Dehydrochlorination of Some Naphthalene Tetrachlorides and Related Compounds. Part III.[1] Structure and Dehydrochlorination of a 1,2,3,4-Tetrachloro-1-phenyltetralin

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Chlorine reacts with 1-phenylnaphthalene in chloroform to give, among other products, a tetrachloride which has been characterised from its ^{1}H n.m.r. spectrum as r-1,c-2,t-3,t-4-tetrachloro-1-phenyltetralin. On alkaline dehydrochlorination, it gives 2,3-dichloro-1-phenylnaphthalene almost exclusively; when heated in carbon disulphide or when treated in nitromethane with an excess of aluminium trichloride, it gives 2,4-dichloro-1-phenylnaphthalene and 2,3-dichloro-1-phenylnaphthalene in a ratio of ca. 2 :1 or greater. The mechanistic implications of these results are discussed.

WE have discussed previously the isomerism, stereo-chemistry, and alkaline dehydrochlorination of some naphthalene tetrachlorides.[1-4] The structural factors that affect the course and rates of these reactions are only partly understood; and, though some other compounds in this series have been prepared, few (if any) have been characterised adequately. 1-Phenylnaphthalene tetrachloride is of interest because of the possible steric influence of the bulky phenyl group, which may also by its conjugating effect favour heterolysis of the C(1)–Cl bond. We now describe some chemical properties of one geometric isomer of this compound.

EXPERIMENTAL

Some of the materials and methods have been described in earlier papers.[1-4] Nitromethane (B.D.H.) was dried

(CaCl$_2$) and fractionally distilled in vacuo; b.p. 101° at 760 mmHg. Carbon disulphide (B.D.H., A.R.), had b.p. 46°.
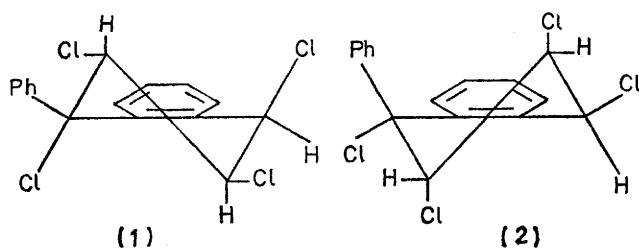
1-Phenylnaphthalene Tetrachloride.—Crude 1-phenyl-naphthalene (16 g), prepared by Weiss' method,[5] was chromatographed on a column of deactivated alumina (280 g), with light petroleum (b.p. 50—70°) as eluant. Fractions free from major amounts of less unsaturated impurities as judged by ^{1}H n.m.r. spectra and by t.l.c. were combined, and a known weight of the resulting viscous oil was dissolved in chloroform. To this solution was added slowly a solution of chlorine (ca. 1·5 mol. equiv.) in chloroform. The mixture was then evaporated in vacuo. Light petroleum (b.p. 50—70°) containing a little methylene chlorine was added, and the remaining solid was filtered off and recrystallised from n-pentane–methylene chloride to give r-1,c-2,t-3,t-4-*tetrachloro*-1-*phenyltetralin* as white

[1] G. W. Burton and P. B. D. de la Mare, *J. Chem. Soc. (B),* 1970, 897 is considered as Part II; the title of this series is now more general.

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

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

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

[5] R. Weiss, *Org. Synth.,* Coll. Vol. III. 1955, p. 729.

needles, m.p. 186—188·5° (16% based on 1-phenylnaphthalene) (Found: C, 55·7; H, 3·5; Cl, 40·5. $C_{16}H_{12}Cl_4$ requires C, 55·5; H, 3·5; Cl, 41·0%), τ [$(CD_3)_2SO$] (first-order analysis) 4·95 (1H, d, J 11·6 Hz), 4·60 (1H, q, J 11·5 and 3·2 Hz), 3·90 (1H, d, J 3·2 Hz), and 3·2—2·4 (9H, m). The ABC n.m.r. spectra of solutions in $CDCl_3$ and in C_6D_6 required computer-simulation, which was carried out by using a version [6] of the program LAOCN3 modified by Dr. G. A. Bowmaker to run on a Burroughs B6700 computer and to include a sub-routine [7] for plotting calculated spectra on a line-printer. The following values for the input parameters reproduced the spacing and intensities of the signals with excellent precision: in $CDCl_3$, ν_3 301·50, ν_4 330·30, $J_{2,3}$ 11·00, $J_{2,4}$ −0·68, $J_{3,4}$ 3·72 Hz; in C_6D_6, ν_2 310·06, ν_3 290·26, ν_4 295·10, $J_{2,3}$ 11·70, $J_{2,4}$ −0·59, $J_{3,4}$ 3·60 Hz. These spectra accord (see Discussion) with the formulation of the tetrachloride as (1). The magnitude of $J_{2,3}$ indicates that very little of the alternative possible conformation (2) is present in the equilibrium mixtures in solution.

(1)   (2)

Other Products of Chlorination of 1-Phenylnaphthalene.—Chromatography of the crude product also gave, as a rapidly eluted fraction, 4-chloro-1-phenylnaphthalene, m.p. 66—68° (Found: C, 80·4; H, 4·8; Cl, 15·2. $C_{16}H_{11}Cl$ requires C, 80·5; H, 4·7; Cl, 14·9%). Another tetrachloride, as yet unidentified, was present in some fractions. The [1]H n.m.r. spectrum of the crude reaction product indicates that the chlorination in chloroform gives products in the following approximate proportions: 4-chloro-1-phenylnaphthalene, 55%; products of addition, 45%. The corresponding reaction in acetic acid gives similarly 4-chloro-1-phenylnaphthalene, 65%; products of addition, 35%.

Dichloro-1-phenylnaphthalenes.—Apparently none of the dichloro-1-phenylnaphthalenes has been reported previously. Two of these compounds can be obtained from the 1-phenylnaphthalene tetrachloride. Alkaline dehydrochlorination gave 2,3-dichloro-1-phenylnaphthalene as white needles, m.p. 94·5—95·5° (from n-pentane–methylene chloride) (Found: C, 70·3; H, 3·9; Cl, 25·7. $C_{16}H_{10}Cl_2$ requires C, 70·4; H, 3·7; Cl, 25·9%), τ ($CDCl_3$) 2·8—2·1 (9H, m), and 1·97 (1H, s).

To obtain the 2,4-isomer, the 1-phenylnaphthalene tetrachloride (0·2 g) was dissolved in CS_2 (*ca.* 50 ml) and solid aluminium trichloride (B.D.H., reagent grade; 0·1 g) was added. After 1 h at reflux temperature the mixture was poured into water. The organic product was recovered in the usual way and chromatographed on a column of alumina, with 5% methylene chloride–light petroleum (b.p. 50—70°) as eluant. The more rapidly eluted material gave 2,4-dichloro-1-phenylnaphthalene as white crystals, m.p. 97—98°

[6] D. F. DeTar, 'Computer Programs for Chemistry,' Benjamin, New York, 1968, vol. 1, p. 1ff.
[7] R. E. Rondeau and H. A. Rush III, *J. Chem. Educ.*, 1970, **47**, 139.
[8] P. T. Cleve, *Ber.*, 1887, **20**, 448.

(from aqueous ethanol) (Found: C, 70·4; H, 3·9; Cl, 26·0%), τ 2·8—2·2 (9H, m) and 1·8—1·6 (1H, m).

The same compound was obtained from the known 2,4-dichloro-1-naphthylamine,[8] which was converted first by the Griess reaction into 2,4-*dichloro-1-iodonaphthalene*, m.p. 88—90° (Found: C, 37·3; H, 1·6; Cl, 22·1; I, 39·2. $C_{10}H_5Cl_2I$ requires C, 37·2; H, 1·6; Cl, 21·9; I, 39·3%). Photolytic decomposition of the latter in benzene [9] gave the required compound, which was purified as before, and was identical (m.p., mixed m.p., i.r. and [1]H n.m.r. spectra, g.l.c. retention time, t.l.c.), with the previous sample.

G.l.c. Analysis of Product Mixtures.—A Varian 1532-2B gas chromatograph was used with a flame-ionisation detector. The carrier gas was nitrogen, and the column (6 ft × 1/8 in) contained 5% Carbowax on 100—120 mesh Chromosorb W, acid-washed and treated with dichlorodimethylsilane. The two dichloro-1-phenylnaphthalenes were well resolved, and their responses to concentration were found to be linear by using synthetic mixtures of known composition.

The products of a number of alkaline dehydrochlorinations were examined, different solvents and different concentrations of sodium methoxide being used. No systematic change of product proportions was noted with change in concentration; the proportion of 2,4-dichloro-1-phenylnaphthalene formed at 25° in 80 : 20 methanol–acetone was 0·73 ± 0·11%; and in 75 : 25 benzene–methanol was 0·92 ± 0·12%. The remainder of the product was essentially all 2,3-dichloro-1-phenylnaphthalene; however a trace of a very rapidly eluted material was observed. The [1]H n.m.r. spectrum of the crude product of dehydrochlorination showed no extraneous signals.

Attempts to detect the build-up of an intermediate chloro-1-phenylnaphthalene dichloride by methods described in an earlier paper [3] were unsuccessful.

Dehydrochlorination induced by Aluminium Trichloride.—Aluminium trichloride has been shown to catalyse geometric interconversions at benzylic centres in the naphthalene tetrachloride system.[10] Consequently we examined the products of reaction of 1-phenylnaphthalene tetrachloride with this reagent, under heterogeneous conditions, in carbon disulphide (with B.D.H. $AlCl_3$) and under homogeneous conditions, in nitromethane (with Riedel de Haen $AlCl_3$). The former reagent had been used to prepare 2,4-dichloro-1-phenylnaphthalene (see above). The results are summarised in the Table.

Products of dehydrochlorination of 1-phenyl-*r*-1,*c*-2,*t*-3,*t*-4-tetrachlorotetralin (1) with aluminium trichloride as catalyst

| Initial molar ratio of $AlCl_3$ to (1)	Solvent	Reaction time	Reaction temp./°C	Product percentages	
				2,3-Dichloro-	2,4-Dichloro-
Excess *	CS_2	1 d	20	Reaction incomplete	
Excess *	CS_2	1 h	46	35	65
0·3	$MeNO_2$	6 d	25	Reaction incomplete	
0·7	$MeNO_2$	6 d	25	Reaction incomplete	
1·0	$MeNO_2$	6 d	25	6	94
1·3	$MeNO_2$	6 d	25	13	87
1·7	$MeNO_2$	6 d	25	15	85

* Reaction mixture was heterogeneous.

[9] W. Wolf and N. Kharasch, *J. Org. Chem.*, 1961, **26**, 283; 1965, **30**, 2493; R. K. Sharma and N. Kharasch, *Angew. Chem. Internat. Ed.*, 1968, **7**, 36.
[10] G. W. Burton, K. R. Bedford, and P. B. D. de la Mare, *Tetrahedron Letters*, 1973, 3205.

T.l.c. of the crude products of reaction in nitromethane showed that the extent of reaction was approximately proportional to the amount of aluminium trichloride present, and ^{1}H n.m.r. spectroscopy showed that the original tetrachloride was unchanged after partial reaction. In separate experiments it was shown that a mixture of 2,3- and 2,4-dichloro-1-phenylnaphthalenes was little changed in composition by treatment with $AlCl_3$ either in CS_2 or in $MeNO_2$ under the conditions of the reaction.

DISCUSSION

Structure of the 1-Phenylnaphthalene Tetrachloride.— The ^{1}H n.m.r. spectrum of this compound in $CDCl_3$ is deceptively simple; but it becomes successively nearer to first-order in C_6D_6 and in $(CD_3)_2SO$. The direction of the solvent-shift is consistent with that observed with other tetrachlorides.[1,4,11] These spectra establish that in this 1-phenylnaphthalene tetrachloride the signals for the two pairs of vicinal protons in the alicyclic ring show one small and one large coupling. Four half-chair structures, (1), (3), (4), and (5) could conceivably give these couplings. Of these, however, only (1) is consistent with the results of alkaline dehydrochlorination. The easiest mode of dehydrochlorination of (4) or (5)


(3)   (4)

(5)
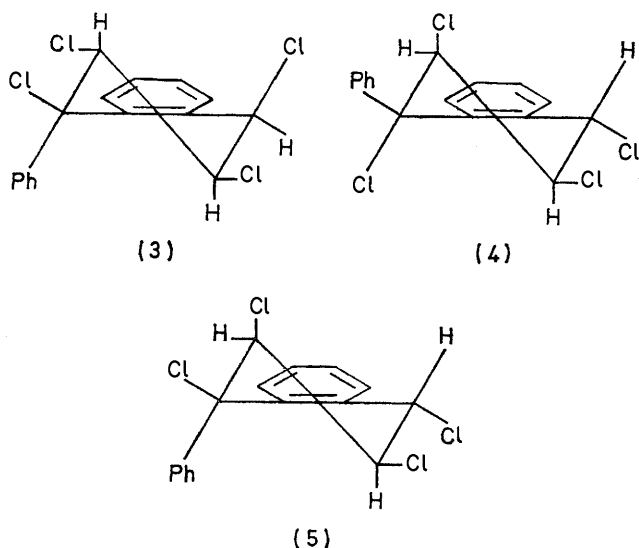
would involve diaxial loss of 3-H and 2-Cl as in naphthalene ε-tetrachloride;[2] subsequent 1,4-dehydrochlorination would then give 3,4-dichloro-1-phenylnaphthalene, which was not detected in the observed product. The only easy possible route from either of these compounds to the observed final product, 2,3-dichloro-1-phenylnaphthalene, involves first loss of 2-H and 1-Cl from the reverse conformation (6) of (5), and this would give the intermediate (7).

Analogues of this compound, also having *trans*-3,4-chloro-substituents, are obtained as intermediates in the dehydrochlorinations of naphthalene γ- and δ-tetrachlorides.[2,3] Like these intermediates, (7) should undergo relatively slow alkaline dehydrochlorination and

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

hence should be easily detectable in the reaction mixture after partial dehydrochlorination. It should also give a mixture of 2,3- and 2,4-dichloro-1-phenylnaphthalene. Since (a) no intermediate was detected in the alkaline

(6)   (7)
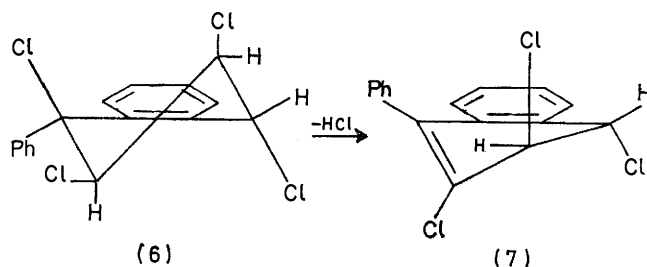
dehydrochlorination of 1-phenylnaphthalene tetrachloride, and (b) the final product is almost exclusively 2,3-dichloronaphthalene, neither structure (4) nor (5) can represent our 1-phenylnaphthalene tetrachloride.

The results of alkaline dehydrochlorination allow the exclusion also of structure (3). This should easily lose a-3-H and a'-4-Cl to form the intermediate (8), which like (7) cannot undergo *trans*-diaxial elimination, and so would be expected to be relatively stable, and readily detectable after partial dehydrochlorination of the original tetrachloride. Since no such intermediate was detected, we assume that it is not formed.

The details of the ^{1}H n.m.r. spectrum in the aromatic region confirm that structure (1) represents the tetrachloride. In $CDCl_3$, a multiplet (τ 3·2—2·8; 1H) is attributable to the signal of the 8-H moved upfield from the remaining aromatic signals by the deshielding effect of the adjacent e'-phenyl substituent. Much less deshielding would be expected for a corresponding a'-phenyl group, as in (3) or (5). We estimate by Johnson and Bovey's method,[12] with geometrical parameters estimated from models and subject to uncertainties because of possible rotation about the Ph–C bond, that the shielding effect of the pseudoequatorial phenyl ring on the adjacent aromatic proton might be in the range 0·6—0·3 Hz, whereas that of the pseudoaxial phenyl group in (3) or (5) could hardly be greater than 0·1 Hz.

Structures of the Dichloro-1-phenylnaphthalenes.—The foregoing discussion depends on the correct identification


(8)
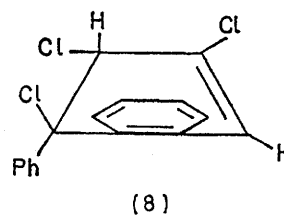
of 2,3-dichloro-1-phenylnaphthalene as the nearly exclusive product of alkaline dehydrochlorination of our tetrachloride. This follows from its ^{1}H n.m.r. spectrum. In substituted naphthalenes, a strong deshielding effect

[12] C. E. Johnson, jun., and F. A. Bovey, *J. Chem. Phys.*, 1958, **29**, 1012; F. A. Bovey, ' Nuclear Magnetic Resonance Spectroscopy,' Academic Press, New York, 1969.

on α-protons, resulting from *peri*-substitution, is generally found.[13] Specifically, 1-chloronaphthalene, and a number of its derivatives which we have examined, all have spectra in which the multiplet associated with 8-H is moved downfield from the signals of the remaining aromatic protons, to τ *ca.* 1·7. This feature is present in our 2,4-dichloro-1-phenylnaphthalene; it is absent in 2,3-dichloro-1-phenylnaphthalene. Here, instead, a singlet (1H) is observed at τ 1·95; this is to be attributed to the uncoupled 4-H. Thus the structure of the latter compound is established.

Reaction Paths in Dehydrochlorination of r-1,c-2,t-3,-t-4-*Tetrachloro-1-phenyltetralin* (1).—The course which we deduce for the alkaline dehydrochlorination is shown in Scheme 1. The main reaction path, we think, involves loss of the 3-H and 4-Cl to give (9), rather than of the 2-H and 1-Cl to give (10); intermediates such as (10) are rather indiscriminate in their further loss of hydrogen chloride,[2] so if much reaction occurred through this path, more 2,4-dichloro-1-phenylnaphthalene would be formed. Reaction through the alternative conformation (2) is clearly not easy; the corresponding reaction of naphthalene α-tetrachloride is known to be partly product-determining,[2] but that of 1-chloronaphthalene tetrachloride is small or absent.[1] It seems that steric congestion around the 1-carbon atom makes such
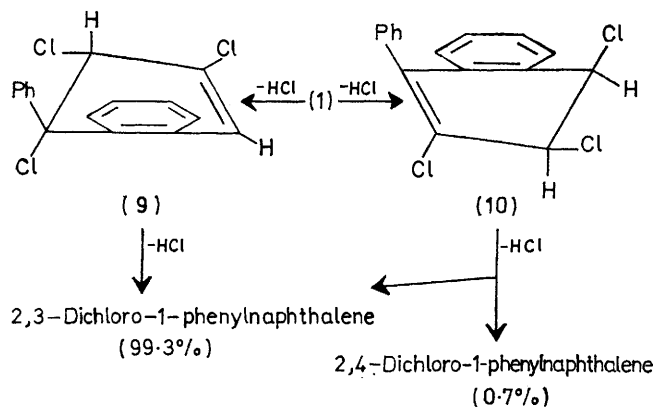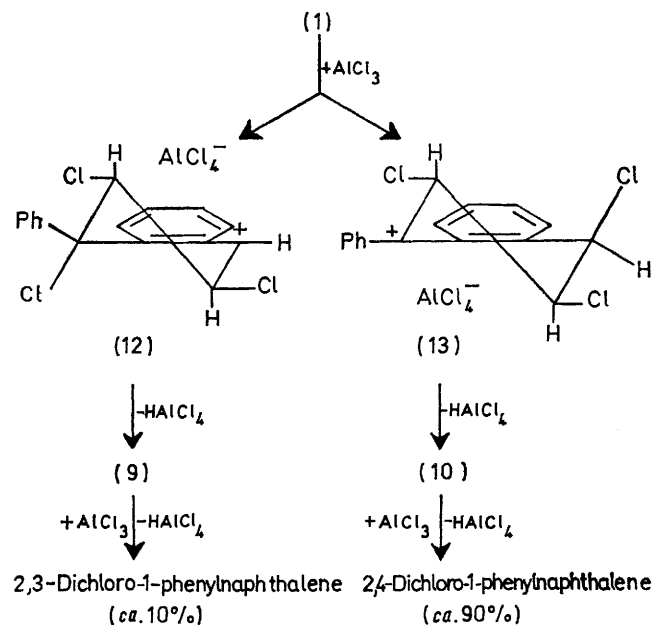

SCHEME 1

structures as (2) less easily accessible; it may also inhibit nucleophilic attack at the 2-position, so increasing the relative importance of reaction through (9).

The corresponding course for dehydrochlorination promoted by aluminium trichloride is shown in Scheme 2. Aluminium trichloride promotes polar reactions of the most ionisable chlorine atoms in naphthalene tetrachlorides; isomerisations involving only the benzylic chlorine atoms have been observed in a number of compounds in this series.[10] The main path now involves the loss of the 2-H and 1-Cl, since the intermediate carbonium ion-pair (13) is stabilised by resonance with the phenyl substituent; and so 2,4-dichloro-1-phenylnaphthalene now comprises about 90% of the product,

[13] A. Zweig, J. E. Lancaster, and M. T. Neglia, *Tetrahedron*, 1967, **23**, 2577; L. M. Jackman and S. Sternhell, ' Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry,' 2nd edn., Pergamon, Oxford, 1969, p. 206.

in marked contrast to reaction by the bimolecular mechanism. Whether the 10% of 2,3-dichloro-1-phenylnaphthalene comes from (13) or from (12) has not been

SCHEME 2

established. The formation of 3,4-dichloro-1-phenylnaphthalene by this reagent is prohibited by the fact that the necessary 1,4-elimination in the first stage of dehydrochlorination would destroy the benzenoid resonance. An excess of aluminium trichloride is necessary to complete the reaction, presumably because the products complex with, and hence deactivate, the aluminium trichloride. This contrasts with the situation in the aliphatic series, where eliminations can be promoted by catalytic amounts of aluminium trichloride.[14]

Chlorination of 1-*Phenylnaphthalene.*—The main tetrachloride (1) derived by chlorination of 1-phenylnaphthalene under relatively polar conditions is analogous to those found for the chlorination of naphthalene,[15] 1-methylnaphthalene,[4] and 1-chloronaphthalene.[1] In all these cases, initial attack by electrophilic chlorine would be expected to be directed to the 4-position, and we think that reaction in each of these cases involves successive stages of *cis*-addition on the opposite faces of the molecule. The proportion of aromatic compound consumed in substitution seems to be much the same as in naphthalene, and the trends observed when the results in acetic acid are compared with those obtained in chloroform[15] are also similar.

[14] A. N. Nesmeyanov, R. Kh. Freidlina, and L. I. Zakharkin, *Quart. Rev.*, 1956, **10**, 330; A. N. Nesmeyanov and N. A. Semenov, *Izvest. Akad. Nauk. S.S.S.R., Org. khim. Nauk.*, 1959, 2119.

[15] 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.