Naphthalene Tetrachlorides and Related Compounds. Part 9.[1] Structures and Reactions of Some 2-Methylnaphthalene Tetrachlorides

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The chlorination of 2-methylnaphthalene in chloroform gives a mixture of tetrachlorides, from which two new 1,2,3,4-tetrachloro-2-methyltetralins have been isolated and characterised. Their structures have been related to that of the known isomer from their ^{1}H n.m.r. spectra, their rates and products of alkaline dehydrochlorination, and their products of reaction with aluminium chloride.

IN earlier papers,[1-12] we have described the use of ^{1}H n.m.r. spectroscopy, of rates and products of alkaline dehydrochlorination, and of isomerisation with aluminium chloride, to establish the structures of isomeric naphthalene tetrachlorides, including those having bulky substituents in the 1-position. In the course of this work, we characterised one of the eight possible tetrachlorides derived by addition to the substituted ring of 2-methyl-naphthalene. This tetrachloride, m.p. 99°, was considered on the basis of its ^{1}H n.m.r. spectrum to be 2-

medium-resolution mass-spectrometer. Details of these and other spectra are given in the Supplementary Publication No. SUP 22864 (52 pp.).†

Compounds.—1-Chloro-2-methylnaphthalene, b.p. 159—161° at 25 mmHg, 1,4-dichloro-2-methylnaphthalene, m.p. 62°, and *r*-1,*c*-2,*t*-3,*c*-4-tetrachloro-2-methyltetralin (1), m.p. 99°, were prepared as in an earlier paper.[4]

Products in Chlorination of 2-Methylnaphthalene.—In a typical experiment, Cl_2 (22.5 g) was passed into a solution of 2-methylnaphthalene (25 g) in chloroform (420 cm³) in the dark at room temperature. After 15 h, solvent, HCl,

(1a)   (1b)
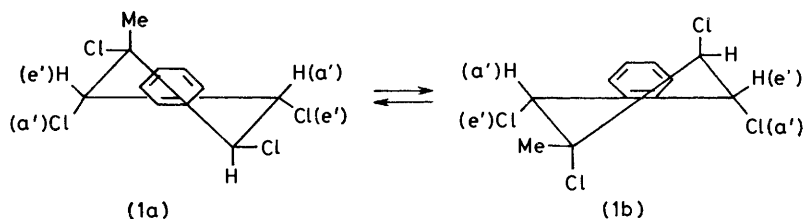
methyl-*r*-1,*c*-2,*t*-3,*c*-4-tetrachlorotetralin (1), existing in solution nearly exclusively in conformation (1a). Its slow rate of dehydrochlorination was, however, a little surprising, since if conformation (1b) were accessible (as might have been expected by analogy with the reactions of the corresponding naphthalene tetrachloride[3,10]) it should lose 1-H,2-Cl readily in a concerted pseudo-axial, axial elimination. We felt that this feature of its chemistry warranted further investigation, and consequently we have examined in more detail the products of chlorination of 2-methylnaphthalene.

EXPERIMENTAL

Most materials and methods have been described in earlier papers. ^{1}H N.m.r. spectra were determined by using a Varian T-60 instrument. Signals were assigned on the basis of their chemical shifts and of the numbers and magnitudes of the vicinal coupling constants by which each signal was split. These were generally determined by inspection of the spectra, solvent shifts being used to obtain spectra approximating sufficiently to first-order character where necessary. Long-range couplings were used also for help in structural assignments; these were obtained in some cases by using a JEOL FX60 spectrometer; appropriate decoupling experiments were used to define the origin of the observed couplings.

Mass spectra were determined by using a Varian CH7

and any residual chlorine were removed *in vacuo*, and the product was chromatographed in portions (5 g) on a column (130 × 3 cm) of silica gel (Kieselgel DGO deactivated with 10% of distilled water). Elution was begun with n-hexane, and thereafter chloroform was added in increments of 5% by volume. The progress of the separation was monitored by ^{1}H n.m.r. spectroscopy. The first fractions contained unchanged 2-methylnaphthalene and 1-chloro-2-methyl-naphthalene which was identified as its picrate, m.p. 106 °C (lit.,[13] 106—107 °C). Three addition products were then

(2a)   (2b)
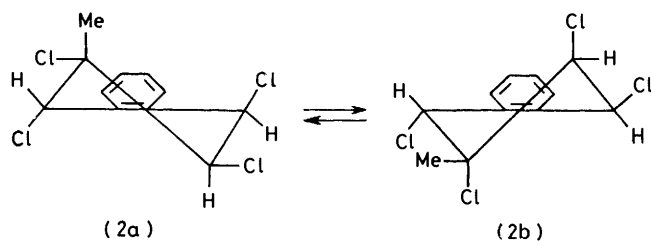
eluted. The first was r-1,c-2,t-3,t-4-*tetrachloro-2-methyl-tetralin*, existing in solution predominantly in conformation (2b). This compound was an oil, which did not crystallise. Its ^{1}H n.m.r. spectrum showed that it contained an impurity, most of which was removed by high-pressure liquid chromatography. A preparative LC/system 500 instru-

ment was used, with two pre-packed (5.7 × 30 cm) silica gel columns in series, and distilled n-hexane at a flow rate of 150 cm³ min⁻¹. The resulting tetrachloride was still an oil
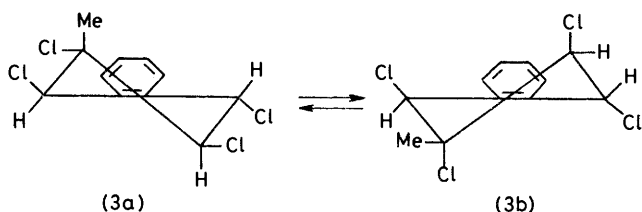
having a purity of ca. 99% as judged by ¹H n.m.r. spectroscopy, details of which are given in Table 1. Ultimate analysis of this tetrachloride was not quite satisfactory

The last tetrachloride to be eluted was the previously known r-1,c-2,t-3,c-4-tetrachloro-2-methyltetralin (1), m.p. 99 °C (lit.,[4,5,6,14] 99—99.5 °C). Its ¹H n.m.r. and mass spectra are given in Table 1 and in SUP 22864.

From separate experiments in which 2-methylnaphthalene was allowed to react with chlorine under controlled conditions, and the products were recovered and chromatographed for ¹H n.m.r. examination of appropriately bulked fractions, the approximate ratios of substitution products and isomeric tetrachlorides can be estimated to be those shown in Table 2.

Isomerisation with Aluminium Trichloride.—Each of the tetrachlorides was treated with aluminium chloride in nitrobenzene following the procedure described elsewhere.[10,11,14] In each case, equilibration occurred to give a

TABLE 1

¹H N.m.r. spectra of some tetrachlorides obtained by chlorination of 2-methylnaphthalene

Compound Solvent	(1)			(2)			(3)		
	CDCl₃	(CD₃)₂CO	C₆D₆	CDCl₃	(CD₃)₂CO	C₆D₆	CDCl₃	(CD₃)₂CO	C₆D₆
τ Values *									
Ar-H (m)	2.1—2.9	2.3—2.6	2.2—2.9	2.2—2.8	2.2—2.7	2.3—3.0	2.2—2.8	2.4—2.8	2.4—3.2
1-H (s)	4.7	4.2	4.8	4.3	4.2	4.7	4.5	4.1	5.2
3-H (d)	4.9	4.9	4.7	5.4	4.9	5.8	5.5	5.2	5.8
4-H(d)	4.8	4.3	4.3	3.9	3.8	4.2	4.8	4.5	5.3
2-CH₃ (s)	8.3	8.3	8.4	7.8	8.0	8.4	8.4	8.4	8.7
Major coupling constants									
³J₃₋ₕ, ₄₋ₕ/Hz	8.8 †	8.5	8.0	4.0	4.0	4.1	9.5	9.5	9.5
Long-range coupling charateristics	Sharp signals showing no obvious long-range couplings			Significant coupling between 1- and 4-H and between both these protons and Ar-H; see Discussion			Significant coupling between 1- and 4-H, and between both these protons and Ar-H; see Discussion		

* s = Singlet, d = doublet, m = multiplet.   † Revised value obtained by computer simulation of the spectrum; we thank Dr. G. A. Bowmaker for his help with this.

(Found: C, 47.3; H, 3.7. C₁₁H₁₀Cl₄ requires C, 46.5; H, 3.6%), but its structure is established by its mass spectrum, which shows it to have the expected cluster of base peaks, m/e 282, 284, 286, 288, and 290, and by its ¹H n.m.r. spectrum, which shows clearly the presence of a methyl group, three alicyclic, and four aromatic hydrogen atoms.

mixture of the three isomers in approximate proportions (1) : (2) : (3) = 8 : 2 : 1. A small proportion of a fourth compound, probably 2-methyl-r-1,t-2,c-3,c-4-tetrachlorotetralin (4) recognised only by the appearance of a singlet at τ 5.3, was also present in each of the isomerised mixtures. Isomerisation of (1) and of (3) occurred very rapidly at

TABLE 2

Estimates of approximate product ratios in chlorination of 2-methylnaphthalene at 0 °C

Solvent	CHCl₃	CHCl₃	CHCl₃	CHCl₃ satd. with H₂O	CHCl₃	MeNO₂	PhCl	CHCl₃– Ph₄AsCl
Atmosphere	N₂	O₂	N₂	N₂	N₂	N₂	N₂	N₂
Illumination	Dark	Dark	Light	Dark	Dark	Dark	Dark	Dark
Catalyst					I₂			
Product proportions (%)								
1-Chloro-2-methylnaphthalene	58	61	54	63	75	50	62	89
Tetrachloride (1)	15	9	11	14	12	9	10	11
Tetrachloride (2)	16	16	11	18	13	4	15	0
Tetrachloride (3)	5	4	3	2	0	5	0	0
Unidentified	6	10	21	3	0	32	13	0

The second tetrachloride to be eluted was r-1,t-2,c-3,t-4-*tetrachloro-2-methyltetralin*, m.p. 135.5 °C. It exists in solution predominantly in conformation (3a) (Found: C, 46.8; H, 3.5; Cl, 49.2. C₁₁H₁₀Cl₄ requires C, 46.5; H, 3.6; Cl, 49.9%). Its ¹H n.m.r. and mass spectra are fully consistent with the given structure.

room temperature; the corresponding reaction of (2) was slower, but was complete after ca. 1 h. After 24 h, some decomposition of the equilibrium mixture had occurred under the further influences of aluminium trichloride, with blackening of the solution. The ¹H n.m.r. spectrum was poorly resolved, but included two methyl signals correspond-

ing with those which characterise 1,3- and 1,4-dichloro-2-methylnaphthalene. A third signal was also present in the same region of the spectrum.

Products of Partial Alkaline Dehydrochlorination.—It had been shown earlier [4] that the first stage of alkaline dehydrochlorination of the tetrachloride (1) is faster than the second, so it was expected that the intermediate chlorodichloride could be characterised by examination of the product of partial dehydrochlorination, as had proved to be

(4a)   (4b)
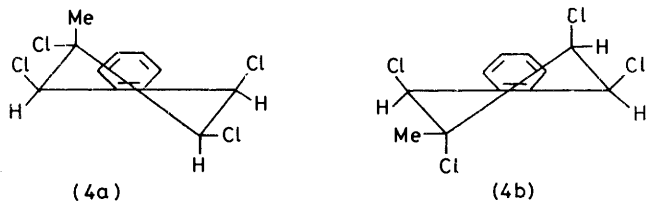
possible for other similar tetrachlorides.[8] Accordingly, when (1) was treated with $NaOCD_3$ in CD_3OH–$CDCl_3$ and the [1]H n.m.r. spectrum was scanned at intervals, alicyclic signals attributable to an intermediate were observed. The mixture was quenched at an appropriate point when most of the tetrachloride had undergone reaction. Extraction into $CDCl_3$ and washing with water gave a solution, the [1]H n.m.r. spectrum of which included signals at τ 4.8 (1 H, d, J 2 Hz), 5.3 (1 H, d, J 2 Hz), and 7.8 (3 H, s). These signals are consistent with those expected for the 4-H, 3-H, and CH_3 protons respectively of *trans*-1,3,4-trichloro-2-methyl-3,4-dihydronaphthalene (5), existing in solution predominantly in conformation (5b).

(5a)   (5b)
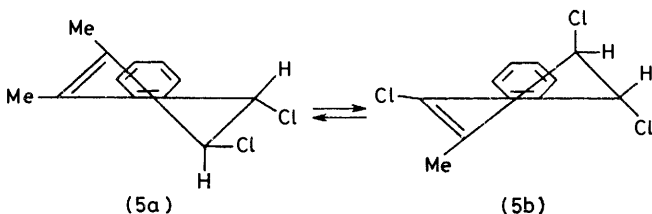
On further treatment with $NaOCD_3$, the intermediate was converted quantitatively into a mixture of 1,4- and 1,3-dichloro-2-methylnaphthalene as judged by [1]H n.m.r. spectroscopy. Dehydrochlorination was interrupted when no starting material was expected to be left, by extracting alkali from the reaction mixture with water. The proportions of the products were measured by [1]H n.m.r. spectroscopy; the reaction was then restarted, and stopped again after an appropriate interval. Results are given in Table 3.

TABLE 3

Proportions of products of successive partial dehydrochlorinations of *r*-1,*c*-2,*t*-3,*c*-4-tetrachloro-2-methyltetralin

Intermediate (%)	1,4-Dichloro-2-methyl-naphthalene (%)	1,3-Dichloro-2-methyl-naphthalene (%)
69	26	5
54	37	9
17	60	23

Treatment of the intermediate with aluminium chloride in nitrobenzene, on the other hand, gave exclusively 1,4-dichloro-2-methylnaphthalene. The intermediate was reasonably stable in solution overnight, but after 5 days it

had decomposed to give a mixture of 1,4- and 1,3-dichloro-2-methylnaphthalene.

Similar treatment of the other tetrachlorides gave no indication of the development of signals attributable to an intermediate chlorodichloride.

Products of Complete Alkaline Dehydrochlorination.—Full dehydrochlorination of the 2-methylnaphthalene tetrachlorides was carried out by treatment with excess of sodium methoxide at several concentrations in 4 : 1 methanol–acetone at 25°. The reagent had no effect over several days on the composition of the resulting product mixtures. These were recovered and analysed by g.l.c., giving the results summarised in Table 4. Good separation was obtained on a capillary column (18 m) coated with SE 30 at a

TABLE 4

Products of alkaline dehydrochlorination of the 1,2,3,4-tetrachloro-2-methyltetralins (1)—(3) with sodium methoxide in 80% methanol–20% acetone

		Proportions of dichloro-2-methyl-naphthalenes	
Compound	[NaOMe]/M	1,4-	1,3-
(1)	0.8	53	47
	0.04	84	16
	0.002	98	2
(2)	0.8	79	21
	0.04	83	17
	0.002	77	23
(3)	0.8	100	0
	0.04	89	11
	0.002	100	0

flow-rate of 0.5 cm³ s⁻¹ and a temperature of 125 °C. The peak attributable to 1,4-dichloro-2-methylnaphthalene was assigned by use of authentic material used as a reference sample.

The other dichloro-2-methylnaphthalene was obtained only as a mixture with the 1,4-isomer (6). Its identity as the 1,3- (7) rather than the 3,4-isomer (8) can be assumed from the fact that it is formed, along with (6), from the intermediate chlorodichloride (5) (Table 3 and accompanying

(6)   (7)   (8)
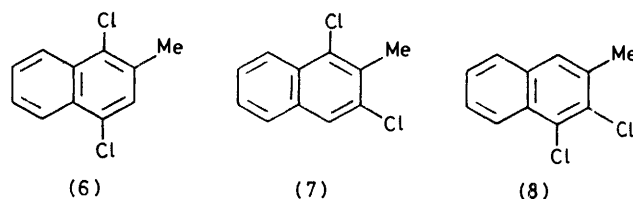
text). This structural assignment is consistent with its [1]H n.m.r. spectrum; this included singlets at τ 7.4 and 2.3 which integrated in the ratio of 3 : 1.

Kinetics of Alkaline Dehydrochlorination.—The rates of alkaline dehydrochlorination at 25° in 80% methanol–20% acetone were determined, as was described elsewhere,[8] potentiometric determination of liberated chloride ion in acetone being used to follow the progress of reaction. For each of the 2-methylnaphthalene tetrachlorides studied in this work, the second stage of elimination was found to be slower than the first. It was necessary, therefore, to determine the individual rate coefficients k_2^I and k_2^{II} for the two successive stages of dehydrochlorination. A method outlined by Swain [15] was used. Results are given in Table 5; some of these are means of several satisfactorily concordant measurements.

Solvolysis of the Intermediate.—In an earlier paper,[10] it was shown that *trans*-1,3,4-trichloro-3,4-dihydronaphthalene, the main intermediate formed in the alkaline dehydrochlorination of *r*-1,*c*-2,*c*-3,*t*-4-tetrachlorotetralin, underwent

TABLE 5

Rate coefficients (k_2/l mol^{-1} s^{-1}) for alkaline dehydrochlorination of some 2-methylnaphthalene tetrachlorides in 80% methanol–20% acetone at 25°

Tetrachloride [$C_{11}H_{10}Cl_4$]/M	[NaOMe]/M	$k_2{}^I$/l mol^{-1} s^{-1}	$k_2{}^{II}$/l mol^{-1} s^{-1}
(1), 0.000 95	0.0635	0.005 78	0.000 70
(1), 0.000 85	0.296	0.005 43	0.000 64
(2), 0.000 82	0.0127	0.247	0.097
(2), 0.000 86	0.006 34	0.275	0.113
(3), 0.0009	0.0631	0.000 455	0.000 141

solvolysis in methanol–acetone at a rate competitive with that of bimolecular reaction with sodium methoxide. We therefore examined the solvolysis of its analogue, the intermediate (5). The 2-methylnaphthalene tetrachloride (1) was dissolved in $CDCl_3$, several drops of $NaOCD_3$ solution were added, and the dehydrochlorination was followed in the usual way by ^1H n.m.r. spectroscopy. When the reaction was approximately half complete, $NaOCD_3$ was removed by extraction with D_2O, containing several drops of dilute nitric acid. The ^1H n.m.r. spectrum of the solution in moist chloroform was then examined over a period of some days. The results are shown in Table 6. They show

TABLE 6

Products of solvolytic decomposition of *trans*-1,3,4-trichloro-2-methyl-3,4-dihydronaphthalene (5) [derived from the tetrachloride (1)] in moist $CDCl_3$

|			Composition (%) of reaction mixture	
Time (days)	2-Methyl-naphthalene tetrachloride (1)	Intermediate (5)	1,4-Dichloro-2-methyl-naphthalene	1,3-Dichloro-2-methyl-naphthalene
0	9	59	32	Trace
7	13	17	70	Trace
14	13	0	87	Trace

that the tetrachloride does not solvolyse under these conditions, but the intermediate loses hydrogen chloride to give nearly exclusively 1,4-dichloro-2-methylnaphthalene.

DISCUSSION

(a) *Structures of the Tetrachlorides.*—The results described above confirm the previous assignment of the structure of the tetrachloride (1) in accord with the following argument. Two tetrachlorides (1) and (3) derived by addition to 2-methylnaphthalene have now been isolated, each having large coupling constants, $^3J_{3-H,4-H}$ 8.5 and 9.5 Hz, respectively. These two tetrachlorides must both have 3- and 4-H axially and pseudo-axially disposed. Four of the eight possible configurations could exist in a conformation having 3- and 4-H disposed in this way; they are (1a), (3a), (9), and (10).

It is known further that the two tetrachlorides which have been isolated are interconverted into the same mixture of tetrachlorides by treatment with aluminium trichloride in nitromethane. This reagent has been shown to act only on benzylic (1- and 4-) chlorine atoms and not upon chlorine atoms in the 2- and 3-positions.

The two compounds must therefore either be (1a) and (3a) or (9) and (10). In either of these pairs, one isomer [(3a) and (10)] has 1- and 4-H both pseudo-axial and therefore oriented as nearly as possible parallel to the

(9)   (10)
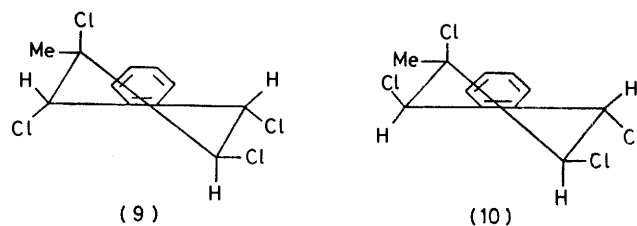
π-orbitals of the double bond and with a dihedral angle between these C–H bonds of nearly 180°. This is the situation in which long-range coupling between these protons would be expected to be seen in the ^1H n.m.r. spectrum. Such couplings have been observed in the spectra of the *r*-1,*t*-2,*c*-3,*t*-4- and *r*-1,*c*-2,*c*-3,*t*-4-tetrachlorotetralins analogous to (3a) and (10) respectively;[16] confirmatory details are included in SUP 22864. Of the 2-methylnaphthalene tetrachlorides having a large value of $J_{3,4}$, only the isomer having m.p. 135.5° shows this type of coupling ($^5J_{1-H,4-H}$ 1.2 Hz). Irradiation at the frequency of 1-H partly collapsed the signal for 4-H, and at the frequency of 4-H partly collapsed the signal for 1-H. The isomer (1), m.p. 99°, was found to have sharp signals for 1- and 4-H, with no indication of long-range coupling. This compound must, therefore, be either (1a) or (9), but if it were (9), then the isomer of m.p. 135.5° would dehydrochlorinate much more rapidly, since it would have to be assigned structure (10), with 1-H and 2-Cl respectively pseudo-axially and axially disposed.

It has been shown, however, that the compound of m.p. 135.5° is much less reactive with sodium methoxide than that having m.p. 99°; and that the latter does lose 1-H and 2-Cl in its first stage of dehydrochlorination. These relative rates of dehydrochlorination, taken together with the long-range {$^5J_{1-H,4-H}$} coupling observed in one isomer and not the other, are therefore inconsistent with assignment of the structures in the series which includes (9) and (10). Instead, they are wholly in accord with the assignment of the isomer having m.p. 99° as having structure (1a), undergoing relatively rapid dehydrochlorination in the first stage of this reaction and with no observable coupling between 1- and 4-H, and the isomer having m.p. 135.5° as having structure (3a), with slow dehydrochlorination in both stages and a relatively large value (1.2 Hz) of $^5J_{1-H,4-H}$.

The 2-methylnaphthalene tetrachloride, isolated as an oil, is shown by its isomerisation with aluminium trichloride to have the same relative configuration of 2- and 3-Cl as (1) and (3). It must therefore be either (2) or (4), each of which could exist in either of the two conformations shown. Any of these conformations would have a relatively low value of the major coupling, $^3J_{3-H,4-H}$; but only one, (2b), would show a long-range homoallylic coupling, $^5J_{1-H,4-H}$. Furthermore, only one conformer of (2) would be expected to have two fast stages of alkaline

dehydrochlorination. For these reasons, the isomer isolated as an oil is assigned structure (2), existing predominantly in conformation (2b).

(b) *Formation of the Tetrachlorides.*—It seems likely that the main products formed from 2-methylnaphthalene and chlorine in chloroform are obtained by heterolytic processes, since the proportions (Table 2) are changed only slightly by the presence of oxygen, nitrogen, or iodine, or by gentle illumination of the reacting mixture. The reaction resembles that of the heterolytic chlorination of naphthalene, in that it divides between substitution and addition (giving rather more substitution); the bulk of the tetrachlorides produced from both substrates are those in which the 2- and 3-chlorine atoms are *trans* to each other. Processes putting chlorine atoms in the 1- and 2- (or 3- and 4-) positions *trans* to each other are relatively more important for 2-methylnaphthalene than for naphthalene.

The *r*-1,*c*-2,*t*-3,*t*-4-tetrachloride (2) is analogous to naphthalene α-tetrachloride, and could be formed by *syn* 1,2- followed by *syn*-3,4-addition. The *r*-1,*c*-2,*t*-3,*c*-4-tetrachloride (1a) analogous to naphthalene δ-tetrachloride could likewise be the result of a first stage of *syn*-1,2-addition, followed in this case by a second stage of *anti*-addition. A possible interpretation of the diversion of the reaction away from the isomer (2) when tetraphenylarsonium chloride is present in the reaction mixture is that chloride ion catalyses *anti*-addition in the second stage of the reaction, and at the same time catalyses loss of hydrogen chloride from the intermediate dichloride. Other explanations based on competing 1,4-additions in the first stage of the reaction are, however, not excluded. The *r*-1,*t*-2,*c*-3,*t*-4-tetrachloride (3), analogous to naphthalene γ-tetrachloride, could be the result of two successive stages of *anti*-addition; it is possible, however, that this very minor component is formed by a homolytic reaction; catalysis by iodine or by tetraphenylarsonium chloride produces a reaction mixture from which this component is absent.

(c) *Conformational and Configurational Isomerism of the Tetrachlorides.*—For each of the isolated tetrachlorides, the main conformation in solution appears to be that which avoids having two substituents in a 1,3- or 2,4-diaxial relationship. This type of steric interaction would be present in (1b), (2a), or (3b) but not in (1a), (2b), or (3a), which are the forms actually adopted; and would be found also in either conformer of (4) which, if it is present in the reaction mixture after isomerisation with aluminium trichloride, certainly is relatively unstable thermodynamically.

As in examples discussed earlier,[10,11,14] only the benzylic chlorine atoms are labile and isomerise when any of these tetrachlorides are treated with aluminium trichloride. The *r*-1,*c*-2,*t*-3,*c*-4-tetrachloride is the thermodynamically favoured isomer at equilibrium; in this compound, unfavourable 1,2- and 1,3-interactions between large groups are minimised, and both 1- and 4-Cl are pseudo-axial and so not compressed against the 8- or 5-H atoms of the aromatic ring.

(d) *N.m.r. Spectra of the Tetrachlorides.*—The [1]H n.m.r. spectra of the tetrachlorides have already been discussed in relation to their structures, which they help to establish. Table 1 shows the effect of change in solvent on the spectra. It has been noted in an earlier paper[7] that the chemical shifts of the proton signals in the spectra of some analogous compounds vary with the solvent. Two types of solvent shift have been noted; some alicyclic signals are moved specifically to higher values of τ in deuterioaromatic solvents, and this has been attributed to the formation of weak, but oriented complexes in which specific hydrogen atoms lie within the deshielding zone of the aromatic ring. This type of shift is observed particularly in the spectra of the 2-methylnaphthalene tetrachlorides (2) and (3). Conflicting with this trend is a general tendency for the signals of the alicyclic protons to move to lower values of τ in more polar solvents, as shown by the comparison of the spectra in deuterioacetone as compared with deuteriochloroform. As the result of the combined changes, the visual appearance of the spectra can vary considerably with the solvent, as is evident for the tetrachloride (1).

The [13]C n.m.r. spectra of these isomers have been recorded, and support the structures assigned to them; presentation and discussion of them are deferred to a later paper.

(e) *Course of Dehydrochlorination of* r-1,c-2,t-3,c-4-*Tetrachloro-2-methyltetralin* (1).—When *r*-1,*c*-2,*t*-3,*c*-4-tetrachloro-2-methyltetralin (1) is treated with sodium methoxide, *trans*-1,3,4-trichloro-2-methyl-3,4-dihydronaphthalene (5) builds up as an intermediate which can be characterised from its [1]H n.m.r. spectrum as existing predominantly in conformation (5b). We have found in other examples that such dichlorodihydronaphthalenes prefer the conformation with the alicyclic chlorine atoms diaxially disposed, thus minimising unfavourable steric compressions between them, and between 4-Cl and 5-H.[8] We have found also that the dehydrochlorination of such compounds gives a mixture of products of loss of 3-H,4-Cl and of 4-H,3-Cl. In conformity with this, the chlorodichloride (5) is further dehydrochlorinated to give a mixture of 1,3- and 1,4-dichloro-2-methylnaphthalene, with the latter in excess (ratio *ca.* 1 : 1, Table 4).

The unimolecular decomposition of the chlorodichloride (5), whether under the catalytic influence of aluminium chloride or under solvolytic conditions, gives almost exclusively 1,4-dichloro-2-methylnaphthalene. A develping carbocationic centre can now be stabilised by conjugation not only with the aromatic ring but also with the double bond; and the axial disposition of the 3-Cl in (5b) ensures that loss of this, rather than of 4-Cl, predominates under conditions favourable for heterolysis.

In accordance with these results, the dehydrochlorination of the 2-methyltetralin (1) with excess of sodium methoxide gives dichloro-2-methylnaphthalenes in a ratio which can be changed, from 1,4 : 1,3 = 53 : 47 when the bimolecular (*E2*) reaction of the intermediate predominates, to 98 : 2 when only the first stage of the dehydrochlorination is bimolecular. These results

accord with, and confirm the conclusions reached elsewhere as to the course of dehydrochlorination of the corresponding (δ) naphthalene tetrachloride;[10] for the latter compound, the major course of dehydrochlorination gives 2,3-dichloronaphthalene, a route not available for its 2-methyl derivative (1).

The first stage of alkaline dehydrochlorination of (1) under standard conditions in 80% methanol–20% acetone at 25° ($k_2{}^I$ 0.0056 l mol^{-1} s^{-1}) is slower than that of r-1,c-2,t-3,c-4-tetrachlorotetralin ($k_2{}^I$ 0.1 l mol^{-1} s^{-1}) by a factor of ca. 18, and this difference can now be interpreted more confidently. Conformation (1a) is not able to undergo rapid elimination, and conformation (1b) is accessible from it only with the expenditure of additional energy which in free energy terms is ca. 7 kJ mol^{-1}. In a previous paper,[8] we calculated by using the value (8.4 Hz) of $^3J_{3\text{-H},4\text{-H}}$ in the ^{1}H n.m.r. spectrum of this compound and comparing it with the largest value (12.4 Hz) of ^3J observed in these highly chlorinated tetrachlorides that conformation (1b) might comprise 23% of the equilibrium mixture between these conformers in solution. We believe now, however, that calculations of this kind are suspect for tetralins containing large substituents, because of distortions resulting from intramolecular steric repulsions.[1,12] The implication for the present example would be that conformation (1a) is distorted (perhaps particularly by the 1,3-interactions 1-Cl,3-H and 2-Me,4-H) so that the dihedral angle between 3- and 4-H does not have the idealised value (ca. 170°) but instead has a value of ca. 145°.

The rate of the second stage of alkaline dehydrochlorination of (1) [i.e., of the alkaline dehydrochlorination of the naphthalene dichloride (5); $k_2{}^{II}$ 0.0007 l mol^{-1} s^{-1}] is close to what would be expected from the rate of dehydrochlorination of 1,2,4-trichloro-1,2-dihydronaphthalene, which is approximately that of the second stage of dehydrochlorination of r-1,t-2,c-3,t-4-tetrachlorotetralin (0.0017 l mol^{-1} s^{-1}).[3,10]

(f) Course of Alkaline Dehydrochlorination of r-1,c-2,t-3,t-4-Tetrachloro-2-methyltetralin (2).—This compound, as would be expected from its structure and main conformation (2b) in solution, undergoes rapid bimolecular dehydrochlorination in both stages of the reaction. The rate of the first stage ($k_2{}^I$ 0.26 l mol^{-1} s^{-1}) is rather faster that that for the first stage of dehydrochlorination of the corresponding unsubstituted tetrachlorotetralin (0.05 or 0.10 l mol^{-1} s^{-1}, depending on whether or not the rate of the second stage is similar to that of the first). A difference in this direction would be expected, since the latter tetrachloride exists predominantly in the conformation analogous with (2a), but from the products of alkaline dehydrochlorination reacts substantially through the conformation analogous with (2b).

The second-order rate coefficients for the alkaline dehydrochlorination of (2b), calculated throughout the liberation of two molecular equivalents of hydrogen chloride, are not constant. Their fall is consistent with the interpretation which we have adopted (Table 5), namely that the second stage of dehydrochlorination is

slower than the first ($k_2{}^{II}$ ca. 0.1 l mol^{-1} s^{-1}). An intermediate (either 1,r-3,c-4-trichloro-2-methyl-3,4-dihydronaphthalene or r-1,c-2,4-trichloro-2-methyl-1,2-dihydronaphthalene, with r-1,c-2,3-trichloro-2-methyl-1,2-dihydronaphthalene, or a mixture perhaps containing all three components) should build up during the course of dehydrochlorination to a maximum concentration of 27% of the concentration of the total products of elimination. We were unable to verify in the usual way from the ^{1}H n.m.r. spectrum after partial reaction that such an intermediate or mixture of intermediates was produced; this failure can reasonably be attributed to the small proportion of intermediates produced and to their instability under work-up prior to examination of the ^{1}H n.m.r. spectrum.

The final products of dehydrochlorination of the tetrachloride (2) were found to be 1,4- and 1,3-dichloro-2-methylnaphthalenes in the ratio 4 : 1, these proportions varying little with concentration of base. The corresponding naphthalene tetrachloride behaves similarly; it gives rather more 1,3-dichloronaphthalene, as might have been expected, since some of the product is derived from the conformation analogous with (2a) by loss of 2-H,1-Cl, a reaction impossible for the 2-methyl-substituted compound.

(g) Course of Alkaline Dehydrochlorination of r-1,t-2,c-3,t-4-Tetrachloro-2-methyltetralin (3).—This compound, having no alicyclic hydrogen and chlorine atoms trans to each other on adjacent carbon atoms, reacts slowly with alkali in both stages of dehydrochlorination ($k_2{}^I$ 0.000 455, $k_2{}^{II}$ 0.000 141 l mol^{-1} s^{-1}). These rates are less by small factors (5, 12) than those for the corresponding dehydrochlorinations of the analogous naphthalene tetrachloride. Since the rate for the second stage is not the same as that for the second stage of the reaction of the tetrachloride (1), the intermediate chlorodichloride is not (5). The reason why (3) reacts so slowly in the first stage of dehydrochlorination is probably the rigidity imposed by the introduction of the 2-methyl group, which prevents adjustment of its geometry towards that which would be favourable for elimination of 4-H,3-Cl. Very little 1,3-dichloro-2-methylnaphthalene is produced, whether high or low concentrations of base are used.

(h) Mass Spectra of the Tetrachlorides.—Details of these are given in SUP 22864. All three isomers have spectra and fragmentation patterns consistent with the proposed structures. The peaks occurring at highest mass (m/e 282, 284, 286, 288, and 290) are as expected for the molecular ion of a tetrachloride $C_{11}H_{10}Cl_4$. The remainder of each spectrum is characterised by prominent peaks occurring at intervals of 35 or 36 mass units, as expected for loss of Cl or HCl. A metastable peak at m/e 218 is associated with the formation from (1) and from (3) of $C_{11}H_{10}Cl_3{}^+$ by loss of Cl from the molecular ion. The peaks at m/e 172 and 174 require the loss of fragments having m/e 110, consistent with decomposition by the reverse Diels–Alder process [i.e., either loss of MeC(Cl) : CHCl or of HCl and MeC : CCl in succession]. This type of fragmentation has been recorded for other tetralins.[17,18]

and here competes with other modes of decomposition involving loss of Cl and of HCl. The three isomers have generally similar fragmentation patterns, the most notable difference being that in the spectrum of r-1,c-2,t-3,t-4-tetrachloride (2) the cluster of peaks at m/e 247, 249, and 251 (corresponding with loss of Cl from the molecular ion) is of relatively low intensity. This probably reflects conformational differences, but further comment would be speculative.

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