Naphthalene Dichloride and its Derivatives. Part III.[1] *trans*-1,2-Dichloro-1,2-dihydronaphthalene and a New Naphthalene Tetrachloride, *r*-1,*c*-2,*c*-3,*t*-4-Tetrachlorotetralin

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The photochemical chlorination of naphthalene with equimolar amounts of chlorine in carbon disulphide at low temperatures gives *trans*-1,2-dichloro-1,2-dihydronaphthalene, which on heterolytic chlorination in methylene chloride gives a new (fifth) geometric isomer of naphthalene tetrachloride, *r*-1,*c*-2,*c*-3,*t*-4-tetrachlorotetralin. On alkaline dehydrochlorination in a mixture of methanol and acetone this tetrachloride gives, as the main intermediate, *trans*-1,2,4-trichloro-1,2-dihydronaphthalene. Some reaction through other intermediates, one of which can decompose unimolecularly, is indicated also. Further dehydrochlorination of *trans*-1,2,4-trichloro-1,2-dihydronaphthalene gives approximately equal amounts of 1,3- and 1,4-dichloronaphthalene by a bimolecular route, which is accompanied by a unimolecular pathway giving nearly exclusively 1,4-dichloronaphthalene. The results throw new light on the courses taken in the dehydrochlorination of the naphthalene tetrachlorides; comparisons are made of the reactivities of some naphthalene *trans*-dichlorides in bimolecular and unimolecular eliminations. Treatment of the new naphthalene tetrachloride with aluminium trichloride in nitrobenzene effects nearly complete conversion into naphthalene ε-tetrachloride, consistent with the view that this isomerisation involves heterolysis of 1- and 4-, but not of 2- and 3-chlorine substituents.

ALTHOUGH a number of workers have claimed to have isolated naphthalene dichloride (for a summary see ref. 2), their reports have not been substantiated; attempts involving heterolytic pathways have so far been frustrated by the fact that the product first formed is trapped by further chlorine to give naphthalene tetrachlorides, in which the α-isomer (1) predominates, accompanied by the δ-isomer (2).† Homolytic pathways, however, have not been investigated extensively; they are known [3] to give a mixture of geometric isomers in which the γ- and ε-tetrachlorides [(3) and (4) respectively] predominate; the presence of traces of (5) had been suspected.

Further investigation of homolytic chlorination, using low temperatures and carbon disulphide as the solvent, has now enabled us to characterise an authentic naphthalene dichloride for the first time. It is reasonably stable in solution but unstable on removal of the solvent, so our best sample was of *ca.* 90% purity. Its u.v. spectrum and its further reactions characterise it as *trans*-1,2-dichloro-1,2-dihydronaphthalene, and its ^{1}H n.m.r. spectrum shows that it exists in solution almost entirely in conformation (6a).

Its reactions, including its heterolytic chlorination, have now been studied. These investigations have led to the preparation and characterisation of a new naphthalene tetrachloride (5), and have thrown some new light on the paths that can be taken in the dehydrochlorination of naphthalene di- and tetra-chlorides.

EXPERIMENTAL

Materials and Methods.—Some of the materials and methods have been described in earlier papers.[1-8] Light

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† Formulae given in this paper imply compounds existing as racemic mixtures of enantiomorphs wherever these are different.

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

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

[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, R. Koenigsberger, and J. S. Lomas, *J. Chem. Soc.* (*B*), 1966, 834.

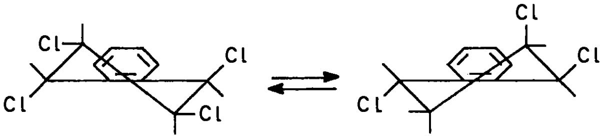
[5] G. Cum, P. B. D. de la Mare, J. S. Lomas, and M. D. Johnson, *J. Chem. Soc.* (*B*), 1967, 244.

[6] P. B. D. de la Mare and H. Suzuki, *J. Chem. Soc.* (*C*), 1967, 1586; G. Cum, P. B. D. de la Mare, and M. D. Johnson, *ibid.*, p. 1590.

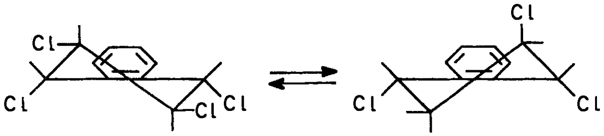
[7] G. W. Burton and P. B. D. de la Mare, *J. Chem. Soc.* (*B*), 1970, 897.

[8] G. W. Burton, P. B. D. de la Mare, L. Main, and B. N. B. Hannan, *J.C.S. Perkin II*, 1972, 265.

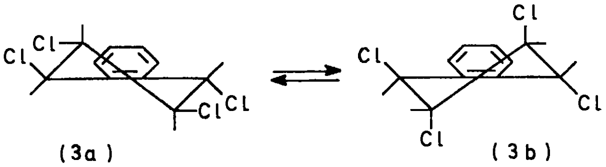
petroleum (b.p. 60—70°) was distilled before use. Silica gel used for column chromatography was Riedel–de Haen Kieselgel S and was deactivated with 15% water. 4 : 1 (v/v) Methanol–acetone was used as solvent in the estimation of the kinetics and products of dehydrochlorination at 25°. I.r. spectra were recorded by using Perkin-Elmer 237 or 337 spectrophotometers, and ^{1}H n.m.r. spectra by using Varian T60 or A60 spectrometers. For g.l.c., we used a Varian Aerograph model 1532-2B equipped with a flame ionisation detector, and an aluminium column (160 × 0·32 cm) packed with 10% Bentone 34–DC-550 (1 : 1) on acid-washed Celite (100—120 mesh) operated with nitrogen (0·5 ml s^{-1}) at 170°. Peak areas were measured by using a disc integrator attached to the chart-recorder. New reference samples of the dichloronaphthalenes were prepared; their properties agreed with those described previously.[4] Tests on synthetic mixtures showed that for each isomer the area of the peak relative to the total area gave the concentration of the isomer within experimental error. The methoxynaphthalenes, also used for reference, were prepared by standard methods from the appropriate naphthols; the 2-isomer had m p. 72°, and the 1-isomer was an oil.



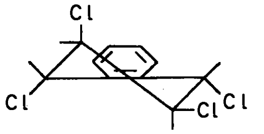
(1a) (1b) α



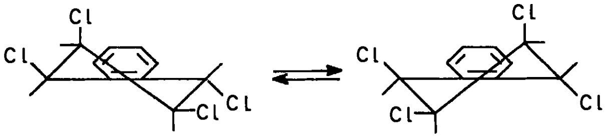
(2a) (2b) δ



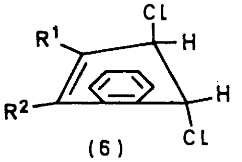
(3a) (3b) γ



(4) ε



(5a) (5b) ζ



(6)

a; $R^1 = R^2 = H$
b; $R^1 = H, R^2 = Cl$
c; $R^1 = Cl, R^2 = H$

The New ζ-Naphthalene Tetrachloride.—The photochemical chlorination of naphthalene with excess of chlorine in CCl_4 is known[1,3] to give the ε-, γ-, and δ-naphthalene tetrachlorides (4), (3), and (2) in relative proportions (4) > (3) ≫ (2). The new ζ-isomer (5) was first obtained in very low yield by repeated chromatography of the residues from such a chlorination. It was recrystallised from methanol and gave crystals of r-1,c-2,c-3,t-4-*tetrachlorotetralin* (5), m.p. 91—92° (Found: C, 44·6; H, 3·05; Cl, 52·4. $C_{10}H_8Cl_4$ requires C, 44·5; H, 3·0; Cl, 52·5%), τ ($CDCl_3$) 5·40 (1H, q, $J_{2.3}$ 2·4, $J_{3.4}$ 8·3 Hz, 3-H), 5·10 (1H, q, $J_{1.2}$ 3·6, $J_{2.3}$ 2·4 Hz, 2-H), 4·50 and 4·46 (2H, 2 × d, 1- and 4-H), and 2·8—2·2 (4H, m, ArH). I.r. spectra of (5) and somewhat impure (6a) are listed in Supplementary Publication No. SUP 20930 (2 pp.).*

In a better method of preparation, naphthalene (1·45 g) in CS_2 (25 ml) was cooled to *ca.* −70°, and to it was added a cold solution of chlorine (0·57M) in CS_2 (20 ml). The mixture, held at −70°, was irradiated with a Phillips Sunray lamp. After *ca.* 10 min, the colour of chlorine had disappeared. The solvent was removed *in vacuo;* the resulting oil was from its ^{1}H n.m.r. spectrum (see below) mainly *trans*-1,2-dichloro-1,2-dihydronaphthalene, contaminated with a little naphthalene and naphthalene γ-tetrachloride.

This oil was purified by dissolving it in n-pentane and cooling it to −70°. The mother liquor, containing most of the naphthalene, was decanted. The remaining crystalline material was dissolved in CCl_4 and held at −20° overnight. Most of the naphthalene γ-tetrachloride crystallised out; the mother liquor contained *trans*-1,2-dichloro-1,2-dihydronaphthalene still contaminated with naphthalene (5%) and naphthalene γ-tetrachloride (7%). It was treated with excess of chlorine in methylene chloride at room temperature for *ca.* 45 min. The product after removal of solvent contained from its ^{1}H n.m.r. spectrum naphthalene γ-, ε-, ζ-, and δ-tetrachlorides in approximate proportions 35 : 30 : 25 : 10. It was added to light petroleum; much of the γ-isomer remained as an insoluble residue. A preliminary chromatographic separation on silica gel deactivated with water (15%) removed most of the ε-isomer, and a further chromatographic separation with light petroleum containing chloroform (1—6%) as eluant on a similar column, a loading ratio of 300 : 1 being used, gave pure naphthalene ζ-tetrachloride (5). Our best yield in a number of experiments of this kind was *ca.* 10% based on the naphthalene used.

Properties and Further Reactions of trans-*1,2-Dichloro-1,2-dihydronaphthalene.*— *trans*-1,2-Dichloro-1,2-dihydronaphthalene was chlorinated also in acetic acid. The tetrachlorides were formed in similar proportions, and were accompanied by two acetoxy-trichlorides (*ca.* 40%), both having ^{1}H n.m.r. absorptions at τ 3·72 (1H, d, *J* 8 Hz). The naphthalene acetoxy-trichloride reported earlier[3] had similar signals, the downfield shift being attributable to the adjacent acetoxy-groups.

trans-1,2-Dichloro-1,2-dihydronaphthalene in the slightly

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* For details of Supplementary Publications see Notice to Authors No. 7 in *J.C.S. Perkin II*, 1972, Index Issue. Items less than 10 pp. are supplied as full size copies.

impure form in which we obtained it had a characteristic pungent odour, and was stable in CS_2 at $-20°$ for many weeks. It decomposed slowly at room temperature, however, and was decomposed by chromatography both on deactivated silica gel, when 1-chloronaphthalene (98%) was the main product, and on g.l.c. under the conditions used for analysis of the dichloronaphthalenes, when 1- and 2-chloronaphthalene were formed in the ratio 87 : 13. The position of the double bond was established by its u.v. spectrum, which in cyclohexane had the expected band [$\lambda_{\max.}$ 274 nm (ε 51,542)] indicating conjugation with the aromatic ring, τ (CCl_4) 5·17 (1H, q, $J_{1,2}$ 2·2, $J_{2,3}$ 5·9 Hz, 2-H), 4·80 (1H, q, $J_{1,2}$ 2·2, $J_{1,3}$ 1·3 Hz, 1-H), 3·90 (1H, octet, $J_{2,3}$ 5·9, $J_{3,4}$ 10·0, $J_{1,3}$ 1·3 Hz, 3-H), 3·31 (1H, d, $J_{3,4}$ 10·0 Hz, 4-H), and 2·70 (4H, m, ArH). The compound clearly contains two vinylic protons, with signals lying well downfield from those of the other alicyclic protons. The low value of the coupling constant, $J_{1,2}$ 2·2 Hz, indicates that (6) is the main conformation in solution. The value $J_{2,3}$ 5·9 Hz is as expected for a pseudo-equatorial hydrogen adjacent to a vinyl hydrogen, and the long-range coupling, $J_{1,3}$ 1·3 Hz, compares well with the similar value observed in 1,2,4-trichloro-1,2-dihydronaphthalene (J 1·3 Hz).[1]

Its alkaline dehydrochlorination (0·04M-NaOMe) in 4 : 1 methanol–acetone gave mainly 1-chloronaphthalene (85%), together with 2-chloronaphthalene (5%). Its solvolytic decomposition in the same solvent again gave mainly 1-chloronaphthalene (89%); under these conditions, only a trace (1%) of 2-chloronaphthalene was formed. These results suggested that the naphthalene dichloride undergoes mainly unimolecular solvolysis, and this was confirmed kinetically. The first-order rate coefficient, determined by the usual procedure, was substantially constant over at least 90% reaction in 4 : 1 methanol–acetone at 25°: $k_1 = 6{\cdot}2 \times 10^{-5}$ s^{-1}, increased only to $6{\cdot}8 \times 10^{-5}$ s^{-1} by the inclusion of NaOMe (0·042M) in the reaction medium. The rate of the bimolecular reaction with methoxide ion derived from these values is $k_2 =$ *ca.* $1{\cdot}4 \times 10^{-4}$ l mol^{-1} s^{-1}, subject to much uncertainty because salt effects of unknown magnitude could affect the result. It seems, however, from the products of the reactions, that more 2-chloronaphthalene is formed by bimolecular than by unimolecular elimination, and this is apparent also in its reaction with potassium t-butoxide (0·2M) in 4 : 1 dimethyl sulphoxide–t-butyl alcohol, which gives 63% of 2-chloronaphthalene.

The remainder of the product of solvolysis in 4 : 1 methanol–acetone was identified by g.l.c. and ^1H n.m.r. spectroscopy as 1-methoxynaphthalene, comprising *ca.* 10% of the mixed products of dehydrochlorination. Solvolysis in methanol was, as expected, faster ($k_1 = 1{\cdot}15 \times 10^{-4}$ s^{-1}) than in 4 : 1 methanol–acetone.

Further Reactions of the New Naphthalene Tetrachloride (5).—Elsewhere,[9] we have reported that any of the α-, δ-, and γ-isomers of naphthalene tetrachloride (1)—(3) on treatment with aluminium trichloride in a suitable solvent gives an equilibrium mixture of these isomers by isomerisation involving heterolysis of the 1- and 4-, but not the 2- and 3-chlorine atoms. Naphthalene ε-tetrachloride (4) is unchanged under these circumstances; accordingly, naphthalene ζ-tetrachloride (5) dissolved in $CDCl_3$ gives (4) almost exclusively on being treated with a few drops of aluminium trichloride in nitrobenzene; none of the other isomers, nor any extraneous signals, were detected in the ^1H n.m.r. spectrum of the product observed directly after reaction for 10 min.

Partial dehydrochlorination of the new tetrachloride (5) was first examined by using the method described in Part II.[1] When dissolved in CCl_4 and treated with the optimum amount of *ca.* 5M-NaOMe, the signals of the parent compound disappeared and were replaced by those expected for *trans*-1,2,4-trichloro-1,2-dihydronaphthalene (6c). The ^1H n.m.r. spectrum of this has been reported earlier, since it is an intermediate in the alkaline dehydrochlorination of naphthalene γ-tetrachloride.[1,4] Other signals in the ^1H n.m.r. spectrum of this sample were consistent with the presence also of *trans*-1,2,3-trichloro-1,2-dihydronaphthalene (6b), the intermediate known to be derived from naphthalene δ-tetrachloride.[1,4]

The formation of intermediates in the alkaline dehydrochlorination of the new tetrachloride (which, like all its isomers, is not solvolysed under our conditions if alkali is absent) was confirmed by kinetic measurements, made as before in 4 : 1 methanol–acetone at 25°. The concentration of organic chloride was typically 6×10^{-4}M, and the total reaction volume was 99·3 ml. Aliquot parts (4·86 ml) were removed, and quenched in distilled acetone (100 ml) containing aqueous nitric acid (2M; 1 ml). The quenched sample was titrated potentiometrically against standardised $AgNO_3$ (0·001M). Appropriate correction was made for blank values. The rate coefficient of the very rapid first stage of the reaction was found to be $k_2 = 1{\cdot}97$ l mol^{-1} s^{-1} ($[NaOMe]_{initial}$ 2×10^{-3}M).

The Dehydrochlorination of 1,2,3- *and* 1,2,4-*Trichloro*-1,2-*dihydronaphthalene*.—The final, relatively slow, alkaline dehydrochlorinations of naphthalene δ-, γ-, or ζ-tetrachloride all involve the formation of the trichloro-1,2-dihydronaphthalenes (6b and c). Previously, we and other workers[10] have presumed that these reactions were bimolecular eliminations; but the discovery that *trans*-1,2-dichloro-1,2-dihydronaphthalene reacts unimolecularly under our conditions required reconsideration of this assumption. Naphthalene γ-tetrachloride (3) ($2{\cdot}6 \times 10^{-3}$M) was allowed to react with sodium methoxide (0·08M) in 4 : 1 methanol–acetone at 25°. After 92 min, a known volume of 4 : 1 methanol–acetone containing excess of aqueous nitric acid (16M; 0·4 ml) was added; an aliquot part was removed for determination of chloride. Reaction of the intermediate *trans*-1,2,4-trichloro-1,2-dihydronaphthalene was then allowed to proceed to completion (7 days); aliquot parts were removed at intervals for titration. First-order plots of the progress of reaction after acidification, the appropriate infinity being used, were satisfactorily linear, with a value of $k_1 = 2{\cdot}95 \times 10^{-5}$ s^{-1}. The products at the end of this reaction contained 1,3- (17%) and 1,4-dichloronaphthalene (83%).

Similar partial dehydrochlorination of (2) gave a mixture of trichloro-1,2-dihydronaphthalenes, of which about 23% was found to undergo solvolysis; this proportion agrees well with our estimate from the ^1H n.m.r. spectrum.[1] The remainder was *trans*-1,2,3-trichloro-1,2-dihydronaphthalene, which was not solvolysed at all after 10 days under the same conditions.

Partial dehydrochlorination of the ζ-tetrachloride similarly gave a product which underwent solvolysis with $k_1 = 2{\cdot}5 \times 10^{-5}$ s^{-1}, liberating chloride ion in amount

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

[10] F. Schütz and K. Hahnfeld, *Chem. Ber.*, 1952, **85**, 131.

which indicated that *ca.* 75% of *trans*-1,2,4-trichloro-1,2-dihydronaphthalene had been formed. The kinetic behaviour suggested, however, that a small proportion of the material undergoing solvolysis was a still more reactive intermediate.

Products of Alkaline Dehydrochlorination of the Naphthalene Tetrachlorides.—The naphthalene tetrachlorides were dehydrochlorinated by treatment with excess of sodium methoxide at several concentrations in 4 : 1 methanol–acetone at 25°, and with potassium t-butoxide in 4 : 1 dimethyl sulphoxide–t-butyl alcohol at 25°. Neither reagent had any effect on the composition of mixtures either of the dichloronaphthalenes or of the monochloronaphthalenes. The products, recovered and analysed by g.l.c., were as shown in the Table. From naphthalene ζ-tetrachloride, but not from any of the other isomers, several new peaks appeared in the chromatograms. The retention times of the materials responsible were similar to those of the dichloronaphthalenes, so that only maximum values can be given for the minor components, and even the values for the major components may in this case be slightly uncertain.

Products of alkaline dehydrochlorination of the naphthalene tetrachlorides at 25°

Naphthalene tetrachloride	Solvent *	NaOMe or KOBu^t/ M	Proportions of dichloronaphthalenes: 1,2	1,3	1,4	2,3	Other products
(1)	B	0·19		0·57	0·33	0·10	
	A	0·75		0·50	0·45	0·05	
	A	0·0425		0·50	0·46	0·04	
	A	0·00204		0·51	0·46	0·03	
(2)	B	0·19		0·14	0·06	0·80	
	A	0·75		0·19	0·08	0·73	
	A	0·0425		0·17	0·11	0·72	
	A	0·00204		0·11	0·18	0·71	
(3)	B	0·19		0·93	0·07		
	A	0·75		0·58	0·42		
	A	0·080		0·50	0·50		
	A	0·0425		0·42	0·58		
	A	0·00204		0·06	0·94		
(4)	B	0·19	0·10	0·85	0·05		
	A	0·75	0·51	0·49	Trace	Trace	
	A	0·0425	0·52	0·47	Trace	0·01	
	A	0·00204	0·65	0·33	0·01	0·01	
(5)	B	0·19	Trace	0·92	0·08	Trace	
	A	0·75	0·01	0·56	0·39	0·04	
	A	0·0425 †	0·02	0·40	0·46	0·12	Trace
	A	0·00204 †	0·08	0·16	0·65	0·07	0·04

* Solvents: A, 4 : 1 methanol–acetone; B, 4 : 1 dimethyl sulphoxide–t-butyl alcohol. † Product proportions may be affected by reaction to give methoxy-containing products, overlapping with the usual peaks and having a different response to concentration.

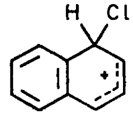
The alkaline dehydrochlorinations of 1,2,3-trichloro-1,2-dihydronaphthalene prepared as described earlier,[1] were examined also. They gave the 1,3- and 2,3-dichloronaphthalenes in the ratios 0·12 : 0·88 (in 4 : 1 methanol–acetone) and 0·08 : 0·92 (in 4 : 1 dimethyl sulphoxide–t-butyl alcohol).

DISCUSSION

trans-1,2-*Dichloro*-1,2-*dihydronaphthalene.*—This, the first authentically described naphthalene dichloride, is formed as a nearly exclusive product of photochemical addition of chlorine to naphthalene in carbon disulphide at −70°. It is reasonably stable in solution, but unstable on removal of the solvent. Its u.v. spectrum shows that its structure is as shown in (6a); its products of further chlorination establish that it is the *trans*-isomer; and its ^{1}H n.m.r. spectrum indicates through the low coupling between the signals for the 1- and 2-hydrogens that these are disposed as in (6a).

Further addition of chlorine to this compound under homolytic conditions at −70° gives almost exclusively (3); but at higher temperatures a mixture is obtained containing mainly (3) and (4), by *trans*-addition to the remaining double bond. Addition under heterolytic conditions in methylene chloride, however, proceeds by a mixture of *cis*- and *trans*-addition to give all four possible isomers (2)—(5); the last is formed in sufficient amount to make this a practicable route for isolation of reasonable quantities of this isomer. A similar mixture is obtained in acetic acid, and is accompanied by two acetoxy-chlorides, which have not been examined further but are probably the products of *trans*-(3-chloro,4-acetoxy) addition.

The dichloride undergoes unimolecular solvolytic decomposition in 4 : 1 methanol–acetone. Such a reaction would be expected to involve the carbonium ion (7) rather than (8) by analogy with the well known preference for attack by electrophiles at the α-position in naphthalene. Consequently 1-chloronaphthalene is the main product of the decomposition. This is accompanied by 1-methoxynaphthalene, which could have been produced from (7) by capture of methanol at the 4-position, followed by 1,4-dehydrochlorination. Alternatively, the solvolysis may give not only (7) but also about 10% of (8) and the latter may then capture methanol to give ultimately 1-methoxynaphthalene, or lose a proton to give 2-chloronaphthalene. In the latter case, the partition ratio between proton loss and capture of methanol must be very different for (7) and (8), since no other methoxy-signals were detected in the ^{1}H n.m.r. spectrum of the product, and so capture by methanol at the 2-position of (7) must be disfavoured. A combination of the two routes is also possible.



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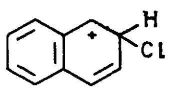

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Comparison of the Dehydrochlorinations of trans-1,2-*Dichloro*-1,2-*dihydronaphthalene and its* 3- *and* 4-*Chloro-derivatives.*—The rates of unimolecular solvolyses of three *trans*-dichlorides (6a—c) have been compared; they are respectively $k_1 = 6{\cdot}2 \times 10^{-5}$; $2{\cdot}95 \times 10^{-5}$; and $<1 \times 10^{-8}$ s^{-1} in 4 : 1 methanol–acetone at 25°. These results illustrate that a chlorine atom introduced into the γ-position of an allylic system has a relatively small effect on its rate of unimolecular heterolysis, because of the opposing conjugative and inductive effects of the halogen,[11] but a chlorine atom similarly introduced

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[11] C. A. Vernon, *J. Chem. Soc.*, 1954, 423.

into the β-position strongly retards the rate of heterolysis, since now only the electron-withdrawing inductive effect can come into play.

The composition of the product of unimolecular solvolysis (6b) can be approximated also from the variation in product ratio in the alkaline dehydrochlorination of naphthalene γ-tetrachloride (3). The results given in the Table show that, even at the lowest concentration of base, only 6% of 1,3-dichloronaphthalene is formed. Under these conditions, the rate of bimolecular elimination from this trichloro-1,2-dihydronaphthalene ($k_2 = 1{\cdot}7 \times 10^{-3}$ l mol^{-1} s^{-1})[4] is sufficient to contribute rather more than 10% to the initial rate of solvolytic decomposition by $E2$ and $E1$ mechanisms ($k_1 = 2{\cdot}95 \times 10^{-5}$ s^{-1}). So reaction by the $E1$ route must give much less than 6%, and probably as little as 1% or less of 1,3-dichloronaphthalene, just as *trans*-1,2-dichloro-1,2-dihydronaphthalene similarly gives no more than 1% of 2-chloronaphthalene.

The alkaline dehydrochlorination of the same three *trans*-1,2-dichloro-1,2-dihydronaphthalenes can be compared also. The rates of these reactions in 4 : 1 methanol–acetone at 25° are approximately (6a) $k_2 = 0{\cdot}1 \times 10^{-3}$; (6b) $1{\cdot}2 \times 10^{-3}$; and (6c) $2{\cdot}5 \times 10^{-3}$ l mol^{-1} s^{-1}, the first two values being subject to some uncertainty because they are rate coefficients dissected from the composite rate of a reaction involving more than one concurrent path. The polar influences of the nearby vinylic chlorine atoms appear to have produced the expected modest acceleration of these eliminations. The orientation of elimination can be composite, involving attack both on the 1- and on the 2-hydrogen atom (this paper and refs. 1 and 4); it will have been noted (*cf.* also ref. 9) that attack on the 2-hydrogen atom, and consequent removal of the 1-chlorine atom, is much more marked in the bimolecular than in the unimolecular eliminations.

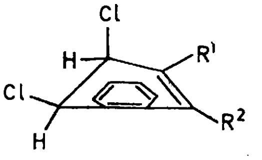
Although *trans*-1,2-dichloro-1,2-dihydronaphthalene gives some 10% of product of substitution (S_N1) accompanying elimination ($E1$), no such product was detected from the unimolecular reaction of its 4-chloro-derivative; this mechanism accompanies the bimolecular reaction in the alkaline dehydrochlorination of (3).

Structure and Reactions of the New Naphthalene Tetrachloride (5).—The structure of the new ζ-naphthalene tetrachloride, *r*-1,*c*-2,*c*-3,*t*-4-tetrachlorotetralin, is established by its ^{1}H n.m.r. spectrum. This clearly is that of a compound with four alicyclic hydrogen atoms in different magnetic environments. Only two of the six possible tetrachlorides fall into this category, and one [*viz.* (2)] is already well characterised. The remaining one, (5), is consistent with the ^{1}H n.m.r. spectrum, (5a) being the main component in solution. The 3,4-vicinal coupling, though large, does not reach its maximum value, so the system either contains a contribution from the conformer (5b) or is distorted by intramolecular compressions.

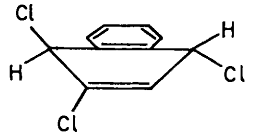
The behaviour of the compound on alkaline dehydrochlorination confirms the above structure. The compound reacts with alkali rapidly in the first stage of dehydrochlorination, as is consistent with concerted *trans*-(1-H, 2-Cl) or *trans*-(2-H, 1-Cl) elimination. The rate coefficient for this reaction is some 10 times greater than that of any of its known isomers; the corresponding benzene tetrachloride is similarly more reactive than its isomers, as has been shown by Orloff and Kolka.[12] At the end of the first stage, signals expected for *trans*-1,2,4-trichloro-1,2-dihydronaphthalene are dominant in the spectrum, so that most of the reaction involves the main conformation (5a), as is true also for the corresponding benzene tetrachloride.[4]

The second stage of alkaline dehydrochlorination follows slowly, as expected for the necessary *cis*-elimination, and gives both 1,3- and 1,4-dichloronaphthalene. The product ratio for reaction at the highest concentration of alkali approximates to that obtained from naphthalene γ-tetrachloride as far as the major components are concerned. A little reaction has probably given 1,2,3-trichloro-1,2-dihydronaphthalene, but the amount cannot exceed *ca.* 5%.

Since the variation in the product ratio, 1,3- : 1,4-dichloronaphthalene, with concentration of alkali does not follow that observed for naphthalene γ-tetrachloride, the dehydrochlorination cannot wholly involve the same intermediate, and a further mode of dehydrochlorination of the ζ-tetrachloride is indicated. This is confirmed by the kinetic form of the reaction and by the identification of the presence of products other than the dichloronaphthalenes by g.l.c. It is possible that there is a significant contribution from the formation of (9; R^1 or R^2 = Cl) by *cis*-elimination in the first stage of the dehydrochlorination. These compounds, however, are intermediates in the bimolecular reactions of the α-tetrachloride, which give quite normal products, and so these intermediates, though possibly responsible for the change in isomer ratios, cannot be responsible for the formation of the extraneous products. Reaction in part through (10), however, represents a pathway analogous to that found for naphthalene ε-tetrachloride, namely a 2,3-elimination to give in the present case a *trans*-1,2,4-trichloro-1,4-dihydronaphthalene. The unimolecular reactions of the compound would be expected to be complex, and might give 1,2- and 1,3-dichloronaphthalenes ($E1$); methoxy-derivatives (S_N1, S_N1'); and 1,2,3-trichloro-1,2-dihydronaphthalene (S_Ni). Bimolecular reactions could give 1,2- and 1,3-dichloronaphthalenes ($E2$), and methoxy-derivatives (S_N2, S_N2'). Its course of dehydrochlorination is likely to be



(9)



(10)

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[12] H. J. Orloff and A. J. Kolka, *J. Amer. Chem. Soc.*, 1954, **76**, 5484; H. J. Orloff, *Chem. Rev.*, 1954, **54**, 347.

quite different from that of its *cis*-isomer implicated in the dehydrochlorination of the ε-tetrachloride.

The fact that (5) is converted into (4) by treatment with aluminium trichloride in nitrobenzene confirms our view[9] that geometric isomerisation of this kind involves regiospecific heterolysis of the benzylic 1- and 4-chlorine atoms rather than of the 2- or 3-chlorine substituents. This would theoretically be expected if this reaction involves a Lewis acid-catalysed heterolysis, $RCl + AlCl_3 \rightleftharpoons [R^+AlCl_4^-]$. The fact that (5) is clearly much less thermodynamically stable than (4) probably arises through unfavourable intramolecular repulsions in (5), and the resulting distortions may explain the accessibility of the rather unusual minor path found in its dehydrochlorination.

Alkaline Dehydrochlorination of the Other Naphthalene Tetrachlorides.—The results given in this paper for the naphthalene tetrachlorides known previously differ significantly from those reported earlier[4,10] only in respect of the additional complications revealed by the discovery that unimolecular (*E*1) modes of solvolysis can become significant for certain types of intermediate. We have already dealt with the case of naphthalene γ-tetrachloride (3); for this, the variation in product composition with concentration of alkali (Table) is diagnostic of this complication, and a corresponding smaller change for naphthalene δ-tetrachloride indicates that the intermediate (6b) plays a minor, but significant role here also.

The fact that naphthalene α-tetrachloride (1) gives substantially the same ratio of products at different concentrations of base suggests that the *cis*-1,2-dichloro-1,2-dihydronaphthalenes involved as intermediates in these dehydrochlorinations[4] undergo wholly bimolecular eliminations. The small change in product proportions from the ε-isomer, on the other hand, makes it possible that the very reactive intermediate *cis*-1,2,4-trichloro-1,4-dihydronaphthalene important in the reaction path for this tetrachloride[4] may include a unimolecular component in its dehydrochlorination. The same may be true of some other complex dehydrochlorinations.[5,6]

The reaction of naphthalene γ-tetrachloride (3) with 0·75M-NaOMe in 4 : 1 methanol–acetone must be nearly completely bimolecular; it goes almost entirely *via* *trans*-1,2,4-trichloro-1,2-dihydronaphthalene and gives 58% 1,3-dichloronaphthalene (Table). The change towards the formation of even more 1,3-dichloronaphthalene (93%) by changing to the more powerful reagent, potassium t-butoxide in 4 : 1 dimethyl sulphoxide–t-butyl alcohol, is unlikely to be the result of a change in the first stage of dehydrochlorination of the tetrachloride. It seems, therefore, that attack on the β-hydrogen of *trans*-1,2,4-trichloro-1,2-dihydronaphthalene is considerably favoured at the expense of attack on the α-hydrogen by change to a more powerfully basic reagent. A similar trend was evident in the reactions of *trans*-1,2,3-trichloro- and *trans*-1,2-dichloro-1,2-dihydronaphthalene (see Experimental section).

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