_5O$ . The NMR spectrum exhibits non-coupled signals for one chloromethine proton and two dissimilar Me groups (cf. Table 3). The UV absorption maximum at 227 mµ and the IR carbonyl absorption at 1746 cm<sup>-1</sup> virtually exclude the presence of a carbonyl group conjugated to a double bond as in :



For this compound UV and IR carbonyl absorption maxima of 250 mµ<sup>+</sup> and 1705 cm<sup>-1</sup> were calculated. Agreement with the spectral data is obtained by structure 4 with one equatorial and one axial chlorine in  $\alpha$ -positions and a calculated carbonyl frequency of 1747 cm<sup>-1</sup>. Reduction of 4 with LAH gave 2,6-dimethyl-3,4,5-trichlorophenol, indicating aromatization with loss of 2 Cl atoms. By carrying out this reduction at 0° a different and sharply melting product of unidentified structure was obtained. On the other hand, reduction with zinc and acetic acid, or, hydrogenation with Pd/C, yielded 2,6-dimethyl-3,4-dichlorophenol. Dehalogenation of 4 with sodium in liquid ammonia regenerated the parent compound, 2,6-dimethylphenol, involving a loss of five Cl atoms!

2,6-Diphenylphenol. The chlorination gave a crystalline compound of composition  $C_{18}H_{12}Cl_4O$ . The NMR spectrum in addition to ten aromatic protons of the two phenyl substituents, indicates one chloromethine and one vinylic proton, weakly coupled to each other as found for compound 2. The IR spectrum indicates a nonconjugated carbonyl group and a double bond with one Cl atom. Structure 5 is in accord with these observations. The experimental carbonyl frequency of 1758  $cm^{-1}$  lies between the calculated values of 1766  $cm^{-1}$  (two equatorial Cl atoms) and 1747 cm<sup>-1</sup> (one axial and one equatorial Cl atom). Therefore, on this basis a choice is impossible. The equatorial-equatorial chlorine arrangement is improbable because of steric strain due to the two axial phenyl groups. The equatorial-axial arrangement is supported by the UV spectrum. The n- $\pi^*$  transition has a much higher molar extinction coefficient as compared with those of compounds 4 and 6 (cf. Table 2). The corresponding molar extinction coefficient of trans-2,6-diphenylcyclohexanone (220 l. mol<sup>-1</sup>  $\cdot$  cn<sup>-1</sup>) is also much higher than that of the *cis*-isomer (44 l. mol<sup>-1</sup> · cm<sup>-1</sup>).<sup>19</sup> It follows that compound 5 probably has the trans-configuration, i.e. the two  $\alpha$ -Cl atoms are in the equatorial-axial position.

2,5-Dimethylphenol. The chlorination gave a crystalline compound with composition  $C_8H_7Cl_5O$ . The IR spectrum indicates a monochlorinated double bond and a nonconjugated carbonyl group, the latter being corroborated by the UV spectrum. The

<sup>†</sup> Calculated according to the "rules of Woodward".18

	n cm <sup>- 1</sup>	၂		1644	1616	1623
	IR, vii	Ŷ		1780	1776	1746
24		velength on (n-π*)	МеОН	u.		305 (23-2)
E DERIVATIVE	and s <sup>6</sup>	Long wa absorpti	i-Octane	•	•	307 (22-1)
YCLOHEXANON	UV, J	velength ption	МеОН	•	•	227 (7972)
HLORINATED C		Short wa absor	i-Octane	209 (9770)	228 (8614)	227 (7924)
OME UNSATURATED C		Structural formula				
TABLE 2. UV AND IR DATA OF S		Product		<pre>2 = 2,2,4,5,6,6-hexachloro-3-cyclohexen- 1-one</pre>	<b>3</b> = 2,2,3,4,5,6,6-heptachloro-3- cyclohexen-1-one	4 = 2,3,4,5,6-pentachloro-2,6-dimethyl-3- cyclohexen-1-one
		Parent phenol		₹-	δ-	H, C,

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- · Further characteristic IR absorptions are given in the Experimental.
  - <sup>h</sup>  $\lambda$  in mpt,  $\varepsilon$  (in parentheses) in 1.mol<sup>-1</sup>. cm<sup>-1</sup>.
    - ' Not measured.
- " Absorption peak not measured due to overlap with other band.
- · In MeOH the absorption peak changed with time, while a new peak appeared at 214 mp. Probably a reaction occurred with MeOH.
  - / Absorption peak below 210 mµ.

Compound	Solvent	Vinylic protons	Chloromethine protons	Methyl protons or phenyl protons
2	CCI.	6.46, (d) $J = 1.5$ , 1H	4.92, (d) $J = 1.5$ , 1H <sup>b</sup>	
3	CDCl <sub>3</sub>		5.13	
4	CDCl,		4·83, (s), 1H	2·12, (s), 3H. 1·94, (s), 3H.
5	CDCl <sub>3</sub>	6.30, (d) $J = 1.5$ , 1H	5.38, (d) $J = 1.5$ , 1H	6.67-7.25, (m), 10H
6	CDCl <sub>3</sub>		4·77, (m) <sup>4</sup> , 1H	2.28, (d) $J = 0.4$ , $3H^{d}$ . 1.93, $3H^{d}$
7	CCl <sub>4</sub>			2.50

TABLE 3. NMR DATA OF SOME UNSATURATED CHLORINATED CYCLOHEXANONE DERIVATIVES<sup>47</sup>

<sup>a</sup> Tetramethylsilane used as internal standard with  $\delta = 0$  ppm. Coupling constants expressed in Hz. s = singlet, d = doublet and m = multiplet.

<sup>b</sup> Comparison with an internal standard, p-dichlorobenzene, gave 1.7 protons per molecule.

<sup>c</sup> Comparison with an internal standard, p-dichlorobenzene, gave 10 proton per molecule.

<sup>4</sup> The chloromethine proton is coupled with both Me groups. In double resonance experiments, decoupling of the chloromethine proton leads to a singlet for the vinylic methyl group and to signal narrowing for the other Me group. Decoupling of the latter methyl group transforms the signal of the methine proton into a clear-cut quartet (J = 0.4 Hz), due to homoallylic coupling with the vinylic Me group, and decoupling of the vinylic methyl group transforms the signal of the methine proton into a rather broad singlet, due to a very weak interaction with the Me group at position 6 (coupling less than 0-2 Hz).

NMR spectrum shows signals for 2 dissimilar Me groups and one chloromethine proton. In addition a weak coupling (0.4 Hz) between the chloromethine proton and one of the Me groups is present (cf. Table 3). This suggests a homoallylic coupling.<sup>20</sup> Therefore structure 6 is proposed for this compound, which is in accord with all spectroscopic data. The probable conformation of the  $\alpha$ -Cl atom at position 6 can be obtained from the IR frequency of the carbonyl absorption at 1758 cm<sup>-1</sup> (calculated  $1753 \text{ cm}^{-1}$ , when this Cl atom is assumed to be axial). With regard to the conformation at carbon atom 5, some information may be derived from the NMR data. The homoallylic coupling constant amounts to 0.4 Hz only, while usually values of 1.9-3.0 Hz are found in cyclic systems.<sup>20</sup> According to Sternhell this may be attributed to a conformation in which the C-H bond at position 5 is more or less parallel to the plane of the double bond.<sup>20</sup> Inspection of a Dreiding and a Stuart-Courtauld model shows a conformation intermediate between the half chair form<sup>†</sup> and one of the two extreme boat forms to be favourable. Then, the C-H bond at position 5 is nearly parallel to the plane of the double bond, the tertiary  $\alpha$ -Cl atom is axial, while steric interaction between the Cl atoms is absent.

3,5-Dimethylphenol. The chlorination gave a crystalline compound of composition  $C_8H_6Cl_4O$ . The NMR spectrum shows only one signal for the Me groups. Therefore, the Me groups are equivalent and a plane of symmetry should be present in this product. The IR spectrum shows a conjugated carbonyl group. On the basis of these results we assigned structure 7 to this product, in accordance with Auwers *et al.*,<sup>21</sup> Müller and Linde<sup>2</sup> and Fort.<sup>10</sup>

<sup>†</sup> In cyclohexene derivatives a proper chair form is not possible.<sup>16</sup>

### **Reaction mechanism**

For the chlorination of pentachlorophenol Denivelle and Fort accepted the following reaction path:<sup>8</sup>



This can be applied to the present chlorination reaction and will be used in a more extended form. The chlorination of phenol at room temperature gives first 2,4,6-trichlorophenol which is very slowly converted to 2 (see Eqs 2 and 3).



In Eq. 3 the addition of the chlorine molecule probably takes place by a 1,4-addition.<sup>8</sup> If a 1,2-addition occurs, two different products can be formed, one with a  $\beta$ , $\gamma$ -double bond as in the present product, the other with an  $\alpha$ , $\beta$ -double bond, which has not been isolated. The residual double bond is presumably prevented from further chlorination by steric hindrance.

When the chlorination of phenol is carried out at  $90^{\circ}$  the final product differs from that at  $25^{\circ}$  in having only one hydrogen. Probably, at  $90^{\circ}$  one of the metapositions has also been chlorinated giving 2,3,4,6-tetrachlorophenol. That metasubstitution is indeed possible is indicated by the bromination of 2,6-dimethylphenol leading to 3,4-dibromo-2,6-dimethylphenol. Instead of a second metachlorination, reaction 4 occurs, in which the chlorine molecule attacks the less heavily substituted side of the tetrachlorophenol.



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	Structural	d.N.		Elemental an	alyses			6272
Compound	formula	ې		%C	Н%	%a	M.W.	
<b>2—2,2,4,5,6,6-hexa</b> chloro-3-cyclohexen-1-one		oil (impure)	Found Calc. for C <sub>6</sub> H <sub>2</sub> Cl <sub>6</sub> O	25-5 23-80	0-98 0-67	66-5 70-25		L. V(
3-2,2,3,4,5,6,6-heptachloro-3-cyclohexen-1-one		66-16	Found Calc. for C <sub>6</sub> HCl,O	21.3 21.37	0-25 0-30	73-3 73-59		ollbracht, W.
4.2,3,4,5,6-pentachloro-2,6-dimethyl-3-cyclohexen-1- one		120-123	Found Calc. for C <sub>6</sub> H,CI <sub>5</sub> O	32-5 3241	2.48 2.38	59-0 59-80	301† 296	G. B. HUYSMANS
<b>5</b> —2,4,5,6-tetrachloro-2,6-diphenyl-3-cyclohexen - 1 - one		160-162	Found Calc for C <sub>18</sub> H <sub>12</sub> Cl <sub>4</sub> O	55-9 55-99	3.29 3.13	36-4 36-73		s, W. J. Mus and
<b>62,4,5,6-penta</b> chloro-3,6-dimethyl-3-cyclohexen- 1-one		131-133	Found Calc. for C <sub>8</sub> H,Cl <sub>5</sub> O	32.7 32.41	2.48 2.38 2.38	59-5 59-80		H. J. HAGEMAN
7=2,4,4.6-tetrachloro-3,5-dimethyl-2.5-cyclohexadien- 1-one		104-107	Found Calc. for C <sub>6</sub> H <sub>6</sub> Cl <sub>4</sub> O	37.1 36 <b>.9</b> 6	2:31 2:33	5 75 75 75		

+ By Rast.

By a subsequent 1,4-chlorine addition, compound 3 is obtained. The other possibility, that 2 is produced first and the vinylic hydrogen is then replaced by chlorine, is highly improbable because the allylic hydrogen is more likely to be substituted.

In the chlorination of 2,6-dimethylphenol a para- as well as meta-position are assumed to be substituted. The mechanism then leads directly to structure 4.

The chlorination of 2,6-diphenylphenol gives structure 5, which resembles structure 2 in having two H atoms in the central ring. It follows that the *meta*-positions of this ring have not been substituted, probably for steric reasons.

The chlorination of 2,5-dimethylphenol first gives 2,5-dimethyl-4,6-dichlorophenol. Before *meta*-substitution occurs, reaction 5 proceeds, in which the chlorine molecule again attacks the less heavily substituted side of this phenol.



By a further 1,4-chlorine addition structure 6 is obtained.

The chlorination of 3,5-dimethylphenol gives compound 7 of a different structure. According to Fort,<sup>10</sup> this is formed by isomerization at room temperature of the initial *ortho*-quinoid structure into the more stable *para*-quinoid structure (cf. 6), which is inert toward further chlorination. In this case, 1,4-chlorine addition is



retarded as both ends of the diene system are substituted. Therefore, the side reaction 6, possibly present to a slight extent in other instances (see in this respect Ref 8), now becomes the main reaction.

#### EXPERIMENTAL

All m.ps are uncorrected. UV spectra were recorded on a Beckman DK 2A spectrometer, IR spectra on a Perkin-Elmer 221 g spectrometer and a Hitachi EPI-G 2 spectrometer, and the NMR spectra on a Varian A-60 spectrometer with a Varian spin decoupler, model V-6058 A, using TMS as internal reference ( $\delta = 0$ ppm). Commercial AcOH (Baker) was used without further purification. Chlorine was obtained from NEPA/KRIS. All phenols, with the exception of 2,6-diphenylphenol, were from Fluka (purum) and used without further purification. 2,6-Diphenylphenol was gratefully obtained from Dr. B. H. Bibo.<sup>22</sup>

#### Reaction procedure

Chlorine gas was bubbled through an approximately 10% (w/v) AcOH soln of the phenol at room temp. Initially, a temp rise to about  $40^{\circ}$  was observed. The reaction was followed by TLC (eluent benzene, detection phosphor molybdic acid soln in EtOH). Usually 24 hr were sufficient to complete the conversion. In case of phenol however, the chlorination at  $90^{\circ}$  required 2 days, while at room temp the reaction was stopped after 14 days. The AcOH in all experiments was evaporated *in vacuo* at  $50^{\circ}$  and the crystalline

mass, formed after standing overnight, was recrystallized from a little pet ether and the purity checked by m.p. and TLC. Yields varied from 40–70%. Chlorination of phenol at room temp gave an oily product, which could not be crystallized even after purification by column chromatography (Merck silica gel 0.2-0.5 mm, eluent benzene). This oil was subjected to spectroscopic analysis. 2,6-Dimethylphenol was chlorinated in CCl<sub>4</sub>, nitromethane and in a water suspension. In the two organic solvents the same product and yield were obtained as in AcOH, but in water 3,3', 5,5'-tetramethyldiphenoquinone was formed, in all likelihood from oxidation by HOCL<sup>23</sup>

#### Additional IR data<sup>†</sup>

In addition to the data given in Table 2, the following absorption maxima have been observed (strong and medium only, unless stated otherwise).

Substance 2 (pure liquid): 3060 (weak, olefinic C-H stretch), 2980 (weak, aliphatic C-H stretch), 1325, 1172, 872, 760, 748, 699 cm<sup>-1</sup>.

Substance 3 (CCl<sub>4</sub>/CS<sub>2</sub>): 2985 (weak, aliphatic C—H stretch), 1166, 1128, 1000, 870, 782, 750, 712, 660 cm<sup>-1</sup>.

Substance 4 (CCl<sub>4</sub>): 1445, 1382, 1331, 1220, 1195, 1112, 1073, 1045, 1023, 700, 655 cm<sup>-1</sup>. Substance 5 (CDCl<sub>3</sub>/CS<sub>2</sub>): 1585, 1445, 1313, 894, 761, 745, 732, 695, 674 cm<sup>-1</sup>. Substance 6 (CCl<sub>4</sub>/CS<sub>2</sub>): 1375, 1080, 797, 762, 730, 680, 628 cm<sup>-1</sup>.

Substance 7 (CCl<sub>4</sub>/CS<sub>2</sub>): 1380, 1210, 1050, 930, 720, 690 cm<sup>-1</sup>.

#### Bromination of 2,6-dimethylphenol

2,6-Dimethylphenol (10 g; 82 mmoles) was dissolved in 100 ml AcOH and brominated at room temp by the slow addition of 22 ml (410 mmoles) Br<sub>2</sub>. The AcOH and the excess Br<sub>2</sub> were removed *in vacuo* and the crystalline mass recrystallized from pet ether. The product was 2,6-dimethyl-3,4-dibromophenol, yield 72%; m.p. 88-0-88.5°, lit. 86°.<sup>24</sup> IR (CCl<sub>4</sub>): 3625 (s) OH stretch, 1600 (vw) 1560 (w) arom. skelet, 1455 (m), 1200 (s) 1175 (s) ether C—O stretch, 1000 (m), 870 (m) 860 (m) 1,2,3,4,5-arom. subst. NMR (CS<sub>2</sub>): 2·17 (Me, doublet J = 0.7 Hz,<sup>‡</sup> 3H), 2·37 (Me, doublet J = 0.5 Hz,<sup>‡</sup> 3H), 4·65 (OH, singlet, 1H), 7·25 (arom. H, septet J = 0.6 Hz,<sup>‡</sup> 1H). (Found: C, 34·4; H, 3·00; Br, 57·3. C<sub>8</sub>H<sub>8</sub>Br<sub>2</sub>O requires: C, 34·32; H, 2·88; Br, 57·09%).

#### **Reactions with compound 4**

Reduction with LAH. To a suspension of LAH (1.5 g; 40 mmoles) in ether (30 ml) 3 g of 4 (10 mmoles) were added and the mixture heated under reflux. Residual LAH was destroyed with EtOH, the Al salts filtered off and the filtrate acidified with dil HCl and extracted with benzene, the extract evaporated *in vacuo* and the residual mass recrystallized from pet ether; m.p. 183–184°. The product appeared to be 2,6-dimethyl-3,4,5-trichlorophenol. IR (CCl<sub>4</sub>/CS<sub>2</sub>): 3615 (s) OH stretch, 1590 (w) 1550 (w) arom. ring, 1445 (w), 1410 (w), 1395 (m), 1350 (w) CH<sub>3</sub> symm. def., 1285 (m), 1208 (s) ether C—O stretch, 1035 (m), 988 (m), 790 (m), 746 (m). NMR (CS<sub>2</sub>): 2·28 (Me, singlet, 6H), 4·67 (OH, singlet, 1H). If the same reaction was carried out at 0–10°, an unidentified product was obtained (m.p. 102–103°).

Reduction with Zn/acetic acid. 1 g (3 mmoles) of 4 was dissolved in 20 ml AçOH and 1 g Zn added with stirring. After 1 hr stirring at room temp the mixture was filtered and the AcOH removed *in vacuo*. The crystalline residue was recrystallized from pet ether, m.p. 87–88°. The product appeared to be 2,6-dimethyl-3,4-dichlorophenol. IR (CCl<sub>4</sub>): 3615 (s) OH stretch, 1600 (w) 1575 (w) 1560 (w) arom. skelet., 1218 (s) 1198 (s) ether C—O stretch, 1015 (m), 868 (m) 1,2,3,4,5-arom. subst. NMR (CS<sub>2</sub>): 2·17 (Me, doublet J = 0.7 Hz, ‡ 3H), 2·28 (Me, doublet J = 0.5 Hz, 3H), 4·54 (OH, singlet, 1H), 6·98 (arom. H, septet J = 0.6 Hz, 1H). Mol. wt, by Rast = 180; calc. 191. (Found: C, 50·3; H, 4·24; Cl, 37·2. C<sub>8</sub>H<sub>8</sub>Cl<sub>2</sub>O requires: C, 50·29; H, 4·22; Cl, 37·10%).

Reduction with hydrogen and Pd/C. 0.6 g (2 mmoles) of 4 was dissolved in 3 ml EtOH and 75 mg of Pd/C (DODUCO Carbonor 18/20, 2% Pd) added with magnetic stirring. Overnight, 107 ml of hydrogen (ca. 4.4 mmoles) were absorbed at room temp. After work-up the product again appeared to be 2,6-dimethyl-3,4-dichlorophenol.

Dehalogenation with sodium in liquid ammonia. To a soln of 1.84 g (80 mmoles) of Na in ca. 250 ml liquid

<sup>†</sup> Assignment of the C—Cl vibrations was not possible due to the complicated nature of the absorption pattern.

<sup>1</sup> Splitting is caused by a long range coupling between the aromatic proton and the two Me groups.<sup>25</sup>

ammonia 4.74 g (16 mmoles) of 4 in 20 ml ether was added. After addition a colour change from blue to brown was observed. After evaporation of the ammonia 15 ml ethanol and 5 ml 4N HCl were added successively and the mixture extracted with benzene. The benzene soln was freed from tarry maternal by passage through a column of silica gel (Merck, 02-05 mm). After evaporation of the filtrate the residue appeared to be 2,6-dimethylphenol.

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### REFERENCES

- <sup>1</sup> R. Stroh, Houben-Weyl 5/3, 679.
- <sup>2</sup> H. Müller and H. Linde, J. Prakt. Chem. 4, 69 (1956).
- <sup>3</sup> A. W. Burgstahler, T. B. Lewis and M. O. Abdel-Rahman, J. Org. Chem. 31, 3516 (1966).
- 4 C. J. Moye and S. Sternheil, Austral. J. Chem. 19, 2107 (1966).
- <sup>5</sup> L. Denivelle and R. Fort, Bull. Soc. Chim. Fr. 1834 (1956).
- <sup>6</sup> L. Denivelle and R. Fort, C.R. Acad. Sci., Paris 242, 2359 (1956).
- <sup>7</sup> L. Denivelle and R. Fort, Bull. Soc. Chim. Fr. 724 (1957).
- <sup>8</sup> L. Denivelle and R. Fort, *Ibid.* 459 (1958).
- <sup>9</sup> L. Denivelle and R. Fort, Ibid. 392 (1959).
- <sup>10</sup> R. Fort, Ann. Chim. Paris 203 (1959).
- <sup>11</sup> H. Labhart and G. Wagnière, Helv. Chim. Acta 42, 2219 (1959).
- <sup>12</sup> L. N. Ferguson and J. C. Nnadi, J. Chem. Educ. 42, 529 (1965).
- <sup>13</sup> E. L. Eliel, N. L. Allinger, S. J. Angyal and G. A. Morrison, *Conformational Analysis* p. 463. Wiley, N.Y. (1965).
- <sup>14</sup> Ref. 13, p. 197.
- <sup>15</sup> C. N. R. Rao, Chemical Applications of IR Spectroscopy p. 218. Academic Press, London (1963).
- <sup>16</sup> Ref. 13, p. 109.
- <sup>17</sup> R. Norman Jones and C. Sandorfy, Technique of Organic Chemistry, Vol. IX, Chemical Application of spectroscopy p. 371; Interscience, New York (1956).
- <sup>18</sup> H. I. Scott, Interpretation of UV spectra of natural products p. 58. Pergamon, London (1964).
- <sup>19</sup> B. H. Bibo, Thesis p. 82. Delft (1967).
- <sup>20</sup> S. Sternhell, Rev. Pure and Appl. Chem. 14, 15 (1964).
- <sup>21</sup> K. V. Auwers, E. Murbe and K. Sauerwein, Fortschr. Chem. Phys. 18, 20 (1924).
- <sup>22</sup> Ref. 19, p. 69.
- <sup>23</sup> W. J. Mijs, O. E. van Lohuizen, J. Bussink and L. Vollbracht, Tetrahedron 23, 2253 (1967).
- <sup>24</sup> S. W. Gleed and E. T. Peters, J. Chem. Soc. 209 (1948).
- <sup>25</sup> W. G. B. Huysmans and H. Angad Gauer, to be published.