

Naphthalene Tetrachlorides and Related Compounds. Part IV.¹ Photochemical Chlorination of 1-Chloronaphthalene

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The photochemical chlorination of 1-chloronaphthalene gives a mixture of dichlorides, which on further chlorination give several new 1-chloronaphthalene tetrachlorides. The structures of the latter have been elucidated by using ¹H n.m.r. spectroscopy and by isomerisation with aluminium trichloride as the 1,1,*r*-2,*t*-3,*c*-4- and 1,1,*r*-2,*c*-3,*t*-4-pentachlorotetralins; and the *r*-1,*t*-2,*t*-3,*c*-4,5-; *r*-1,*t*-2,*c*-3,*c*-4,5-; and *r*-1,*t*-2,*c*-3,*t*-4,5-pentachlorotetralins. Evidence is presented to suggest that the last compound, because of internal non-bonding strain, exists predominantly in an unusual 'half-boat' conformation. The results are compared with those obtained by heterocyclic chlorination, from which another isomer, *r*-1,*c*-2,*t*-3,*t*-4,5-pentachlorotetralin, is a minor product. The course and products of alkaline dehydrochlorination have been used to support some of the assignments of structure. The heterolytic chlorination of 1,2-dichloronaphthalene has been examined also; the major product is *r*-1,*t*-2,*c*-3,*t*-4,5,6-hexachlorotetralin, which also exists in a 'half-boat' conformation.

THE heterolytic chlorination of naphthalene gives substitution products together with a mixture of tetra-

chlorides, of which a major component, *r*-1,*c*-2,*t*-3,*t*-4-tetrachlorotetralin (1),[†] appears to have been formed by

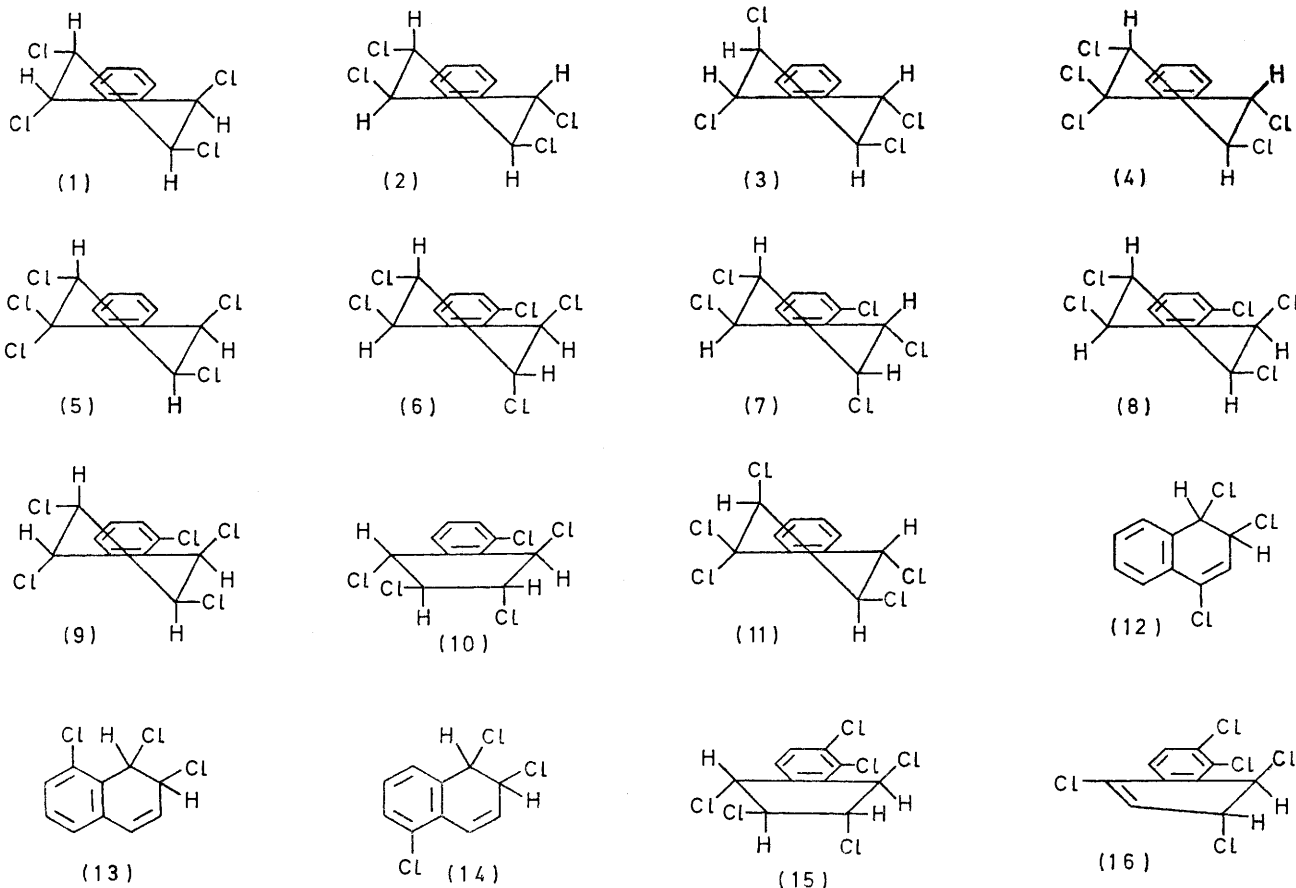
[†] Specification of stereochemistry follows the I.U.P.A.C. 1968 Tentative Rules E-3.1 to E-3.4.² Structures given in this paper imply the enantiomeric structure where chirality is possible.

¹ Part III, K. R. Bedford, G. W. Burton, P. B. D. de la Mare, and H. Suzuki, *J.C.S. Perkin II*, 1974, 459; the title of this series is now generalised still further.

² As described in *J. Org. Chem.*, 1970, **35**, 2849.

a succession of *cis*-1,2-additions.^{3,4} The corresponding photochemical chlorination, however, does not give (1); instead, the major components are the *r*-1,*t*-2,*c*-3,*t*-4- and the *r*-1,*t*-2,*t*-3,*c*-4-isomers (2) and (3) respectively which would be expected if this mode of chlorination proceeded characteristically with *trans*-stereochemistry. The heterolytic chlorinations of several 1-substituted naphthalenes have been shown^{1,5,6} also to give products of substitution together with adducts analogous to (1), but no careful investigation of the corresponding homolytic chlorinations has been made. In this paper we

Publication No. SUP 21132 (8 pp.); * the absorption pattern in the region 1670—2000 cm^{-1} can be used^{8,9} to determine the pattern of substitution in a substituted benzene, and in the present examples allowed distinction to be made between 1,2- and 1,2,3-substituted compounds. ^1H N.m.r. spectra were determined by using a Varian A-60 or T-60 instrument. Signals were assigned on the basis of their chemical shifts, and by the number and magnitudes of the vicinal coupling constants by which each signal was split. These were determined by inspection of the spectra where this was possible, and otherwise by computer-simulation of the spectra.¹ Confirmatory details are recorded in Supple-



describe the preparation, properties, and structures of compounds obtained by photochemically activated homolytic chlorination of 1-chloronaphthalene. A preliminary report which describes the properties of one of the isomeric tetrachlorides has been published elsewhere.⁷

EXPERIMENTAL

Most of the materials and methods have been described in earlier papers.²⁻⁶ I.r. spectra are given in Supplementary

* 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.

³ P. B. D. de la Mare, M. D. Johnson, J. S. Lomas, and V. Sanchez del Olmo, *J. Chem. Soc. (B)*, 1966, 827.

⁴ P. B. D. de la Mare, A. Singh, E. A. Johnson, R. Koenigsberger, J. S. Lomas, V. Sanchez del Olmo, and A. M. Sexton, *J. Chem. Soc. (B)*, 1969, 717.

mentary Publication No. SUP 21132 (8 pp.).* Alkaline dehydrochlorinations were carried out at 25° in methanol-acetone (80 : 20), with 0.04M-NaOMe except where otherwise stated.

1,1,*r*-2,*t*-3,*c*-4-Pentachlorotetralin (4).—In a typical reaction, chlorine (39 g, 0.55 mol) in CCl_4 (500 ml) was added to 1-chloronaphthalene (44 g, 0.27 mol), also dissolved in CCl_4 (200 ml), and the solution was irradiated with a Phillips sunlamp for 40 min. The ^1H n.m.r. spectrum of a

⁵ G. Cum, P. B. D. de la Mare, and M. D. Johnson, *J. Chem. Soc. (C)*, 1967, 1590.

⁶ G. W. Burton and P. B. D. de la Mare, *J. Chem. Soc. (B)*, 1970, 897.

⁷ K. R. Bedford, G. W. Burton, and P. B. D. de la Mare, *Tetrahedron Letters*, 1973, 3205.

⁸ C. W. Young, R. B. Duvall, and N. Wright, *Analyt. Chem.*, 1951, **23**, 709.

⁹ L. J. Bellamy, 'The Infrared Spectra of Complex Molecules,' Methuen, London, 1958, p. 52.

sample of the oily residue, obtained after the solvent was removed *in vacuo*, showed two complex patterns of absorption in the regions τ 5.8—4.3 and 2.9—2.0; the absence of the characteristic signal of 1-chloronaphthalene at τ 1.87 indicated that reaction was complete. Addition of n-hexane to the residue, followed by cooling, gave crystals (11.5 g) which were recrystallised from hot methanol to give 1,1,*r*-2,*t*-3,*c*-4-pentachlorotetralin,⁷ m.p. 137°. Its ¹H n.m.r. spectrum (ref. 7 and Supplementary Publication No. SUP 21132 *) allowed its structure and predominant conformation in solution to be assigned unambiguously as (4). The signal for 4-H was found to be further split by coupling with the adjacent aromatic hydrogen atoms, as has been observed also for related compounds possessing axial benzylic hydrogens. Its alkaline dehydrochlorination was, as expected, fast in the first stage (k_2^I 2.00 l mol⁻¹ s⁻¹, with 2.04×10^{-3} M-NaOMe) and slow in the second stage (k_2^{II} 0.032 l mol⁻¹ s⁻¹). The reaction gave 1,2,3- and 1,2,4-trichloronaphthalene in the ratio 97 : 3.

The pentachlorotetralin (4) (*ca.* 0.15 g) was dissolved in CDCl₃ (*ca.* 0.6 ml) and several drops of a concentrated solution of aluminium chloride in nitrobenzene were added. The solution was maintained at *ca.* -1° for 45 h. The ¹H n.m.r. spectrum showed that the reaction mixture then contained trichloronaphthalenes (52%), starting material (14%), and 1,1,*r*-2,*t*-3,*t*-4-pentachlorotetralin (5) (34%). Treatment of (5) with the same reagent has been reported previously⁷ to give a similar mixture.

r-1,*t*-2,*t*-3,*c*-4,5-Pentachlorotetralin (6).—Solvent was removed *in vacuo* from the mother liquors of the products of chlorination. The residue was dissolved in aqueous methanol. Crystals slowly appeared on cooling the solution; these were filtered off (6.3 g) and recrystallised from hot methanol. The small crystals (3.2 g) had m.p. 106.5—107° (Found: C, 39.4; H, 2.4; Cl, 58.6. C₁₀H₇Cl₅ requires C, 39.45; H, 2.3; Cl, 58.25%). The ¹H n.m.r. spectrum in CDCl₃ clearly indicated the presence of four aliphatic hydrogens and, from the integral, three aromatic hydrogens. The spectrum was notable for the low-field resonance at τ 4.42, assigned to 4-H, which occurred at a significant distance downfield from the corresponding absorption in related compounds without additional substituents in the aromatic ring. This deshielding of 4-H was attributed to its close proximity to 5-Cl. The large value of $J_{1,2}$ (10.0 Hz) indicated that 1- and 2-H were *trans*-diaxial, whereas the low value for $J_{2,3}$ (2.4 Hz) and the axial disposition of 2-H indicated that 2- and 3-H must be axial-equatorial. The low value for $J_{3,4}$ (3.4 Hz) would be consistent with either a diequatorial or an equatorial-axial relationship between 3- and 4-H. The chlorine atoms could then be disposed in either the *r*-1,*t*-2,*t*-3,*c*-4- (6) or *r*-1,*t*-2,*t*-3,*t*-4- configurations (7).

Treatment of the compound in CDCl₃ with a few drops of aluminium trichloride in nitromethane caused no observable change in its ¹H n.m.r. spectrum. Analogy with the corresponding naphthalene tetrachlorides^{7,10} suggests that (7) should isomerise under these conditions, whereas (6) should not; intramolecular repulsions are less unfavourable in the latter case. Accordingly, we consider that the compound is *r*-1,*t*-2,*t*-3,*c*-4,5-pentachlorotetralin. Examination by ¹H n.m.r. spectroscopy of the product of partial alkaline dehydrochlorination in CDCl₃ with NaOMe (*ca.* 5M) showed no evidence for the build-up of an intermediate.

* See footnote on p. 1909.

¹⁰ G. W. Burton, P. B. D. de la Mare, and M. Wade, *J.C.S. Perkin II*, 1974, 591.

This result supports the structural assignment as (6) rather than (7) by analogy with the behaviour of the analogous naphthalene tetrachlorides.¹⁰

r-1,*t*-2,*c*-3,*c*-4,5-Pentachlorotetralin (8).—Solvent was removed *in vacuo* from the remainder of the product of chlorination. The residue (60 g) was chromatographed on silica gel (450 g) deactivated with water (15%), using light petroleum containing dichloromethane (2—7%) as eluant. The progress of the chromatogram was monitored by t.l.c. and ¹H n.m.r. Over 100 fractions (*ca.* 15 ml) were collected. A large portion of the fractions (24—64) comprised a mixture of compounds. Fractions 65—75 contained 1,1,*r*-2,*t*-3,*c*-4-pentachloro-1,2,3,4-tetrahydronaphthalene. Fractions 78—93 were found to contain mainly one compound; the residue from these fractions was dissolved in n-pentane-dichloromethane and cooled; a small amount of fine crystals was obtained, m.p. 107°. The ¹H n.m.r. spectrum (CDCl₃) showed the presence of four aliphatic hydrogens and, from the integral, three aromatic hydrogens; a low-field signal at τ 4.34 was again assigned to 4-H. Large values for $J_{1,2}$ (8.7) and $J_{2,3}$ (12.1 Hz) implied that the pairs of hydrogens 1- and 2-H, and 2- and 3-H were both *trans*-diaxial. The low value for $J_{3,4}$ (3.3 Hz) and the axial disposition of 3-H indicated that 3- and 4-H were axial-equatorial. The compound could then be assigned as *r*-1,*t*-2,*c*-3,*c*-4,5-pentachlorotetralin (8) (Found: C, 39.6; H, 2.5; Cl, 58.3%). Treatment with aluminium chloride in nitromethane gave the expected extensive isomerisation; the major new signals accorded with those of *r*-1,*c*-2,*t*-3,*t*-4,5-pentachlorotetralin (9) described below.

r-1,*t*-2,*c*-3,*t*-4,5-Pentachlorotetralin (10).—The earlier fractions of the chromatogram were combined and a sample (6 g) was chromatographed on alumina (870 g) deactivated with HCl (1.5M; 5% w/w) light petroleum containing dichloromethane (1—6%) being used as eluant. A small amount of 1,4-dichloronaphthalene, followed by a small amount of 1,5-dichloronaphthalene, was found in the first fractions; the next set of fractions contained mainly one compound. The residue from these was dissolved in a mixture of n-pentane and dichloromethane and cooled; fine crystals were obtained, m.p. 53° (Found: C, 39.8; H, 2.4; Cl, 58.0%). The ¹H n.m.r. spectrum in CDCl₃, discussed in more detail later, showed the presence of four aliphatic hydrogens and, from the integral, three aromatic hydrogens ($J_{1,2}$ 9.3, $J_{2,3}$ 3.3, $J_{3,4}$ 2.7 Hz). These coupling constants are consistent with a number of structures, but reaction with aluminium trichloride in CDCl₃ containing MeNO₂ gave further information. The solution darkened, and its ¹H n.m.r. spectrum showed immediate changes in the aliphatic region (τ 4—6), which became very extensive after a period of *ca.* 10 min. The reaction was quenched with water after *ca.* 20 min, and the solution was extracted several times with small amounts of water and finally D₂O to remove the catalyst and the nitromethane. The ¹H n.m.r. spectrum of the solution showed it to contain (8) and (9), with the former in slight preponderance, and only a small amount of the original isomer. It was apparent from the early spectral changes that (8) was formed prior to (9). A slight amount of decomposition also accompanied the reaction.

These changes show that the original pentachlorotetralin is neither (6) nor (7), but instead is a relatively thermodynamically unstable isomer from the series of compounds to which (8) and (9) belong; all these compounds can be converted into an equilibrium mixture by geometric

isomerisation about the 1- and 4-positions. It must therefore be *r-1,t-2,c-3,t-4,5-pentachlorotetralin*, existing predominantly in the strained conformation (10).*

1,1,r-2,c-3,t-4-Pentachlorotetralin (11).—It was suspected that further new compounds were present, together with mixtures of the known compounds, in some chromatographic fractions. Fractional crystallisation of some samples from a mixture of *n*-pentane and dichloromethane yielded a small amount of a crystalline compound. Its ¹H n.m.r. spectrum in CDCl₃ showed it to have three aliphatic and four aromatic hydrogens, with an absorption at τ 2.2–1.8, characteristic of an aromatic hydrogen opposite a geminal dichloro-substituted carbon atom, as found in earlier isomeric examples, also present. The aliphatic sub-spectrum was an ABC multiplet in both CDCl₃ and (CD₂)₂CO; however, in C₆D₆ the resonances of the individual hydrogens could be recognised and were treated by approximate first-order analysis. Improved values for the parameters of the aliphatic portion of the spectrum were obtained from the computer-simulated spectrum, which matched each line of the actual spectrum with excellent precision (difference \gt 0.05 Hz). From the coupling constants ($J_{2,3}$ 2.5, $J_{3,4}$ 8.9 Hz), the compound was tentatively assigned as *1,1,r-2,c-3,t-4-pentachlorotetralin* (11). Its ¹H n.m.r. spectrum showed no evidence of isomerisation on treatment with aluminium trichloride in nitromethane for 7 days at room temperature.

Heterolytic Chlorination of 1-Chloronaphthalene; Formation of r-1,c-2,t-3,t-4,5-Pentachlorotetralin (9).—In a complementary investigation, the chlorination of 1-chloronaphthalene in chloroform, catalysed by a trace of iodine, was studied. Addition of chlorine was found to comprise 44% of the reaction. 1,4-Dichloronaphthalene and the well-known ⁶ *1,1,r-2,t-3,t-4-pentachlorotetralin* (5) were, as expected, the main products; there was, however, a small amount of another tetrachloride which comprised *ca.* 16% of the total adduct. Fractional crystallisation followed by chromatography gave a little *1,1,r-2,t-3,c-4-pentachlorotetralin* (4), and *r-1,c-2,t-3,t-4,5-pentachlorotetralin* (9), m.p. 150.5–151.5° (Found: C, 39.65; H, 2.35; Cl, 57.45%). Its ¹H n.m.r. spectrum was similar to, but not identical with, that of *1,2,3,4-tetrachloro-5-chloromethyltetralin* ⁵ in CDCl₃, and could be reproduced to a good approximation by using a large value for $J_{2,3}$ (11.2 Hz) and small values (3.7 and 3.4 Hz) for $J_{1,2}$ and $J_{3,4}$ respectively. On treatment with AlCl₃ in nitromethane, it was converted slowly into an equilibrium mixture containing (8) (56%) and (9) (44%). These results establish that it has the structure and predominant conformation shown in (9).

Intermediate Dichlorides.—These were investigated in outline only. Excess of 1-chloronaphthalene was dissolved in CS₂. The solution was cooled to *ca.* –70°, and to it was added a cooled solution of Cl₂. The ¹H n.m.r. spectrum of the product obtained after several minutes irradiation was largely free from tetrachlorides; it included an absorption pattern recognisable as that of *trans-1,2,4-trichloro-1,2-dihydronaphthalene* ¹¹ (12). From the ratio of aliphatic to olefinic absorption it could be calculated that this compound comprised 34% of the total dichlorides, and this value was confirmed within experimental error by comparison of the ratio of the integral of the aliphatic signals from this dichloride to that of the signals from other di-

chlorides. The remaining chloro-dichlorides must then be compounds in which addition has occurred to the unsubstituted ring of 1-chloronaphthalene. A singlet at τ 4.47 was considered to be that of the 1-H of 1,2,8-trichloro-1,2-dihydronaphthalene (13), shifted downfield by the *peri*-chlorine substituent. The integral of this signal was not sufficiently large to account for all the remaining dichloride; probably therefore, *trans-1,2,5-trichloro-1,2-dihydronaphthalene* (14) is present also.

Heterolytic Chlorination of 1,2-Dichloronaphthalene.—The chlorination of 1,2-dichloronaphthalene (10 g) with chlorine (6.3 g) in chloroform (150 ml) in the dark for two days gives products of substitution, together with two tetrachlorides, which were separated by chromatography and fractional crystallisation. The major product had m.p. 73–74° (Found: C, 35.6; H, 1.7; Cl, 62.6. C₁₀H₆Cl₆ requires C, 35.45; H, 1.8; Cl, 62.75%). Its ¹H n.m.r. spectrum ($J_{1,2}$ 9.1, $J_{2,3}$ 3.1, $J_{3,4}$ 2.9 Hz) was very similar to that of *r-1,t-2,c-3,t-4,5-pentachlorotetralin*. The compound is therefore considered to be *r-1,t-2,c-3,t-4,5,6-hexachlorotetralin*, existing in the strained conformation (15) analogous to (10). Its isomerisation, initiated with a few drops of a concentrated solution of aluminium trichloride in nitrobenzene, was slow, requiring 10 days for complete reaction, but eventually it underwent changes similar to those undergone by (10). Its dehydrochlorination with NaOMe (2.04 \times 10⁻³M) in methanol-acetone (80 : 20) proceeded in two stages, with rates k_2^I 1.6 and k_2^{II} 0.018 l mol⁻¹ s⁻¹. Partial dehydrochlorination gave an intermediate with a ¹H n.m.r. spectrum consistent with its formulation as *trans-1,2,4,7,8-pentachloro-1,2-dihydronaphthalene* (16), $J_{1,2}$ 2.2, $J_{2,3}$ 6.9 Hz.

DISCUSSION

Course of Photochemical Chlorination.—The course of the photochemical chlorination of 1-chloronaphthalene appears, from the intermediates and products identified in the reaction mixture, to follow the pattern observed for naphthalene.³ No substitution products are formed, and intermediate dichlorides can be recognised in the partly chlorinated product obtained by reaction at low temperature. Since all the intermediate produced by attack on the substituted ring was accounted for as the *trans*-dichloride (12), no initial attack occurs at the 1-position, and the amount of (12) formed (34%) suggests that attack on unsubstituted α -positions is nearly indiscriminate.

Further reaction of (12) then proceeds to give the expected products, (4) and (11), of a second stage of *trans*-addition, both of which were identified in the products of reaction with two molecular equivalents at room temperature.

The intermediates (13) and (14) also give the expected products of further *trans*-addition, (6) and (10), both of which were identified as components of the reaction mixture obtained by photochemical chlorination at room temperature. Under these conditions, naphthalene gives a small proportion of products which could be formed by *cis*-addition; and accordingly, we isolated the tetrachloride (8), which could be formed by *cis*-

* In considering these geometric isomerisations, one should remember that these compounds have all been obtained as mixtures of enantiomers.

¹¹ G. W. Burton, M. D. Carr, P. B. D. de la Mare, and M. J. Rosser, *J.C.S. Perkin II*, 1972, 710.

addition to *trans*-1,2,5-trichloro-1,2-dihydronaphthalene (14). We did not succeed in isolating the corresponding product from (13), *r*-1,*c*-2,*t*-3,*c*-4,5-pentachlorotetralin, but it may well have been present in the reaction mixture.

Although we cannot exclude completely that some reaction might have proceeded by way of the *cis*-analogues of (13) and (14), we did not detect the formation of (9) in the reaction product, and so think that these routes are unlikely to have been significant.

Course of Heterolytic Chlorination.—The products of heterolytic chlorination of 1-chloronaphthalene, like those of naphthalene, differ from those of homolytic chlorination not only because products of substitution are formed in major amount (56%), but also in the stereochemistry of the adducts. The main product of addition to the already substituted ring is not (4) or (11) (products obtainable by homolytic *trans*-addition) but instead (5), which could be formed by way of an initial *cis*-3,4-addition. We have now isolated also a product of addition to the unsubstituted ring; and this is not (6), (10), or (8), products of initial *trans*-3,4-addition, but instead is (9), formed by an initial *cis*-5,6- or 8,7-addition.

Isomerisation by Aluminium Trichloride.—The results obtained by treatment of the various chlorotetrachlorides with aluminium chloride present a pattern which is consistent with that obtained^{7,10} for the naphthalene tetrachlorides. The structures of the *gem*-dichlorides (4), (5), and (11) have been assigned on the basis of the ¹H n.m.r. spectra. Isomerisation of (4) gives (5), and the ratio by which the latter predominates (2.4 : 1) is a measure of the preference of the (4-*ax'*-Cl, 4*eq'*-H) over the (4*eq'*-Cl, 4*ax'*-H) arrangement adjacent to a (3*eq*-Cl, 4*ax*-H) group; it results almost certainly from relief of non-bonding strain between the 4-Cl and the 5-H atoms. Attempted isomerisation of (11) gives no evidence for isomerisation. Neither (4) nor (5) is formed, and (11) is not formed from either (4) or (5), results which confirm that the result of treatment with aluminium trichloride involves only geometric isomerisation about the benzylic carbon atoms. That (11) is unchanged accords with the fact that the analogous naphthalene ϵ -tetrachloride¹⁰ (3) is also unchanged; in both series the all-*cis*-tetrachloride remains elusive, and presumably is thermodynamically unstable relative to its isomers under treatment with aluminium trichloride.

For the products of addition to the unsubstituted ring of 1-chloronaphthalene, we have in part used the results of treatment with aluminium trichloride to assign structures, so in discussing the results it is important to avoid circular arguments. The isomer (6) can be assigned unambiguously to the *r*-1,*t*-2,*t*-3-series. It is unchanged on treatment with aluminium trichloride [and is not formed on similar treatment of any of its isomers (8)—(10)]; so we presume that it is the

¹² P. B. D. de la Mare and H. Suzuki, *J. Chem. Soc. (C)*, 1968, 1159.

r-1,*t*-2,*t*-3,*c*-4-5-compound by analogy with the similar behaviour of naphthalene ϵ -tetrachloride and of (11) above. The isomers (8)—(10) are interconverted (and partly dehydrochlorinated) with aluminium trichloride. Since the structures of (8) and (9) can be assigned unambiguously from their ¹H n.m.r. spectra, (10) can also be assigned to the *r*-1,*t*-2,*c*-3-series. The predominant conformations and relative stabilities are as expected; in all these compounds the 4-Cl atom displays a marked preference for the *ax'*-position, thus relieving as far as possible the non-bonding repulsions between the 4- and 5-Cl substituents.

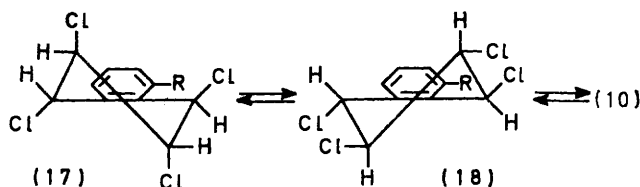
Because of this strain, the *r*-1,*t*-2,*c*-3,*t*-4,5-isomer, analogous in structure to naphthalene γ -tetrachloride (2), cannot adopt the conformation (18; R = Cl) preferred by the latter compound (2), *i.e.* (18; R = H). In the alternative half-chair conformation (17; R = Cl), however, there are two relatively unfavourable 1,3-Cl...Cl non-bonding repulsions. Accordingly, it seems from its ¹H n.m.r. spectrum that this conformation is not adopted either; instead, the strained 'half-boat' conformation (10) is preferred. This is the first example of a naphthalene tetrachloride to be recognised as existing in a conformation other than the half-chair arrangement, and its structure is discussed in the next section.

¹H N.m.r. Spectra.—The lower-field absorptions of the aliphatic signals of the various naphthalene tetrachlorides and their derivatives have been assigned as those of the hydrogens immediately adjacent to the aromatic ring. This has been verified by deuterium labelling in two cases.¹²

The asymmetry introduced into the isomers of 1,2,3,4,5-pentachlorotetralin by the presence of 5-Cl greatly assisted the assignment of configuration in these compounds. The proximity of 5-Cl resulted in the deshielding of 4-H, whose chemical shift is often coincident with that of 1-H in the ¹H n.m.r. spectra of the naphthalene tetrachlorides. The absorptions of the aliphatic hydrogens were then usually amenable to first-order analysis. For each isomer this also led to the detection of long-range coupling between the axial 1-H and its adjacent aromatic proton. Thus the long-range splittings of the signals belonging to 1-H of the isomers of 1,2,3,4,5-pentachlorotetralin revealed variations in the intensities and line-widths which were anomalous, considering the small value of the coupling constant and the large chemical shift difference of the aromatic and aliphatic protons involved. This was most obvious in the spectrum of *r*-1,*t*-2,*c*-3,*t*-4,5-pentachlorotetralin (10) in CDCl₃, in which both signals of the doublet belonging to 1-H were split into apparent 1 : 1 : 2 triplets. It seemed that the presence of an additional long-range coupling, involving 1- and 6-H, would most probably account for this effect.¹³ This was confirmed by double

¹³ L. M. Jackman and S. Sternhell, 'Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry,' Pergamon, Oxford, 1969, 2nd edn., pp. 330ff; typical values of coupling constants between benzylic methyl protons and *ortho*- and *para*-protons are 0.6–0.9 and 0.5–0.6 Hz respectively. Values for *meta*-coupling are smaller (<0.4 Hz).

irradiation at the expected position of resonance of 6-H; both triplets belonging to 1-H then became doublets ($J_{1,8}$ 1.1 Hz). Also, approximate computer-simulation of the tightly-coupled aromatic resonance, with inclusion of appropriate values for the long-range coupling between 1- and 8-H and 1- and 6-H, reproduced the non-first-order splitting observed in the well-separated resonance of 1-H, thus apparently confirming the origin of the phenomenon. In the ^1H n.m.r. spectrum of the compound in C_6D_6 , however, it was possible to assign the resonances of all seven hydrogens. Inspection of the individual aromatic resonances confirmed beyond doubt the suspected origin of the long-range couplings with the aliphatic hydrogens; double-resonance experiments enabled unambiguous assignments of the couplings to be made and led to values for $J_{1,8}$ (1.2), $J_{1,6}$ (0.8), and $J_{4,8}$ (0.6 Hz). The fine structure of each signal of 1-H now appeared as a 1 : 2 : 1 triplet, as expected for two closely similar coupling constants. Precise values for the parameters of the aromatic hydrogens and their



associated long-range coupling constants were obtained by computer simulation of the entire aromatic portion of the spectrum; each signal was matched with excellent precision.

Details of the spectrum are given in Supplementary Publication No. SUP 21132 and accord with the unusual conformation (10) assigned to this compound. This highly asymmetric structure would be expected to exhibit quite different chemical shifts for each of its alicyclic hydrogens, as is found; and inspection of the model shows that the dihedral angles between the various vicinal hydrogens are, indeed, consistent with the approximate values implied by the individual vicinal

coupling constants. In particular, it can be seen that the *trans*-configuration of 2- and 3-H, shown in all other compounds through a large vicinal coupling constant, is no longer discernible by this means, because of the low value of the corresponding coupling constant. The near perpendicularity of 1-H to the aromatic ring is confirmed by the observation of long-range coupling with the *ortho*-(8-H) and *para*-(6-H) hydrogens in the adjacent aromatic ring;¹³ slightly smaller values were also observed for the pseudo-axial hydrogens in the half-chair conformations of its isomers. The near coplanarity of the equatorial 4-H with the aromatic ring was confirmed by the observation of a long-range coupling¹³ with 8-H. Also consistent with the unusual conformation of the compound is the long-range coupling observed between 2- and 4-H, the configuration of which the model shows to be approximately in a **W** like relationship.^{13,14}

It is interesting to note that ^1H n.m.r. spectroscopy has been used to show that constraint of a different nature in methyl substituted *cis*-cyclohex-4-ene-1,2-dicarboxylic anhydrides causes these compounds to adopt half-boat conformations.¹⁵

The major adduct (15) formed by heterolytic chlorination of 1,2-dichloronaphthalene has a ^1H n.m.r. spectrum in the alicyclic region similar in all essential details to that of (10), and so is regarded as having the same stereochemistry. It isomerised similarly on being treated with aluminium trichloride, and its behaviour on alkaline dehydrochlorination also supports our assignment of structure: partial reaction gives an intermediate dihydronaphthalene, the ^1H n.m.r. spectrum of which is consistent with its identification as the *trans*-dichloride (16). The rates of both stages of alkaline dehydrochlorination are fast, as is consistent with the strained ground states of the dichlorotetralin and of the intermediate derived from it.

We thank Mr. D. Calvert for technical assistance, and the U.G.C. for a postgraduate scholarship (to K. R. B.).

[4/1250 Received, 24th June, 1974]

¹⁴ J. D. Remijnse, B. G. M. Vandeginste, and B. M. Wepster, *Rec. Trav. chim.*, 1973, **92**, 804.

¹⁵ H. Werner, E. Kleinpeter, A. Zshuncke, and G. Mann, *Org. Magnetic Resonance*, 1973, **5**, 179.