

Naphthalene Tetrachlorides and Related Compounds. Part V.¹ Chlorination of 1,5-Dichloronaphthalene; Conformations affected by Intramolecular Non-bonding Repulsions

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The chlorination of 1,5-dichloronaphthalene in chloroform or in dichloromethane is heterolytic in character, but gives little or no trichloronaphthalene. The main tetrachloride product is 1,1,2,3,4,5-hexachlorotetralin, previously thought to be its *t*-4-isomer. The latter compound has been prepared by isomerisation of the former with aluminium trichloride. The structures have been established by using ¹H n.m.r. spectroscopy together with reactions with aluminium trichloride and with sodium methoxide. The former tetrachloride exists in a deformed conformation as the result of intramolecular non-bonding repulsions. *trans*-1,2,4,8-Tetrachloro-1,2-dihydronaphthalene is an intermediate in the chlorination.

THE naphthalene tetrachlorides and their derivatives appear generally to exist in half-chair conformations, as is consistent with studies of their ¹H n.m.r. spectra,^{2,3} and this has been confirmed for selected cases by use of X-ray crystallography.^{4,5} One exception has been claimed; it has been suggested¹ that, because of intramolecular non-bonding repulsions involving the chlorine substituents, *r*-1,2,3,4,5-pentachlorotetralin exists in a distorted half-boat conformation.

Following Schütz and Hahnfeld's⁶ pioneer investigation of the naphthalene tetrachlorides, we have used the rates and products of alkaline dehydrochlorination to help in the necessary assignments of structure.^{3,7-10} More recently,^{11,12} we have found that isomerisation about the benzylic carbon atoms can also be diagnostic. Recognition of the possible consequences of internal strain has led us to reconsideration of the structures of derivatives of 1,5-dichloronaphthalene to which two of us¹⁰ earlier assigned structures on the basis of the vicinal coupling constants between the ¹H n.m.r. signals for the alicyclic hydrogen atoms.

EXPERIMENTAL

The methods and many of the materials have been described in earlier papers.^{1-3,7-12} Further details of some of the ¹H n.m.r. spectra are given in Supplementary Publication No. SUP 21132 (8 pp.),† together with the i.r. spectra of most of the new compounds described. 1,1,2,3,4,5-Hexachlorotetralin (1) ‡ (see Scheme), m.p. 84–86°, was

† For details of Supplementary Publications see Notice to Authors No. 7 in *J.C.S. Perkin II*, 1973, Index issue. Items less than 10 pp. are supplied as full-size copies.

‡ As usual, structures given in this paper imply also the enantiomer where chirality is possible. Evidence relating to the unusual conformation of this compound and the new structural assignment follows; we had previously¹⁰ regarded this compound as its *t*-4-isomer (2).

¹ Part IV, J. W. Barnett, K. R. Bedford, G. W. Burton, P. B. D. de la Mare, S. Nicolson, and H. Suzuki, preceding paper.

² P. B. D. de la Mare, M. D. Johnson, J. S. Lomas, and V. Sanchez del Olmo, *J. Chem. Soc. (B)*, 1966, 827.

³ G. Cum, P. B. D. de la Mare, J. S. Lomas, and M. D. Johnson, *J. Chem. Soc. (B)*, 1967, 244.

⁴ M. A. Lasheen, *Acta Cryst.*, 1952, 5, 593.

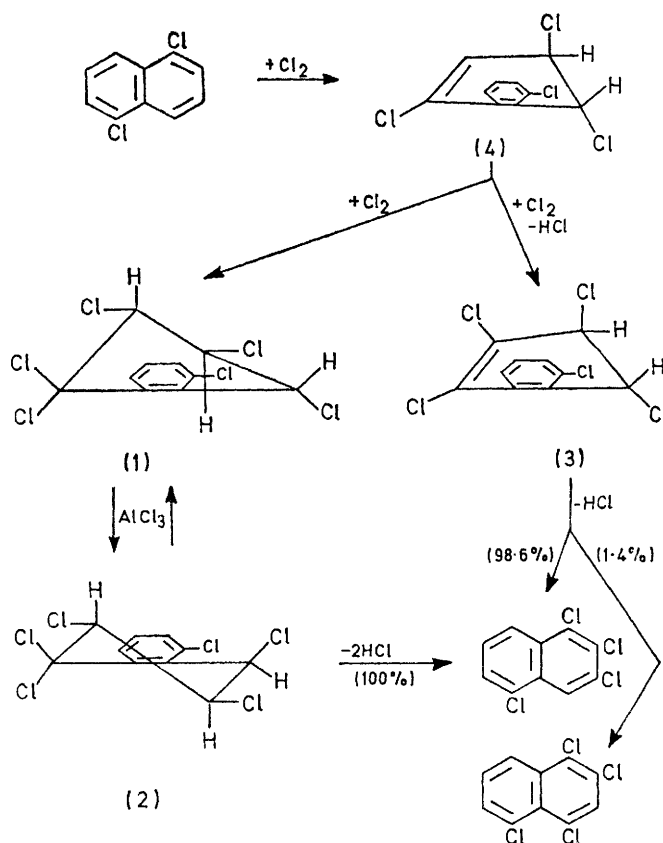
⁵ J. E. Godfrey and J. M. Waters, *Cryst. Struct. Comm.*, 1973, 2, 677.

⁶ F. Schütz and K. Hahnfeld, *Ber.*, 1952, 85, 131.

⁷ P. B. D. de la Mare, R. Koenigsberger, and J. S. Lomas, *J. Chem. Soc. (B)*, 1966, 834.

⁸ G. W. Burton and P. B. D. de la Mare, *J. Chem. Soc. (B)*, 1970, 897.

prepared^{10,13} from 1,5-dichloronaphthalene. The ¹H n.m.r. spectrum has been given previously,¹⁰ and details are included in Supplementary Publication No. SUP 21132.



SCHEME Inter-relationships between products derived from chlorination of 1,5-dichloronaphthalene

Its dehydrochlorination with sodium methoxide in methanol-acetone (80 : 20) was fast in the first stage and

⁹ K. R. Bedford, G. W. Burton, P. B. D. de la Mare, and H. Suzuki, *J.C.S. Perkin II*, 1974, 459.

¹⁰ P. B. D. de la Mare and H. Suzuki, *J. Chem. Soc. (C)*, 1968, 1159.

¹¹ K. R. Bedford, G. W. Burton, and P. B. D. de la Mare, *Tetrahedron Letters*, 1973, 3205.

¹² G. W. Burton, P. B. D. de la Mare, and M. Wade, *J.C.S. Perkin II*, 1974, 591.

¹³ O. Widman, *Bull. Soc. chim. France*, 1877, (2), 28, 505; A. Atterberg and O. Widman, *Ber.*, 1877, 10, 1841; *Bull. Soc. chim. France*, 1877, (2), 28, 513; W. P. Wynne, *J. Chem. Soc.*, 1946, 61.

slower in the second. The rate-coefficients for the two stages, $2.04 \times 10^{-3} \text{M-NaOMe}$ at 25° being used, were $k_2^I 6.7$ and $k_2^{II} 0.35 \text{ l mol}^{-1} \text{ s}^{-1}$. Partial dehydrochlorination gave an intermediate, the ^1H n.m.r. spectrum of which was identical with that of the known^{10,13} 1,2,3,4,8-pentachloro-1,2-dihydronaphthalene, which we now must formulate as having the *trans*- (3), rather than the *cis*-configuration, as we had previously speculated.¹⁰ The rate of dehydrochlorination of the latter compound was determined independently as being $0.32 \text{ l mol}^{-1} \text{ s}^{-1}$, in reasonable agreement with the indirect measurement. A 5-bond coupling (*ca.* 0.5 Hz) between 1- and 5-H, which was confirmed by double-resonance experiments, and could be observed directly in the spectrum in C_6D_6 , could be recognised in the spectra of the isolated product of chlorination and of the product of partial dehydrochlorination of the tetrachloride, and helped to confirm the identity of these substances.

Complete dehydrochlorination of (1) has already been shown¹⁰ to give mainly 1,2,3,5-tetrachloronaphthalene. Analysis of the products (g.l.c.) revealed the presence of a small amount (1.4%) of a further component which we consider to be 1,2,4,5-tetrachloronaphthalene.

The dichlorotetrachloride (1) (0.15 g) was dissolved in CDCl_3 (*ca.* 0.6 ml) and several drops of a concentrated solution of AlCl_3 in PhNO_2 were added. The solution was maintained at *ca.* -1° for several weeks. Periodically its ^1H n.m.r. spectrum was examined; conversion into a predominant proportion of a new isomer was noted. The products were worked up by adding the solution to water, extracting with ether, washing the ether layer several times with water, and removing the ether *in vacuo*. Aqueous ethanol was added to the residue and then removed *in vacuo* to assist the removal of the small amount of nitrobenzene present. Finally, CCl_4 was added to the residue and then removed *in vacuo* to help remove any remaining ethanol. The ^1H n.m.r. spectrum of the residue showed that the tetrachloride had undergone some dehydrochlorination [36%, assuming the products to be tetrachloronaphthalenes (see below)]; the remaining tetrachlorides were composed of the new isomer (96%) and the original isomer (4%).

The products of dehydrochlorination were separated from the tetrachlorides by preparative t.l.c. The material isolated from the lower band, shown by ^1H n.m.r. to contain the new tetrachloride, was recrystallised from *n*-pentane in the cold to give fine crystals of 1,1,*r*-2,*t*-3,*t*-4,5-hexachlorotetralin (2) (0.0349 g, 23% overall yield), m.p. $125-127^\circ$ (Found: C, 35.85; H, 1.95; Cl, 62.35. $\text{C}_{10}\text{H}_6\text{Cl}_6$ requires C, 35.45; H, 1.8; Cl, 62.75%). The ^1H n.m.r. spectrum ($J_{2,3} 11.6$, $J_{3,4} 3.5$ Hz) was very similar in the aliphatic region to that of 1,1,*r*-2,*t*-3,*t*-4-pentachlorotetralin,^{3,8} apart from the deshielding of 4-H, caused by the presence of 5-Cl, and was affected similarly by change of solvent from CDCl_3 to C_6D_6 .

The material obtained from the top band of the preparative t.l.c. plate was shown by g.l.c. to comprise predominantly 1,2,3,5-tetrachloronaphthalene, and after recrystallisation from cold *n*-pentane had m.p. $138-139^\circ$ (lit.,¹⁴ 141°); there was a minor peak with a considerably shorter retention time which, perhaps, corresponded to a trichloronaphthalene, but there was no peak corresponding to the presence of 1,2,4,5-tetrachloronaphthalene.

The alkaline dehydrochlorination of 1,1,*r*-2,*t*-3,*t*-4,5-hexachlorotetralin (2) differed from that of its isomer (1). It showed a simple kinetic form over the whole course of loss of two mol. equiv. of HCl, with no indication of the interven-

tion of an intermediate; k_2 (composite) $0.33 \text{ l mol}^{-1} \text{ s}^{-1}$. The sole product was 1,2,3,5-tetrachloronaphthalene.

Chlorination of 1,5-Dichloronaphthalene.—Further aspects of the chlorination of 1,5-dichloronaphthalene were elucidated. Reaction in CHCl_3 in the dark with chlorine (1 mol. equiv.; 13 days) gave a product, the ^1H n.m.r. spectrum of which (CCl_4) showed it to contain much unchanged starting material together with the expected (1) (29%), (3) (21%), and a further compound (50%) characterised by a quartet at $\tau 3.7$ (J 6 and 1 Hz) similar to that given by the aliphatic protons of *trans*-1,2,4-trichloro-1,2-dihydronaphthalene.¹⁵ The compound was stable to chromatography on silica gel, but we did not succeed in separating it from (3). Its properties are consistent with those of the proposed¹⁰ intermediate in the chlorination, *trans*-1,2,4,8-tetrachloro-1,2-dihydronaphthalene (4). Similar chlorination using chlorine (2 mol. equiv.) gave a product containing a much smaller proportion of this compound. In the ^1H n.m.r. spectra of the products from these reactions, weak signals attributable to the 2-H doublet of (2), present in trace amount, could be recognised.

The reaction in glacial acetic acid as solvent appeared to be considerably faster; the ^1H n.m.r. spectrum in CCl_4 of the products, recovered after a period of two days, showed not only the signals of the usual products, but also two acetoxy-singlets at $\tau 7.96$ and 7.83 , which comprised *ca.* 17% of the total non-aromatic signal.

No substitution products derived directly from 1,5-dichloronaphthalene were detected in the reaction mixtures from chlorination in chloroform. This feature was investigated further, since with 1-chloronaphthalene the absence of products of substitution distinguishes a homolytic from a heterolytic process.¹ Dichloromethane was used as solvent, and was passed through a column of activated alumina immediately before being used. Chlorine (1.4×10^{-3} mol) and 1,5-dichloronaphthalene (0.0988 g, 5.01×10^{-4} mol) in CH_2Cl_2 (21 ml) was allowed to stand in the dark (20 days). The solvent was then removed *in vacuo* and the residue was weighed. The ^1H n.m.r. spectrum (CCl_4) showed that *ca.* 32% of the 1,5-dichloronaphthalene had been consumed, forming the usual adducts, (1) (51%), (3) (32%), (4) (17%), and (2) (trace). The increased weight of the residue, calculated on the basis of this amount of reaction and these proportions of adducts (0.118 g) was in fair agreement with that actually found (0.124 g). The mixture of products was treated with NaOMe (0.14M) in methanol-acetone (80 : 20) at 25.6° for *ca.* 2 h. The products were analysed by g.l.c., and contained major amounts of 1,5-di-, and 1,2,3,5- and 1,2,4,5-tetra-chloronaphthalene, together with traces of two further products appearing in the chromatogram between the peaks for the di- and tetrachloro-naphthalenes. These are probably to be ascribed to 1,3,5- and 1,4,5-trichloronaphthalene formed by dehydrochlorination of (4), known to be present in the original reaction mixture.

In a similar experiment, chlorine (1.3×10^{-3} mol) was allowed to react with 1,5-dichloronaphthalene (0.089 g, 4.54×10^{-4} mol) in CH_2Cl_2 in which a trace of iodine had been dissolved. The solution was allowed to stand in the dark for 3.5 days, after which time the colour of iodine was still present. The solvent was then removed *in vacuo* and the residue carefully weighed, after taking the normal precautions to ensure removal of any remaining traces of solvent. The small amount of iodine present was not regarded as significantly affecting the weight of the residue. The ^1H

¹⁴ E. G. Turner and W. P. Wynne, *J. Chem. Soc.*, 1941, 243.

n.m.r. spectrum of the residue in CCl_4 showed that (1) (85%) and (3) (15%) were the only products detectable. The increased weight of the residue, calculated using these proportions of adducts (0.151 g) was in good agreement with the actual value found (0.149 g). Dehydrochlorination gave only 1,2,3,5- and 1,2,4,5-tetrachloronaphthalene in the expected proportions.

The same reaction, carried out in chloroform with a five-fold excess of chlorine, and also with a trace of iodine, was complete after *ca.* 16 h, and again gave only the tetrachloride (75%) and the dichloride (25%) as products. Thus, iodine not only markedly catalyses the reaction; it also causes a significant increase in the ratio of tetrachloride to dichloride formed to occur; from 1.6 : 1 in dichloromethane, in the absence of iodine, to 5.7 : 1 in the presence of iodine.

The photochemical chlorination of 1,5-dichloronaphthalene in CCl_4 or in CS_2 at room temperature was considerably slower than the corresponding reactions of naphthalene and of 1-chloronaphthalene. Signals attributable to (1) and to (4) were apparent in the ^1H n.m.r. spectrum of the products from incomplete chlorination. The reaction mixture also contained a substantial amount of a product (or products) not found in the 'dark' reaction with chlorine.

(Table 2) to show no evidence of the formation of an intermediate. The two stages of alkaline dehydrochlorination of a compound having the *t*-3,*c*-4 configuration shown in (1) would, on the other hand, be expected by similar analogies to be faster in the first than in the second stage, and therefore to allow the build-up of a recognisable intermediate in the reaction. Table 1 shows that Widman's compound behaves just in this way.

It is evident that non-bonding repulsions between the 5-Cl and the pseudo-axial 4-Cl in (2) would help to maintain the half-chair conformation. The related interaction in (1) is even more severe, since it involves instead pseudo-equatorial 4-Cl, and would tend to deform the flexible ring in the opposite direction. The resulting twist appears to be sufficient to reduce the coupling constants between the ^1H n.m.r. signals for 3- and 4-H to *ca.* 5 Hz; according to the Karplus relationship with the constants as estimated earlier,¹⁵ the relevant dihedral angle must have been reduced from *ca.* 170 to *ca.* 130°. The distortion is, however, not quite as great as that in the *r*-1,*t*-2,*c*-3,*t*-4,5-pentachlorotetralin, which adopts a

TABLE 1

^1H N.m.r. spectra, and rates of alkaline dehydrochlorination, of some substituted naphthalene tetrachlorides having *trans*-2,3-chlorine substituents

Compound	^1H N.m.r. spectrum (CDCl_3) ^a						Rates of alkaline dehydrochlorination ^b			Refs.	
	τ_1	τ_2	τ_3	τ_4	$J_{1,2}$	$J_{2,3}$	$J_{3,4}$	$k_2^I/1 \text{ mol}^{-1} \text{ s}^{-1}$	$k_2^{II}/1 \text{ mol}^{-1} \text{ s}^{-1}$		$k_2/1 \text{ mol}^{-1} \text{ s}^{-1}$
<i>r</i> -1, <i>c</i> -2, <i>t</i> -3, <i>t</i> -4-Tetrachlorotetralin	4.28	4.93	4.93	4.28	3.5	10.8	3.5			0.04	2, 7
1,1, <i>r</i> -2, <i>t</i> -3, <i>t</i> -4-Pentachlorotetralin		4.82	5.30	4.58		12.0	3.8			0.11	1, 3, 8
1,1, <i>r</i> -2, <i>t</i> -3, <i>t</i> -4,5-Hexachlorotetralin, m.p. 126–127° (2)		4.75	5.32	4.30		11.6	3.5			0.33	This paper
<i>r</i> -1, <i>t</i> -2, <i>c</i> -3, <i>t</i> -4-Tetrachlorotetralin	4.64	5.6	5.6	4.64	8.0	8.0	8.0	0.0022	0.0017		2, 7, and this paper
1,1, <i>r</i> -2, <i>t</i> -3, <i>c</i> -4-Pentachlorotetralin		5.41	5.40	4.68		11.7	9.2	2.0	0.03		1
1,1, <i>r</i> -2, <i>t</i> -3, <i>c</i> -4,5-Hexachlorotetralin, m.p. 84–86° (1)		5.55	5.04	4.37		11.1	5.0	6.7	0.35		10, and this paper

^a Tetramethylsilane as internal standard; coupling constants in Hz. ^b Solvent, methanol-acetone (80 : 20); temperature, 25°; k_2^I and k_2^{II} , second-order rate coefficients for liberation of first and second mol. equiv. of HCl respectively. For interpretation of the composite rate coefficients k_2 (uniform over the liberation of 2 mol. equiv. of HCl), see refs. 7 and 8.

The kinetics of alkaline dehydrochlorination of 1,1,*r*-2,*t*-3,*c*-4- and 1,1,*r*-2,*t*-3,*t*-4-pentachlorotetralin,^{1,8} structurally analogous to (1) and (2) respectively, were determined also and the results are included in Table 1.

DISCUSSION

Structures of the Tetrachlorides.—Structure (2), which we previously¹⁰ assigned to Widman's¹³ hexachlorotetralin, m.p. 84–86° [now considered to be (1)], is, we believe, correctly to be assigned to the more thermodynamically stable isomer, m.p. 126–127°, derived from (1) by treatment with aluminium trichloride in a dipolar aprotic solvent. The ^1H n.m.r. spectrum of the new compound (Table 1) is as expected for the structure indicated, and in particular the chemical shift of the signal for 1-H is no longer anomalous. Alkaline dehydrochlorination of the new compound takes the course expected for a compound having the *t*-3,*t*-4-configuration of (2), which would be expected by analogy with its structural analogues having similar configurations

'half-boat' form;¹ probably the difference arises because in (1) the geminal 1- Cl_2 forces an extra rigidity upon this end of the flexible ring; (1) in a half-boat form would also be subject to a severe non-bonding interaction between 1- and 4-Cl.

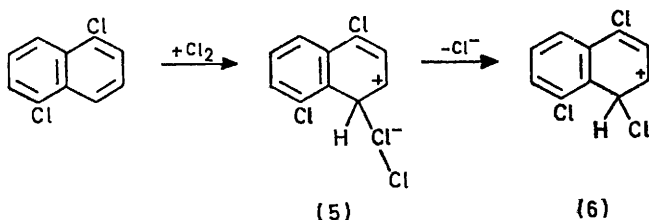
The first stages of the dehydrochlorination of all the compounds in Table 1, except *r*-1,*t*-2,*c*-3,*t*-4-tetrachlorotetralin, can involve loss of *trans*-2-H,1-Cl, as is consistent with the observed products. It is to be noted that the rates cover a considerable range, the greatest value being for the strained compound (1). It is probable that internal strain is as important as polar effects in determining the rates of these dehydrochlorinations.

The high value of τ_2 for Widman's compound is probably a reflection of the structural analogy with naphthalene γ -tetrachloride (*r*-1,*t*-2,*c*-3,*t*-4-tetrachlorotetralin; Table 1), and is no longer anomalous. It is noteworthy also that the value of τ_3 is significantly reduced in this dis-

¹⁵ G. W. Burton, M. D. Carr, P. B. D. de la Mare, and M. J. Rosser, *J.C.S. Perkin II*, 1972, 710.

torted structure, just as are the values for the corresponding signals in the other distorted structures described in Part IV.¹

Chlorination of 1,5-Dichloronaphthalene.—The chlorination of 1,5-dichloronaphthalene in chloroform or in dichloromethane appears to be heterolytic in character, since the product mixtures comprise the same compounds, whether or not iodine is present as catalyst, whereas photochemical chlorination includes other adducts in the reaction mixture. The general course of the reaction is confirmed to be the same as we described earlier,¹⁰ but the stereochemistry of the first stage of reaction has now been shown to involve *trans*- rather than *cis*-addition, giving intermediate (4) (see Scheme).



By analogy with arguments developed elsewhere,¹⁶ the initial sequence of events in the reaction of 1,5-dichloronaphthalene with molecular chlorine would be the formation of the intermediate (5), which then can trap chloride ion to give *cis*-adducts or lose chloride ion to give the further intermediate (6). If this sequence is accepted, several of the unusual features of the heterolytic chlorination of 1,5-dichloronaphthalene can be understood. The reaction gives very little products of direct substitution; proton loss from either (5) or (6) is inhibited by the difficulty encountered by the entering chlorine atom in approaching a tetrahedral arrangement about C-4 and then in reaching coplanarity with the aromatic ring because of steric repulsions involving 5-Cl. A similar steric inhibition of proton loss has been described by Zollinger¹⁷ in 8-substituted derivatives of 2-naphthol.

The change in stereochemistry from the predominantly *cis*-addition observed with naphthalene and 1-chloronaphthalene to nearly exclusively *trans*-addition arises similarly from the changed geometry of the intermediate (5), which instead of capturing the still-bound nucleophilic chlorine, instead loses chloride ion to form (6). This is probably the main source of *trans*-adduct. Iodine catalysis would be expected to favour the formation of (6), and so still further to favour *trans*-addition; it could also change the ratio of addition to substitution in the next stage of the reaction, and so alter the ratio in which (4) is converted into (1) and (3) (see Scheme), as is observed.

Structures of the 1,2-Dihydronaphthalenes.—The 1,2-dihydronaphthalenes (3) and (4) both have the *trans*-configuration, as is established by their relationships to

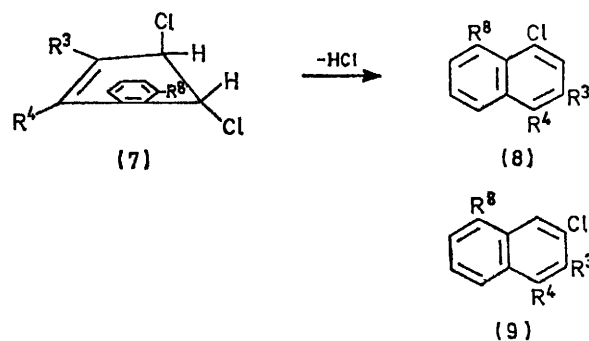
¹⁶ P. B. D. de la Mare, 'The Kekulé Symposium,' Butterworths, London, 1958, p. 219.

¹⁷ H. Zollinger, *Adv. Phys. Org. Chem.*, 1964, **2**, 163.

¹⁸ L. M. Jackman and S. Sternhell, 'Applications of Nuclear Magnetic Resonance in Organic Chemistry,' Pergamon, Oxford, 1969, 2nd edn., p. 333.

the tetrachloride (1). Since both of them have a small coupling constant between the signals for 1- and 2-H, they must exist predominantly in the conformations shown. The pseudo-equatorial rather than pseudo-axial disposition of 1-H in (3) is confirmed by the observation of long-range coupling (0.5 Hz) with the signal for 5-H. Spin-spin couplings through similar pathways are characteristic of essentially planar structures, and fall off rapidly in magnitude with departures from planarity.^{18,19} This coupling is not observed in the spectra of analogues not having 8-Cl, confirming the view that the 1...8 non-bonding interactions affect the conformations of such compounds. A strong preference for the *trans*-*eq,eq'*-disposition of hydrogens (and consequent *ax,ax'*-disposition of chlorines) is apparent generally in the *trans*-1,2-dichloro-1,2-dihydronaphthalene series,^{12,15} and contrasts with the situation in substituted dihydronaphthalenes bearing some other substituents.²⁰

TABLE 2
Bimolecular dehydrochlorinations of some
trans-1,2-dichloro-1,2-dihydronaphthalenes



Elimination with 0.043M-NaOMe
in methanol-acetone (80 : 20)

Substituents in (7)			Products		
R ³	R ⁴	R ⁸	Relative rate ^a	(8)	(9)
H	H	H	ca. 0.05 ^b	ca. 55 ^c	ca. 45 ^c
H	Cl	H	ca. 0.5 ^b	ca. 42 ^c	ca. 58 ^c
Cl	H	H	1.0	12	88
Cl	Cl	H	13	3	97
Cl	Cl	Cl	130	1	99

^a Expressed relative to *trans*-1,2,3-trichloro-1,2-dihydronaphthalene, $k_2 = 2.5 \times 10^{-3} \text{ l mol}^{-1} \text{ s}^{-1}$. ^b Obtained from a composite rate coefficient.¹² ^c Extrapolated values.¹²

In Table 2 we compare the rates and products of bimolecular dehydrochlorinations of *trans*-1,2-dichloro-1,2-dihydronaphthalene and some of its derivatives.

The effect of chlorine substitution on the bimolecular reaction is quite marked; the rate increases approximately 10-fold for each chlorine substituent introduced, and the proportion of the product (9) increases. These trends probably result from a combination of polar and steric influences.

It will be noted from Tables 1 and 2 that the rates of the dehydrochlorinations of 1,2-dihydronaphthalenes

¹⁹ A. F. Janzen and T. Schaefer, *Canad. J. Chem.*, 1971, **49**, 1818.

²⁰ M. J. Cook and N. L. Dassanayake, *J.C.S. Perkin II*, 1972, 1901; H. Lehmkuhl, *Chimia*, 1970, **24**, 182.

involving loss of *cis*-disposed hydrogen and chlorine can in the presence of suitable substituents exceed the rates of *trans*-dehydrochlorinations in the tetrahydronaphthalene series. For this reason, the rate sequence of the two

stages of dehydrochlorination of a substituted naphthalene tetrachloride is more useful as diagnostic of structure than are the individual rate coefficients.

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