Naphthalene Tetrachlorides and Related Compounds. Part 12.[1] Influence of Some 1-Substituents on the Course of Chlorination of Derivatives of 2-Naphthol

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The chlorinations of 1-methyl-2-naphthol, 1-bromo-2-naphthol, 2,2'-dihydroxy-1,1'-dinaphthylmethane, and 6-t-butyl-2-naphthol with excess of chlorine in acetic acid give tetralin-2-ones analogous to that formed from 1-chloro-2-naphthol. 1,6-Di-t-butyl-2-naphthol, however, gives only 1,6-di-t-butyl-1,3-dichloro-1,2-dihydronaphthalene; 1-iodo-2-naphthol gives some 1,1,3,4-tetrachlorotetralin-2-one in acetic acid, whereas in chloroform it gives a mixture from which *r*-1,*c*-2,*t*-3,*t*-4,5,7-hexachlorotetralin-6-ol was isolated. The structures of these products and the pathways leading to them are discussed.

In association with our investigation [1] of the course of chlorination of 2-naphthol, the reactions of a number of 1-substituted naphthols were examined preparatively. Some of these reactions had been studied by earlier investigators; [2,3] uncertainty existed, however, in regard to the stereochemistry of the final stage of these chlorinations. Having established the course taken for 1-chloro-2-naphthol, we now report our findings for some of its analogues, and record the characterization of a number of new products.

Experimental

Many of the materials and methods have been described in earlier papers. 2,2'-Dihydroxy-1,1'-dinaphthylmethane, m.p. 200 °C (lit.,[4] 200 °C), was prepared by the condensation of 2-naphthol with formaldehyde in the presence of potassium acetate. 1-Methyl-2-naphthol, m.p. 110 °C (lit.,[4] 110 °C), was prepared according to Fries and Hübner's method [4] and was separated from the starting material easily by steam-distillation. 1-Bromo-2-naphthol, m.p. 82—84 °C (lit.,[5] 84 °C), was prepared from 2-naphthol by bromination; 1-iodo-2-naphthol, m.p. 93—94 °C (lit.,[6] 94.5 °C) was prepared similarly, hydrogen peroxide being used as oxidizing agent. 6-t-Butyl-2-naphthol, m.p. 118—119 °C (lit.,[7,8] 119—120 °C) and 1,6-di-t-butyl-2-naphthol, m.p. 138—139 °C (lit.,[8] 138—139 °C) were prepared by Contractor *et al.*'s method [7] and were purified by chromatography on a mixture of silica gel and alumina using benzene–light petroleum (b.p. 120—140 °C) (1 : 1 v/v) as eluant.

Chlorinations were normally carried out by passing excess of chlorine into a solution or suspension of the compound in glacial acetic acid at room temperature. The product was if necessary precipitated by the addition of water. From 2,2'-dihydroxy-1,1'-dinaphthylmethane was obtained in nearly quantitative yield 1,1',3,3',4,4'-hexachloro-2,2'-dioxoditetralylmethane (probably a mixture of geometric isomers), m.p. 156—158 °C (Found: C, 49.5; H, 2.9; Cl, 41.6. Calc. for $C_{21}H_{14}Cl_6O_2$: C, 49.4; H, 2.8; Cl, 41.6%). It was soluble only with difficulty in ordinary solvents, but could be crystallized from boiling benzene–light petroleum (b.p. 80—100 °C), or from carbon tetrachloride, which gave a sample, m.p. 170 °C (decomp.), $\nu_{max.}$ 1 753s, 1 309m, 1 258, 1 248s, 1 238, 1 203, 1 186, 1 176, 1 171, 1 139, 1 122, 1 104, 1 087, 1 075, 1 069, 1 047, 1 031, 1 008, 991m, 969,9 26m, 905m, 896, 879, 869, 867, 825m, 812m, 781, 769s, 766s, 756, 733s, 730s, 713s, and 679s cm^{-1}.

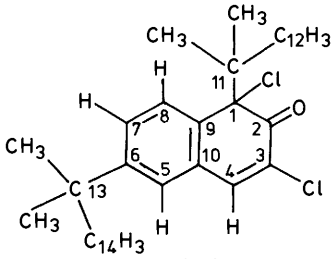
1-Methyl-2-naphthol similarly gave a product, m.p. 76—78 °C (lit.,[2] 78 °C), $\nu_{max.}$ 1 743s, 1 348m, 1 303, 1 294, 1 242, 1 233, 1 215, 1 187, 1 171m, 1 107, 1 088, 1 067, 1 046, 1 013m, 880, 865, 840, 829, 814, 778, 762s, 751s, 702, and 692s cm^{-1}. Previous workers [2] have regarded this as a single compound, but its ^1H n.m.r. spectrum shows that it is a mixture having signals at δ 2.27 and 2.11 (two methyl groups, each s, relative intensity 1 : 1), 5.51 and 5.31 (two CH d, *J* 5.8 Hz), 5.62 and 4.83 (two CH d, *J* 4.5 Hz), and 7.72—8.00 and 8.05—8.40 (m, ArH). The downfield pairs of doublets partly overlap, but the coupling constants can be identified clearly. Since *trans*-addition of chlorine is expected for this acid-catalysed reaction,[1] this product is probably an equimolar mixture of *r*-1,*t*-3,*c*-4- and *r*-1,*c*-3,*t*-4-trichloro-1-methyltetralin-2-one. On being treated with a solution of potassium acetate in acetic acid, it gave 1,3-dichloro-1-methyl-1,2-dihydronaphthalen-2-one as an oil,[2] $\nu_{max.}$ 1 692s, 1 603m, 1 262m, 1 230s, and 759s cm^{-1}. This took up further chlorine slowly, and the product had m.p. 111—113 °C. 1,3,3,4-Tetrachloro-1-methyltetralin-2-one has been prepared before,[2] and is recorded as having m.p. 114—116 °C. Our sample was a mixture of the *r*-1,3,3,*c*-4- and *r*-1,3,3,*t*-4 isomers, as shown by the ^1H and ^{13}C n.m.r. spectra. In the ^1H spectrum, the aromatic, methine, and methyl signals integrated in the proportions 4 : 1 : 3, as expected. The aromatic signals lay between δ 7.25 and 7.95, the two methine signals in ratio 1 : 2.8 lay at δ 5.75 and 5.65, respectively, and the two methyl signals in ratio 1 : 2.9 lay at δ 2.20 and 2.40, respectively. In the ^{13}C spectrum, all eleven signals appeared doubled, with intensities in the approximate ratio established for the ^1H spectrum. They occurred at the following values of δ (p.p.m. downfield from Me_4Si; signal of the minor isomer given first): 30.94 and 32.30 (CH_3), 63.63 and 64.80 (C-1), 66.03 and 65.71 (C-4), 83.66 and 84.96 (C-3), 127.85 and 128.81 (probably C-8), 128.79 and 128.30, 129.44 and 129.70, 130.38 and 130.54, 131.12 and 131.25 (C-4a or -8a), 137.26 and 137.39 (C-8a or -4a), and 189.08 and 189.43 (C-2). We think it likely, but have not established with certainty, that the major product is the *r*-1,3,3,*t*-4- and the minor product is the *r*-1,3,3,*c*-4-isomer, since the dipolar effect would be more important than the size of the substituent in discouraging attack *cis* to one or other of the two 1-substituents.

The corresponding reaction of 1-bromo-2-naphthol with excess of chlorine also gave a product which on recrystallization from light petroleum (b.p. 120—140 °C) appeared to be a single compound, m.p. 106—108 °C (Found: C, 36.4; H, 1.7; Cl, 32.4; Br, 24.4. $C_{10}H_6BrCl_3O$ requires C, 36.5; H,

Table 1. ^{13}C N.m.r. frequencies and coupling constants obtained from the spectra of 1,6-di-t-butyl-1,3-dichloro-1,2-dihydronaphthalen-2-one [a] in $CDCl_3$ at 30 °C

Position of signal [b]	Assignment	Multiplicity Single resonance [c]	LPSF H-8	LPSF Bu^t	Derived coupling constants $^1J_{C-H}$/Hz	$^3J_{C-H}$/Hz	Other couplings
29.056	C-12 or C-14	q; m	q; m	becomes q; s	126.6	4.4	
30.939	C-14 or C-12	q; m	q; m	becomes q; s	126.1	4.9	
34.640	C-11 or C-13	s; m	s; m	s; m			
34.802	C-13 or C-11	s; m	s; m	s; m			
84.020	C-1	s; broad d	becomes s; s	s; d		5.4 (H-8) [d]	
126.287	C-7 or C-4	d; m	d; m	d; m	*ca.* 157		
126.775	C-4 or C-7	d; m	d; m	d; m			
127.654	C-10	s; d	becomes s; s	s; d		6.4 (H-8)	
128.433	C-8	d; s	d; s	d; s	162.1		
135.965	C-9	s; q	s; q	s; q		7.0 (H-7, -4, -5)	
137.585	C-5	d; [e]	d; [e]	d; [e]	*ca.* 156		
142.681	C-3	s; [e]	s; [e]	s; [e]			
154.047	C-6	s; decet	s; octet	becomes s; d		7.3	3.7
185.400	C-2	s; d	s; d	s; d		11.5 (H-4)	

[a] Numbering as in (A).



(A)

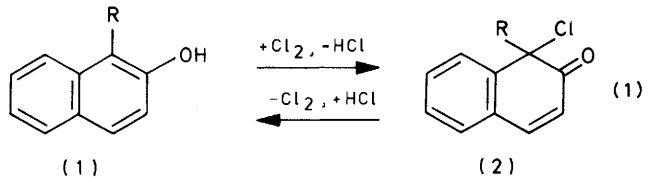
[b] p.p.m. downfield from Me_4Si. [c] Main (^1J) multiplicity given first. [d] The signals were broad and could contain a second minor coupling. [e] Signals overlapped; multiplicity uncertain.

1.8; Cl, 32.4; Br, 24.4%). Its ^1H n.m.r. spectrum showed it to be a mixture of two compounds in approximately equal proportions, δ 5.56 and 5.15 (two d, *J* 5.0 Hz), 5.61 and 5.11 (two d, *J* 3.8 Hz), and 7.52—8.04 and 8.32—8.48 (m, ArH). A small amount of impurity not evident in the analytical results was shown by the presence of an extraneous signal in the ^1H n.m.r. spectrum at δ 4.88. Signals attributable to *trans*-1,1,3,4-tetrachlorotetralin-2-one were absent from the spectrum. It is considered to be a mixture of 1-bromo-*r*-1,*t*-3,*c*-4- and 1-bromo-*r*-1,*c*-3,*t*-4-trichlorotetralin-2-one.

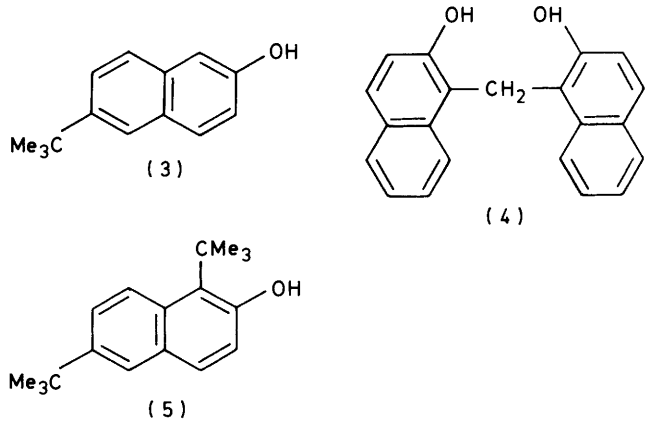
1-Iodo-2-naphthol when chlorinated in acetic acid gave much iodine, and from the resinous product was isolated 1,1,3,4-tetrachlorotetralin-2-one, m.p. 100—102 °C, by repeated extraction with warm light petroleum (b.p. 80—100 °C) from the residue of the resinous material. Similar chlorination in chloroform as solvent also gave much iodine, which was removed with the solvent to give a product containing carbonyl compounds, $\nu_{max.}$ 1 756, 1 708, and 1 690 cm^{-1}, from which by trituration with light petroleum (b.p. 80—100 °C) there was recovered r-1,c-2,t-3,t-4,5,7-*hexachlorotetralin*-6-*ol*, m.p. 149—150 °C (Found: C, 34.0; H, 1.7; Cl, 59.9. $C_{10}H_6Cl_6O$ requires C, 33.9; H, 1.7; Cl, 59.9%), $\nu_{max.}$ 3 460s, 1 416s, 1 349, 1 334, 1 314s, 1 296s, 1 273, 1 253, 1 232s, 1 192s, 966, 901m, 879m, 857m, 806m, 757m, 732s, 709s, and 694 cm^{-1}, δ 4.43 (1 H, q, H-2, *J* 10.1 and 3.1 Hz, alicyclic H), 5.16 (1 H, q, H-3, *J* 10.1 and 4.4 Hz, alicylic H), 5.30 (1 H, d, H-1, *J* 3.1 Hz, alicyclic H), 5.62 (1 H, d, H-4, *J* 4.3 Hz, alicylic H), 6.4br (s, OH), and 7.57 (1 H, s, ArH). Assignments here have been made on the basis of multiplicity and of chemical shift, on the assumption that 5-Cl moves the signals for the nearer protons downfield.

The reaction of 6-t-butyl-2-naphthol with chlorine (1 mol. equiv.) in chloroform gave 1-chloro-6-t-butyl-2-naphthol. The crude product was dissolved in dilute NaOH, filtered, acidified, and distilled in steam. The resulting product solidified, and was filtered off and recrystallized from light petroleum (b.p. 80—100 °C), m.p. 75—76 °C (lit.,[8] 76 °C). Further treatment of this with chlorine (1 mol. equiv.) in chloroform at 0 °C gave a product which after removal of the solvent *in vacuo* was able to be crystallized from light petroleum (b.p. 40—60 °C), to give 6-*t*-*butyl*-1,1-*dichloro*-1,2-*dihydronaphthalen*-2-*one* as prisms, m.p. 95—96 °C (Found: C, 62.6; H, 5.3; Cl, 26.2. $C_{14}H_{14}Cl_2O$ requires C, 62.5; H, 5.2; Cl, 26.3%), $\nu_{max.}$ 1 691s, 1 616, 1 595, 1 360, 1 283, 1 233s, 1 222s, 1 207s, 1 200s, 1 122, 1 099, 1 026, 945s, 918, 894s, 883, 850m, 814m, 759, 712s, and 677 cm^{-1}.

For further chlorination, 6-t-butyl-2-naphthol (3 g) was suspended in acetic acid and treated with excess of chlorine. The resulting solution was poured into water, and the precipi-



(1) (2)



(3) (4) (5)

tate was filtered off and recrystallized from light petroleum (b.p. 80—100 °C). The resulting 6-*t*-*butyl*-1,1,3,4-*tetrachlorotetralin*-2-*one* (4.2 g) had m.p. 102—103 °C (Found: C, 49.5; H, 4.2; Cl, 41.7. $C_{14}H_{14}Cl_4O$ requires C, 49.4; H, 4.1; Cl, 41.7 %), $\nu_{max.}$ 1 750s, 1 607, 1 364, 1 338, 1 294, 1 272, 1 230m, 1 205, 1 189, 1 157m, 1 134, 1 106, 1 038, 1 029, 930m, 907, 896, 873, 854, 833s, 801m, 770 ,760s, 736s, 707, and 672s cm^{-1}, δ 1.42 [9 H, s, $(CH_3)_3C$], 5.55 (1 H, d, *J* 5.2 Hz, H-3), 5.15 (1 H, d, *J* 5.2 Hz, H-4), and 7.65—8.00 and 8.25—8.40 (3 H, m, Ar-H).

1,6-Di-t-butyl-2-naphthol (2.5 g) when treated with excess of chlorine in acetic acid or in chloroform gave 1,6-*di*-*t*-*butyl*-1,3-*dichloro*-1,2-*dihydronaphthalen*-2-*one* (3.1 g) as yellow needles, m.p. 116—117 °C (Found: C, 66.3; H, 6.8; Cl, 21.7. $C_{18}H_{22}Cl_2O$ requires C, 66.5; H, 6.8; Cl, 21.8%), $\nu_{max.}$ 1 693s, 1 599, 1 589, 1 570, 1 389, 1 365, 1 346, 1 309, 1 255m, 1 230s, 1 200, 1 167, 1 105, 1 034, 1 028, 981, 945, 856m, 907, 890, 840m, 816s, 761, 745, 709m, 687s, and 670s cm^{-1}, δ 1.33, 1.36 [18 H, 2 × $(H_3C)_3C$], 7.2 (1 H, s, vinyl H), 7.3—7.5 (3 H, m, ArH), 7.86, 7.97 (1 H, d, ArH, J_{app} = 8 Hz). Its ^{13}C n.m.r. spectra have been included in SUP 23486 (see Part 11[1]) and the essential features are given in Table 1.

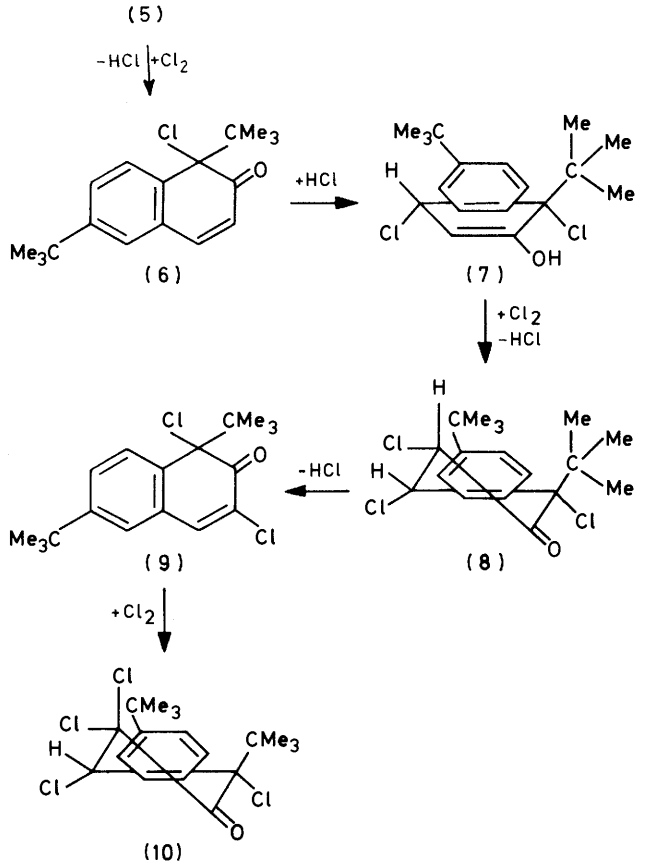
Further chlorination of this (2 g) in acetic acid was slow; after treatment for four days with excess of chlorine, the product was poured into water. The precipitate was filtered off and dissolved in hot light petroleum (b.p. 80—100 °C). After elution through a column of silica gel and concentration of the eluate there was obtained 1,6-*di*-*t*-*butyl*-1,3,3,4-*tetrachlorotetralin*-2-*one* (1.6 g), m.p. 161—162 °C (Found: C, 54.6; H, 5.6; Cl, 34.5. $C_{14}H_{22}Cl_4O$ requires C, 54.6; H, 5.6; Cl, 35.8%), $\nu_{max.}$ 1 739s, 1 604, 1 366, 1 270, 1 221s, 1 199, 1 113, 1 105, 1 080, 1 031, 971, 942, 932, 908, 881, 821, 816, 774s, 765m, 736m, 687s, and 669 cm^{-1}, δ 1.05 [9 H, s, $C(CH_3)_3$], 1.41 [9 H s, $C(CH_3)_3$], 5.77 (1 H, s, CHCl), and 7.56—8.31 (3 H, m, ArH).

Discussion

The course taken in the first stage of chlorination of 1-substituted derivatives of 2-naphthol (1) uniformly seems to involve *ipso*-attack at the activated 1-position, with loss of a proton from the hydroxy group, even when the substituent is the t-butyl group [equation (1)]. These reactions can be classified as bimolecular electrophilic substitutions with rearrangement (S_E2'), and are reversible, though the position of equilibrium seems generally to be well over towards the product (2). The preferred mode of addition to 1,1-dichloro-1,2-dihydronaphthalen-2-one (2; R = Cl) has now been shown[1] to involve HCl-catalysed *anti*-addition under the conditions used in the present study; so the results obtained in the present investigation can be interpreted in a reasonable and self-consistent manner. When the substituent at the 1-position is not too large (*e.g.* Cl, Me, or Br), the expected product is formed. With R = Cl, this is a single compound; but with R = Me and R = Br, two geometric isomers are obtained. We propose that these are both formed by *anti*-addition; the initial attachment of chlorine to the 4-position, by 1,4-addition of HCl initiated at the carbonyl group, occurs with similar ease on either face of the molecule. The two geometric isomers appear to crystallize together and the product is revealed to be a mixture only through its ^1H n.m.r. spectrum. The corresponding reaction starting with 6-t-butyl-2-naphthol (3), however, gave a single product as judged by the ^1H n.m.r. spectrum. The polychloroketone derived from chlorination of 2,2'-dihydroxy-1,1'-dinaphthylmethane (4) was too insoluble in the solvents available for determination of its ^1H n.m.r. spectrum, but the complexity of its i.r. spectrum in the region (650—760 cm^{-1}) expected for C–Cl stretching frequencies suggests that it is probably a mixture. With a sufficiently bulky substituent at the 1-position [*e.g.*, with 1,6-di-butyl-2-naphthol (5)], it is evident from the nature of the final product that the reaction sequence starts out similarly, but that the product of addition undergoes rapid dehydrochlorination. We can see no special reason why either of the products of *anti*-addition should be so unstable if they were formed; but it is known that *syn*- can accompany *anti*-addition in the acid-catalysed chlorinations of acyclic αβ-unsaturated aldehydes.[9] Inspection of models of the intermediate chloroketone (6) shows that the t-butyl group is likely to interfere sterically with attachment of nucleophilic chlorine to the 4-position. Approach of nucleophilic chlorine to the face of the molecule opposite to the t-butyl group will be favoured stereoelectronically also, because this group will be forced towards a pseudo-axial disposition by the *peri*-hydrogen atom, and the chloride ion can then approach pseudoaxially. Attachment of electrophilic chlorine to the 3-position then for steric reasons must occur on the same face, opposite to the t-butyl group. We suggest, therefore, that the course of the chlorination is that shown in Scheme 1. It follows, though this has not been proved, that (10) is the *r*-1,3,3,*c*-4-tetrachloro-isomer, as shown.

The dehydrochlorination of (8) to give (9) is rapid, in contrast with the relatively slow dehydrochlorination of most of the analogous *anti*-adducts, because of the axial, pseudo-axial disposition of 3-H and 4-Cl, and probably also because of steric congestion. The adoption by (8) of the conformation shown, rather than of any other form, seems theoretically likely, because it allows both the 1-t-butyl and the 4-chloro-substituent to lie pseudoaxial rather than pseudoequatorial.

The identification of (9) as the 1,3- rather than as the 1,4-dichloro-isomer could be made independently of assumptions concerning the mechanism of elimination, in two ways. One was from the ^{13}C spectrum of (9), which is discussed separately; the vinylic proton is not significantly coupled with C-1, as it should be if the proton were in the 3-position. The second is by consideration of the chemical shift of the 4-hydrogen atom in the ^1H n.m.r. spectrum of the derived product (10) formed by rather slow addition of chlorine. In 1,1,3,4-tetrachloro-tetralin-2-one (11), for which proof of assignments of the signals is available,[1] that for H-3 lies at δ 4.89, whereas that for

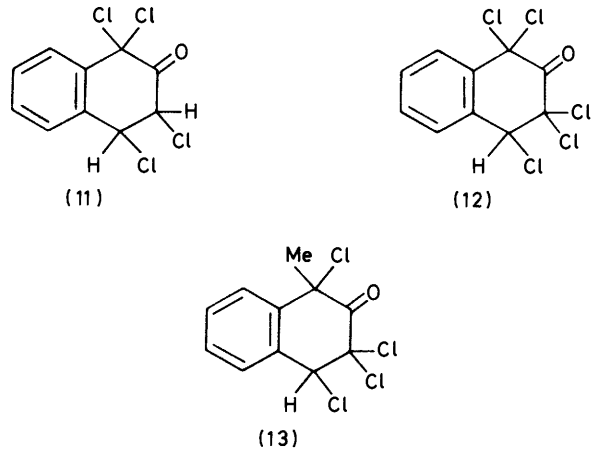


Scheme 1. Proposed course of chlorination of 1,6-di-t-butyl-2-naphthol in acetic acid

H-4 lies at δ 5.33. Consistently, the signal for H-4 in (12), for which the structure is proved by its derivation from 1,3-dichloro-2-naphthol, lies at δ 5.59; and those for H-4 in the two isomers of (13) lie at δ 5.75 and 5.65. Since the signal for the alicyclic proton in (10) lies at δ 5.77, it seems highly probable from this evidence alone that this proton is located at the 4- rather than at the 3-position.

The chlorination of 1-iodo-2-naphthol in acetic acid resulted in the displacement of iodine and ultimately in the formation of 1,1,3,4-tetrachlorotetralin-2-one (11). Either or both of the pathways shown in Scheme 2 could contribute. The yield was poor, and the residue was an intractable syrup.

When the reaction was carried out in chloroform as solvent, a similar product was obtained, from which we isolated *r*-1,-*c*-2,*t*-3,*t*-4,5,7-hexachloro-6-hydroxytetralin (19). Its stereochemistry is established by its ^{1}H n.m.r. spectrum, which shows that both 2- and 3-H are axially disposed ($^3J_{2\text{-C},3\text{-H}}$ 10.1 Hz). The low values of $^3J_{1\text{-H},2\text{-H}}$ and $^3J_{3\text{-H},4\text{-H}}$ (3.1 and 4.4 Hz) make it probable, therefore, that 1- and 4-H atoms lie pseudo-equatorially.[10] It is possible that (19) was formed by way of dehydrochlorination of (18) (Scheme 2), followed by iodine-catalysed addition to the resulting 1,3-dichloro-2-naphthol; but we think that this is unlikely, since chlorination of substituted 2-naphthols usually gives the normal ketopolychlorides.[1] Addition to (18) followed by loss of hydrogen chloride is another possibility; a third is that an unstable iododichloride is formed from 1-iodo-2-naphthol, and this in part reacts to give a product of addition.[11] These reactions are not of preparative importance, but they serve to show that a sufficiently electropositive group such as iodine can be lost in the course of these chlorinations. In contrast, we obtained no preparative evidence for the similar loss of a t-butyl group as the t-butyl cation, or of bromine as Br^+.

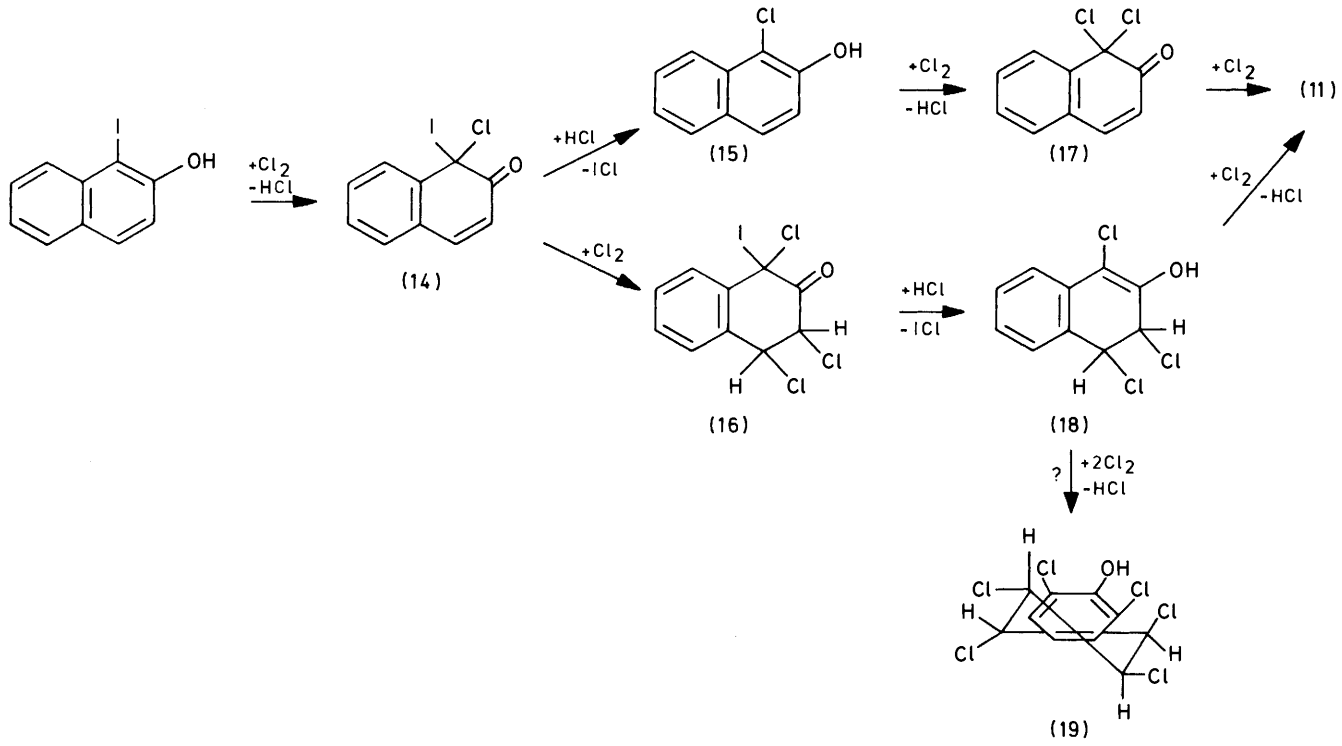


I.r. Spectra.—In this and in the preceding paper, i.r. spectra of a number of polyhalogenotetralin-2-ones and 1,2-dihydronaphthalen-2-ones have been provided, and they accord quite well with expectations. In the tetralins, the carbonyl stretching frequencies all lie in the range 1 739—1 761 cm^{-1}, tending to be at greatest frequencies when more electronegative substituents are present. All these compounds also have several strong absorptions in the region 670—760 cm^{-1} expected for C–Cl stretching frequencies. We have not succeeded in correlating individual frequencies with particular patterns of substitution. Absorptions in the latter region are noted also for the polychloro-1,2-dihydronaphthalen-2-ones; for these compounds, the carbonyl stretching frequency is, as expected, smaller (1 676—1 704 cm^{-1}), again seeming to be at higher frequencies for the more heavily chlorine-substituted compounds.

N.m.r. Spectra.—The ^{1}H n.m.r. spectra of the polychlorotetralin-2-ones recorded in this and in the preceding paper[1] are consistent with the structures assigned to the compounds for which measurements have been made. We have already indicated our reasons for assuming that signals for 3-H lie somewhat upfield from those for 4-H; on the assumption that the present assignments are correct, the ranges in our series are respectively δ 4.89—5.15 and 5.33—5.77. Compounds having hydrogens in both 3- and 4-positions all have vicinal coupling constants in the range 3—5 Hz, and so probably all have e,e′-hydrogen atoms; we assume for reasons already given[1] that all these compounds were formed by *anti*-addition.

A further feature of the spectra of the 1,1-dihalogeno-substituted compounds was that the multiplet for the aromatic hydrogen atoms could be divided into two groups, one below δ 8, and one integrating as a single hydrogen, width δ *ca.* 0.2, in the region δ 8.05—8.50. The latter can be attributed with reasonable confidence to H-8 adjacent to the two bulky electronegative substituents. In the spectra of the 1-chloro-1-methyl-substituted compounds, the two groups of signals overlapped, and the signals for H-8 did not lie so far down field.

The ^{1}H n.m.r. spectrum, no less than the chemical transformations, of 6-t-butyl-1,1,3,4-tetrachlorotetralin-2-one, confirms Buu-Hoi *et al.*'s[8] conclusion concerning the identity of the t-butyl-2-naphthol obtained by Contractor *et al.*'s[7] method. The aromatic part of its spectrum, though not quite first order, was consistent with the assignment, δ 7.72 (1 H, d, H-5, $J_{\text{H-5, H-7}}$ 2 Hz), 7.87 (1 H, dd, H-7, $J_{5\text{H, 7H}}$ 2, $J_{7\text{H,8-H}}$ 8 Hz), and 8.28 (1 H, d, H-8, $J_{7\text{H,8H}}$ 8 Hz). The doublet for H-8, iden-



Scheme 2. Possible pathways to 1,1,3,4-tetrachlorotetralin-2-one by chlorination of 1-iodo-2-naphthol in acetic acid

Table 2. Chemical shifts [δ (p.p.m. downfield from Me_4Si)] of the signals for the alicyclic carbon atoms in the ^{13}C n.m.r. spectra of some substituted tetralin-2-ones

Compound	Configuration	C-1	C-2	C-3	C-4
Tetralin-2-one		44.4	209.2	37.5	27.8
(11)	*r*-3, *t*-4	78.08	187.75	57.43	58.02
(13a)	presumed *r*-1, *t*-4	64.08	189.43	83.66	66.03
(13b)	presumed *r*-1, *c*-4	64.63	189.98	84.96	65.71

tified through its single large coupling to H-7, lay well downfield, whereas that for H-5, less congested by the adjacent substituents in the other ring, but adjacent also to a t-butyl group, is the furthest upfield of the aromatic signals.

The ^1H n.m.r. spectra of only two of the rather unstable polychloro-1,2-dihydronaphthalen-2-ones were examined. That of 1,1-dichloro-1,2-dihydronaphthalen-2-one had the expected signals in the aromatic region. The doublets representing the vinylic protons were centred at δ 6.3 and 7.45 ($^3J_{3H,4H}$ 10 Hz). These can be assigned to H-3 and -4 respectively by analogy with the corresponding assignments in other 1,2-dihydronaphthalenes.[12] Correspondingly, in the spectrum of 1,6-di-t-butyl-1,3-dichloro-1,2-dihydronaphthalen-2-one the signal for the vinylic 4-H lies with the aromatic multiplet, almost certainly at δ 7.19. In both these compounds, signals attributable to 8-H appeared downfield of the remaining aromatic signals, being centred at δ 8.0 for the 1,1-dichloro-compound and at δ 7.9 for the 1-t-butyl-1-chloro-compound. In the latter, as in 6-t-butyl-1,1,3,4-tetrachloro-1,2-dihydronaphthalen-2-one, the aromatic part of the proton spectrum was consistent with coupling constants $J_{7,8}$ 8, $J_{5,7}$ *ca.* 2, $J_{5,8}$ *ca.* 0 Hz, as expected for an aromatic ring with this pattern of substitution.

The ^{13}C spectra of only two of the new tetralin-2-ones have been examined. Chemical shifts for the alicyclic carbon atoms are summarized in Table 2, where the corresponding values for tetralin-2-one [13] and for 1,1,3,4-tetrachlorotetralin-2-one [1] are included.

Effects of substituents on ^{13}C chemical shifts are complex, depending on electronegativities, steric congestion, sterically induced polarization, and other factors. In cyclic systems, they can be significant even when the substituent is δ to the carbon atom concerned. Empirical parameters for calculation of chemical shifts in substituted cyclohexanes are available [14] and can be used as a basis for discussion of the results for the present system. A major feature of these appears to be that the effect of one or more chlorine substituents on the chemical shift of the signal of a directly attached carbon atom is less by at least δ 7 than that which would be expected on the basis of the results for the cyclohexane system. This applies to all three relevant positions (C-1, -3, -4), and in making it, allowance has been made for the effect expected for more distant chlorine substituents. The discrepancy is particularly large (> δ 19) for positions bearing two chlorine substituents, a fact which suggests that substituent chemical shifts are not by any means cumulative in this system.

The carbonyl signals in the spectra of ketopolychlorides lie upfield from those in tetralin-2-ones. Such an effect has been

established in other chloroketones,[15a] and apparantly results from the inductive effect of chlorine on the C^+-O^- dipole, which produces a relatively higher local electron density at the carbonyl carbon atom, with consequent less deshielding.

None of these features help towards determination of the stereochemistry of the two geometric isomers of (13).

The ^{13}C spectrum of only one [*viz.* (9)] of the polychlorodihydronaphthalen-2-ones has been determined. Chemical shifts in this spectrum are approximately as expected, as are the values of $^1J_{C-H}$. The minor coupling constants, however, merit some comment.

(a) The protons of the 6-t-butyl group are strongly coupled with the attached aromatic carbon ($^3J_{H-14,C-6}$ 3.7 Hz; for numbering, see Table 1). Because this value is approximately half the value of $^3J_{H-8,C-6}$, and because of the weakness of the outside signals in what should be a decet, the signal for C-6 is deceptively simple in the single resonance spectrum, but low-power single-frequency decoupling on the t-butyl protons shows clearly its characteristic ^3J coupling with H-8.

(b) Values of the ^3J couplings within the t-butyl groups are between 4 and 5 Hz; similar values have been recorded for related systems.[15,16] No indication of similar coupling with C-1 was, however, noted; the signals (d, coupled with H-8) were somewhat broad, but were not sharpened by low-power single-frequency decoupling on the t-butyl protons. The small magnitude of this expected vicinal coupling to a carbon atom adjacent to a carbonyl group is perhaps confirmatory [1] that the values of such $^1H-C-C-^{13}C$ couplings can be very variable; in the present case it can be noted that the C-1, to which vicinal coupling seems to be reduced, is highly congested, and the bond angles around it may be heavily distorted.

A number of ^3J couplings of vinylic or aromatic protons with carbon atoms have been determined. The largest (11.5 Hz) is the transoid coupling of H-4 with C-2; similarly large couplings with carbonyl carbon have been reported in the coumarin series.[17] The remaining transoid couplings (H-8, C-10; H-8, C-6; H-7, C-9; H-5, C-9; H-4, C-9) are all in the range 6.4—7.3 Hz; the cisoid coupling H-8, C-1 seems to be significantly smaller (5.4 Hz), as has also been noted in the coumarin series. Values of ^2J and of ^4J, expected to be smaller than those of ^3J, are in this series apparently negligible at our level of resolution (*ca.* 1.5 Hz).

Comments on Eliminations from the Ketotetrachlorides.— The naphthalene tetrachlorides undergo 1,2-dehydrochlorination by *E*1 and solvolytic *E*2 mechanisms only rather slowly. With strong bases, however, they characteristically react rapidly, giving mixtures of products.[10,18] Dehydrochlorinations of *trans*-1,2-dichloro-1,2-dihydronaphthalene and its analogues also give mixtures, *e.g.*, mainly the 1-chloro-isomer by solvolysis in methanol, but a mixture containing excess of 2-chloronaphthalene with potassium t-butoxide in t-butyl alcohol. In all these eliminations, therefore, proton loss from both 1- and 2-positions proceed by pathways not very different in rate; the overall result depends on mechanism, and within each mechanism is controlled both by polar and stereoelectronic factors.

The ketotetrachlorides discussed in this work present a rather different situation. Elimination of 3H,4Cl, where this is possible, is greatly preferred over elimination of 4-H,3Cl, presumably because the carbonyl group activates the proton being lost. Although the mechanisms of these reactions have not been studied in detail, our rationalization of the preparative observations is as follows. 1,1,3,4,4-Tetrachlorotetralin-2-one is quite unstable, because it perforce has 4-Cl *anti*- to 3-H. 1,6-Di-t-butyl-1,3,4-trichlorotetralin-2-one is similarly unstable; it is suggested above that steric effects have ensured *syn*- rather than *anti*-addition of chlorine in its formation, and so *anti*-loss of 3-H, 4-Cl is possible. 1,1,3,4-Tetrachlorotetralin-2-one, on the other hand, known to be formed by *anti*-addition, is relatively stable and can be prepared readily by chlorination in hydroxylic solvents. Elimination from it, though probably *E*2 in character, must be well on the *E*1cB side of the mechanistic spectrum. The remaining compounds, formed from 1-methyl-2-naphthol, 1-bromo-2-naphthol, 6-t-butyl-2-naphthol, and 2,2′-dihydroxy-1,1′-dinaphthylmethane, are relatively stable in hydroxylic solvents, and all have been formed by *anti*-addition.

1,3,3,4-Tetrachloro-1-methyltetralin-2-one, though it has hydrogen and chlorine necessarily *anti*, is similarly stable except on treatment with base; because of the absence of hydrogen 'activated' by an adjacent carbonyl group, its chemistry resembles more closely the naphthalene tetrachlorides themselves.

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