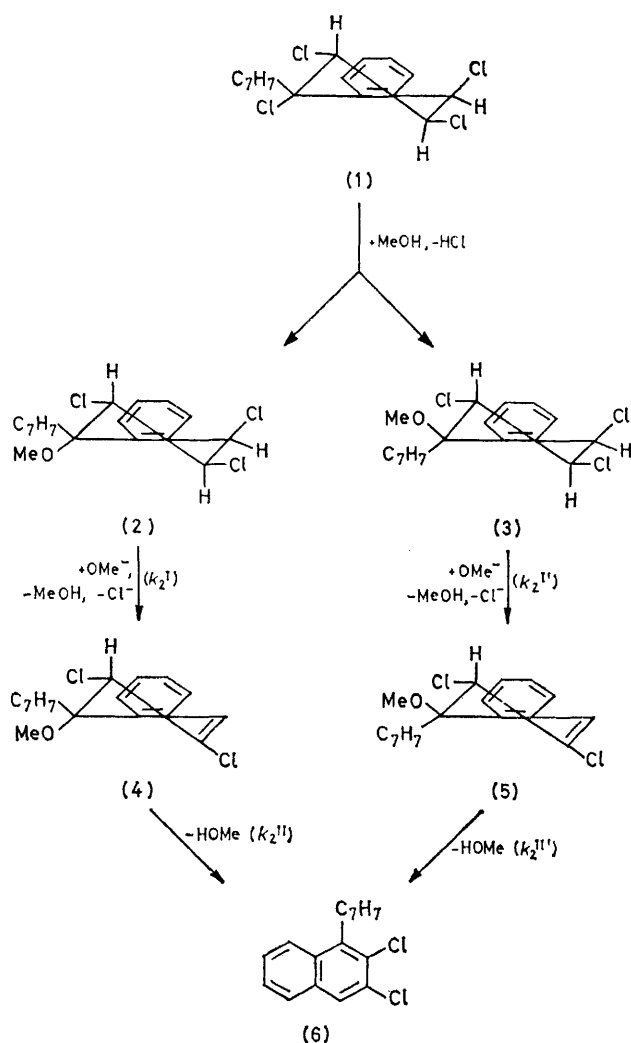


## Naphthalene Tetrachlorides and Related Compounds. Part 7.<sup>1</sup> Products of Methanolysis of a 1-*p*-Tolynaphthalene Tetrachloride; Evidence for a Rapid Bimolecular Elimination of Methanol from the 2,3-Dichloro-1-methoxy-1-*p*-tolyl-1,2-dihydronaphthalenes

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Unimolecular methanolysis of *r*-1-*c*-2-*t*-3-*t*-4-tetrachloro-1-*p*-tolyltetralin gives two isomeric 1-methoxy-1-*p*-tolyl-2,3,4-trichlorotetralins, each of which undergoes bimolecular elimination in two defined stages having similar rates, and giving 2,3-dichloro-1-*p*-tolynaphthalene as the nearly exclusive final product. The intermediate 2,3-dichloro-1-methoxy-1-*p*-tolyl-1,2-dihydronaphthalenes, which can be characterised through signals in their <sup>1</sup>H n.m.r. spectra, must, therefore, undergo bimolecular elimination of methanol at rates which can be estimated from the rates of build-up of their precursors. The theoretical implications of these results are discussed; it is suggested that this elimination must be far on the *E*1cb side of the spectrum of bimolecular eliminations.

THE bimolecular reactions of naphthalene tetrachlorides and their substituted derivatives have had some



SCHEME Solvolysis of 1-*p*-tolynaphthalene tetrachloride, and elimination from the products of this solvolysis

attention.<sup>1-3</sup> They give nearly exclusively the products of elimination of hydrogen chloride in two stages, the second of which is in some cases slow enough for an

intermediate dichloride to build up in a concentration sufficient to be isolable or recognisable from its <sup>1</sup>H n.m.r. spectrum.<sup>4</sup> The corresponding unimolecular processes have been less extensively examined. Isomerisations in the presence of Lewis acids have been recognised;<sup>5</sup> the accompanying eliminations give mixtures of isomeric dichloronaphthalenes in proportions quite different from those obtained in the corresponding bimolecular processes,<sup>6</sup> a result which can be of synthetic value. Only a few replacements have been recorded for compounds in this series.<sup>7</sup>

In an earlier paper,<sup>5</sup> we found that the proportions of products of bimolecular elimination from some of the naphthalene tetrachlorides were affected, if the concentration of methoxide ion in the methanol-acetone solvent was too low, by the incursion of a reaction presumed to be unimolecular. It seemed desirable, therefore, to check that such a reaction was not disturbing the bimolecular reactions of the 1-arylnaphthalene tetrachlorides for which the kinetic comparisons<sup>1</sup> were desired. Investigation of the rate and products of solvolysis of 1-*p*-tolynaphthalene tetrachloride [*r*-1-*c*-2-*t*-3-*t*-4-tetrachloro-1-*p*-tolyltetralin (1); see Scheme] was therefore undertaken, together with some subsidiary experiments on 1-phenylnaphthalene tetrachloride.

### EXPERIMENTAL

**Materials and Methods.**—Most of the materials and methods have been described in earlier publications.<sup>1,3-6</sup> Abbreviations used in describing i.r. spectra are s = strong, m = medium, v = very. For <sup>1</sup>H n.m.r. spectra, the abbreviations are s = singlet, etc.; m = multiplet.

**Products of Solvolysis of 1-*p*-Tolynaphthalene Tetrachloride.**—In a typical experiment 1-*p*-tolynaphthalene tetrachloride (0.1 g) dissolved in acetone (20 cm<sup>3</sup>) and methanol (80 cm<sup>3</sup>) was heated under reflux for 2 h. The products were examined by <sup>1</sup>H n.m.r. spectroscopy; replacement of one chlorine appeared to be complete, and no products of elimination were detected. Two isomeric methoxy-derivatives had been formed, and these proved difficult to separate; fractional crystallisation from a number of solvents gave only partial separation. Pure specimens were obtained by chromatography of the mixture (0.85 g) on alumina (250 g) deactivated with 1.5M-HCl (5% w/w). Light petroleum (b.p. 65–69 °C) was used as

eluant, followed towards the end of the separation by a mixture of this with chloroform (50% by volume). The first fractions removed traces of impurity, and were followed by fractions from which *r*-1-methoxy-1-*p*-tolyl-*c*-2,*t*-3,*t*-4-trichlorotetralin (2) was obtained and recrystallised from *n*-hexane to m.p. 208 °C (Found: C, 60.8; H, 4.7; Cl, 29.6.  $C_{18}H_{17}Cl_3O$  requires C, 60.8; H, 4.8; Cl, 29.9%). Its i.r. spectrum in  $CS_2$  had peaks at 3 020, 2 915, 2 825, 1 343, 1 279, 1 270, 1 223, 1 202, 1 184, 1 166, 1 099, 1 079s, 1 050, 1 020, 990, 834, 818m, 789, 759s, 724, 705s, 656, 632m, 608, 564, 545, and 479  $cm^{-1}$ ; additional absorptions in  $CCl_4$  were observed at 1 463, 1 449, and 1 382  $cm^{-1}$ . Its  $^1H$  n.m.r. spectrum ( $CDCl_3$ ) had signals centred at  $\delta$  2.30 (s, 3 H, Me), 3.35 (s, 3 H, OMe), 4.65 (q, 1 H,  $J_{2,3}$  12.0,  $J_{3,4}$  3.6 Hz, H-3), 5.20 (d, 1 H,  $J_{2,3}$  12.0 Hz, H-2), 5.58 (d, 1 H,  $J_{3,4}$  3.6 Hz, H-4), and 6.8–7.5 (m, 8 H, Ar-H).

Intermediate fractions containing both isomers were rejected; later fractions were combined and the product was recrystallised from *n*-hexane to give *r*-1-methoxy-1-*p*-tolyl-*t*-2,*c*-3,*c*-4-trichlorotetralin (3), m.p. 158–159 °C (Found: C, 61.3; H, 4.6; Cl, 29.5%). The i.r. spectrum ( $CS_2$ ) had absorptions at 3 030, 2 960, 2 830, 1 910, 1 348, 1 256, 1 228, 1 205, 1 186m, 1 098vs, 1 092vs, 1 052, 1 024, 993, 838m, 816s, 808s, 764s, 756s, 727m, 704, 686m, 675m, 644, 635, 612, 565m, 522, and 454  $cm^{-1}$ . Additional absorptions in  $CCl_4$  were observed at 1 465 and 1 449  $cm^{-1}$ . Its  $^1H$  n.m.r. spectrum ( $CDCl_3$ ) had signals centred at  $\delta$  2.40 (s, 3 H, Me), 3.10 (s, 3 H, OMe), 4.83 (d, 1 H,  $J_{2,3}$  11.9 Hz, H-2), 5.16 (q, 1 H,  $J_{2,3}$  11.8,  $J_{3,4}$  3.4 Hz, H-3), 5.58 (d, 1 H,  $J_{3,4}$  3.4 Hz, H-4), and 6.8–7.5 (m, 8 H, Ar-H).

The isomers were differentiated clearly, and recognisable in mixtures, by their  $^1H$  n.m.r. spectra; singlets attributable to the methoxy-group were particularly useful for characterisation. The assignment of configuration as in (2) and (3) cannot be made directly from their  $^1H$  n.m.r. spectra; it has been made tentatively on the basis of other evidence discussed later.

The ratio of (2):(3) formed in solvolysis of 1-*p*-tolyl-naphthalene tetrachloride in methanol-acetone (80:20) at 25 °C was 67:33. When carried out at reflux temperature (*ca.* 62 °C), the ratio was 63:37. The corresponding reaction carried out at room temperature in the presence of an excess (2 mol. equiv.) of silver perchlorate gave mainly (3); appreciable amounts of products of disubstitution were also present in the product mixture.

The first-order rate-coefficient for the solvolysis of (1) was determined by following the rate of production of chloride ion potentiometrically;  $k_1 = 1.14 \times 10^{-5} s^{-1}$  in methanol-acetone (80:20 v/v) at 25 °C. The reaction went to completion within experimental error; first-order rate-coefficients fell slightly over the first 30% of reaction, perhaps through a mass-law effect.

*Alkaline Dehydrochlorination of the 1-Methoxy-1-p-tolyl-r-2,t-3,t-4-trichlorotetralins.*—When either of these compounds (2) or (3) was treated with excess of alkali the product was almost entirely 2,3-dichloro-1-*p*-tolyl-naphthalene (6). Analysis by g.l.c., as in the previous paper,<sup>1</sup> showed that for reaction of (2) (*ca.*  $10^{-3}M$ ) with 0.29M- or with 0.06M-NaOMe in methanol-acetone (80:20 v/v), at 25 °C only a trace (<0.1%) of 2,4-dichloro-1-*p*-tolyl-naphthalene was obtained, whereas (3) gave  $0.8 \pm 0.3\%$  of this isomer. The rates of these reactions were also measured as for the 1-arylnaphthalene tetrachlorides;<sup>1</sup> the values of the second-order rate-coefficients (see Scheme) pertain to the

rate of liberation of chloride ion in methanol-acetone (80:20 v/v) at 25 °C and were for (2), with [NaOMe] 0.28M,  $k_2^I = 0.000 62 \pm 0.000 1$  and  $0.000 65 \pm 0.000 02 l mol^{-1} s^{-1}$  in duplicate experiments; for (3), with [NaOMe] 0.06M,  $k_2^{I'} = 0.001 65 \pm 0.000 04$  and  $0.001 77 \pm 0.000 06 l mol^{-1} s^{-1}$ . Rounded-off mean values have been adopted for the following discussion.

Elimination of chloride ion from (2) or from (3) would give first a 2,3-dichloro-1-methoxy-1-*p*-tolyl-1,2-dihydro-naphthalene, (4) or (5) respectively. This then cannot under mild conditions lose the vinylic 3-chlorine atom; to aromatise the reduced ring it must lose methanol, which we expected to be a slow reaction. The loss of methanol was, in fact, slow enough to allow (4) and (5) to be characterised as intermediates in the reaction of the tetralins with methoxide ion, by examination of the products of partial reaction; but it was of rate similar to that of the dehydrochlorination. Neither intermediate could be obtained easily in a pure state, since we had very little of either starting material to work with. In a typical experiment, reaction of (2) was initiated as usual ([NaOMe]<sub>init</sub> = 0.06M). At time-intervals judged appropriate from separate experiments, the solvent was partly removed under reduced pressure, and the reaction was quenched by pouring the residue into dilute aq. HCl. The product was recovered by extraction ( $Et_2O$ ); the ether layer was washed and dried ( $MgSO_4$ ). The solvent was then removed under reduced pressure, and the products were examined by  $^1H$  n.m.r. spectroscopy. In the product from (2), signals attributable to (2), (4), and (6) could be recognised, in approximate ratio 9:40:51 from the integrals of these signals. The intermediate (4) was characterised clearly by signals at  $\delta(CDCl_3)$  2.42 (s, 3 H, Me), 2.82 (s, 3 H, OMe), 4.33 (s, 1 H, H-2), 6.75 (s, 1 H, H-4), and 7.0–8.0 (m, Ar-H). If it is assumed that under the conditions of the reaction the rates of both the stages of elimination must be pseudo-first-order, the ratio of first-order rate-coefficients  $k_1^I$  and  $k_1^{II}$  can be calculated from the product-ratios after partial reaction by using the equations given by Frost and Pearson;<sup>8</sup>  $k_1^I/k_1^{II} = 1.3$ . This will also be the ratio of the second-order rate-coefficients if both processes are bimolecular; so, since  $k_2^I = 0.000 64 l mol^{-1} s^{-1}$ ,  $k_2^{II} = 0.000 49 l mol^{-1} s^{-1}$ .

The corresponding reaction mixture recovered from partial reaction of (3) had signals attributable to (3), (5), and (6) in ratio (from the spectrum integrals) 7:43:50. The intermediate was characterised by peaks at  $\delta$  2.30 (s, 3 H, Me), 3.17 (s, 3 H, OMe), 5.22 (s, 1 H, H-2), 6.57 (s, 1 H, H-4), and 6.8–8.0 (m, Ar-H). From the proportions of partial reaction, the ratio  $k_2^{I'}/k_2^{II'}$  is 1.5, so that with  $k_2^{I'} = 0.001 68$ ,  $k_2^{II'}$  is  $0.001 2 l mol^{-1} s^{-1}$ .

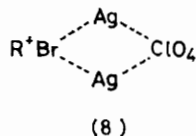
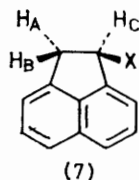
*Solvolysis of 1-Phenylnaphthalene Tetrachloride.*—This reaction was studied only in outline. When 1-phenylnaphthalene tetrachloride (*ca.*  $1.8 \times 10^{-3}M$ ) in methanol-acetone (80:20) had been maintained at 25 °C for 6 days, the  $^1H$  n.m.r. spectrum of the recovered product included two new singlets, the smaller at  $\delta$  3.1 and the larger at  $\delta$  3.35. These were considered to be those of methoxy-groups derived by replacement of Cl by OMe at the 1-position. The rate-coefficient for the very slow solvolysis was  $k_1 = ca. 1 \times 10^{-6} s^{-1}$ . The corresponding reaction catalysed by excess of silver perchlorate gave a product in which the singlet at  $\delta$  3.1 was now larger than that at  $\delta$  3.35; its integral suggested that this component accounted for *ca.* 60% of the monosubstituted product.

The similar reaction of 1-phenylnaphthalene tetra-

chloride with silver perchlorate in acetone-water (72 : 28) at reflux temperature for 6 h gave a product the  $^1\text{H}$  n.m.r. spectrum of which was consistent with the formation of isomeric hydroxy-containing 1-phenyltetralins. It was hoped that this mixture could be converted back into a mixture of 1-phenylnaphthalene tetrachlorides from which a new tetrachloride could be obtained. Treatment with thionyl chloride with or without pyridine, or with triphenylphosphine in  $\text{CCl}_4$ , gave, however, only the original tetrachloride accompanied by products of elimination.

#### DISCUSSION

The structure of the 1-*p*-tolyl-naphthalene tetrachloride (1) used in this work has been established,<sup>1</sup> we think unambiguously. Solvolysis of it gives a mixture of isomeric products (2) and (3) of replacement of the 1-chlorine atom by the methoxy-group. The stereochemistry about C-1 in these isomers does not follow from their  $^1\text{H}$  n.m.r. spectra; evidence is given, however, from the  $^1\text{H}$  n.m.r. spectra of their products of loss of hydrogen chloride. The compounds (4) and (5) derived from (2) and (3) respectively, show a major difference in the position of the singlet attributable to the 2-proton, which in (4) appears at  $\delta$  4.33 whereas in (5) it appears at  $\delta$  5.22. This difference is not reasonably attributable to an inductive effect varying with the stereochemistry about the adjacent carbon atom; in substituted acenaphthenes (7), for example,<sup>9</sup> the signal for  $\text{H}_A$  appears at  $\delta$  3.64 ( $\text{X} = \text{OMe}$ ) and 3.82 ( $\text{X} = \text{Ph}$ ), whereas that for  $\text{H}_B$  appears at  $\delta$  3.31 ( $\text{X} = \text{OMe}$ ) and 3.26 ( $\text{X} = \text{Ph}$ ). Thus interchanging the position of the methoxy and aryl substituents on the 1-position of (4) would not be expected to produce an effect on the chemical shift of H-2 of more than *ca.* 0.2 p.p.m. The observed difference is 0.89 p.p.m. The most likely explanation for the considerable upfield shift in the position of the 2-proton in (4) as compared with (5) is that it arises from diamagnetic shielding by the aryl ring, which in turn implies that the 2-proton is *syn*- to the aryl group as in structure (4). This effect, which has been used by others for the assignment of configuration,<sup>10</sup> is expected to be very critical to the exact conformation adopted by the molecule under investigation; presumably the relatively flexible nature of the dihydronaphthalene system allows close approach of H-2 to the aryl ring.



The assignments of configuration to (4) and (5) made in accordance with the above considerations is supported by the stereochemistry of solvolysis. Consider first the reaction catalysed by silver ions. Here inversion of configuration is commonly observed; Bach and Willis,<sup>11</sup> for example, have found that reaction of 2-bromo-octane with an excess of silver perchlorate in methanol was of

the second kinetic order in silver ion, and gave mostly 2-methoxyoctane of inverted configuration. It was proposed that an intermediate of the form of structure (8) was attacked by solvent preferentially from the rear to give the observed inversion of configuration. Irrespective of the exact nature of the mechanistic sequence and intermediates which could be involved,<sup>12</sup> an interpretation of this kind is consistent with the findings of this work [namely that (1) gives predominantly (3) by replacement with inversion of configuration when treated with silver perchlorate in methanol] provided that the configurational assignment is accepted.

The stereochemistry of the uncatalysed solvolysis supports the above view of the silver-catalysed reaction; inversion of configuration is much less pronounced, and in fact the reaction proceeds with more retention than inversion of stereochemistry at C-1. Unimolecular solvolyses in which configuration-holding groups are absent or not suitably placed stereochemically are normally expected to proceed with predominant inversion;<sup>13</sup> but this is not a universal rule.<sup>12</sup> A 1-arylnaphthalene tetrachloride would seem to provide just the sort of system, somewhat stereochemically rigid and somewhat hindered from the upper face of the molecule, where retention of configuration in a unimolecular solvolysis might be favoured.

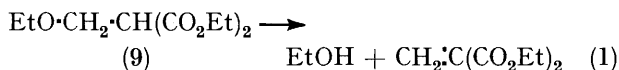
Although the reactions of 1-phenylnaphthalene tetrachloride were investigated only in outline, the results were consistent with those for 1-*p*-tolyl-naphthalene tetrachloride. The rate-coefficients for the solvolyses of the two compounds indicate that a rate-increase by a factor of *ca.* 12 results from introduction of a *p*-methyl group on an aryl ring conjugated with the reacting centre. This ratio supports the mechanistic assignment for the solvolysis as  $\text{S}_{\text{N}}1$ ; for solvolysis of substituted benzhydryl chlorides in methanol,<sup>14</sup> the corresponding ratio is 18, and this ratio would be expected to be reduced somewhat in the 1-arylnaphthalene tetrachloride system because the two activating aryl groups cannot both exert their full conjugative power because of stereochemical constraints.<sup>15</sup>

Earlier,<sup>1</sup> we showed that bimolecular loss of (3-H, 4-Cl) from (1) is favoured by increased electron-withdrawal from the aryl group. It is not unreasonable therefore, that this reaction ( $k_2 = 0.0066 \text{ l mol}^{-1} \text{ s}^{-1}$ ) is faster by a factor of 10 than the corresponding reaction of (2) ( $k_2 = 0.00064 \text{ l mol}^{-1} \text{ s}^{-1}$ ) in which the 1-chlorine atom has been replaced by the less electron-withdrawing methoxy-group. The isomer (3) of (2) undergoes similar bimolecular loss at a similar, slightly faster, rate ( $k_2 = 0.00168 \text{ l mol}^{-1} \text{ s}^{-1}$ ), but we have no other compounds with this disposition of the aryl group for strict comparison.

The reactions of (4) and (5) with base to lose methanol in what appears to be a bimolecular elimination are unusual, and we have been unable to find many precedents. Acid-catalysed eliminations of methanol are of course known;<sup>16</sup> but under these conditions the methoxy-group is presumably protonated, and thereby

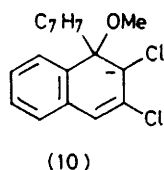
becomes a reasonable leaving group, which normally it is not. Base-catalysed elimination from an ether to give an olefin normally requires forcing conditions.<sup>17</sup>

One reaction which appears to provide an analogy with our base-catalysed elimination is that shown in equation (1), which occurs when the ester (9) is heated.<sup>18</sup>

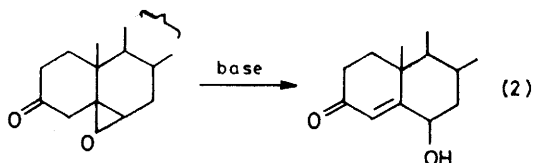


No doubt this reaction proceeds with relative ease because proton-loss from (9) is relatively rapid.

We presume that the bimolecular base-catalysed reactions of (4) and (5) can occur under the mild conditions of our experiments because the 2-proton can be lost to give a carbanion (10) sufficiently easily that assistance from the leaving methoxy-group is not needed.



It seems that the rate of formation of the carbanion (10) is not very critically dependent on the stereochemistry of its precursor, the *syn*-elimination from (5) being only about twice as rapid as the *anti*-elimination from (4). This result in itself accords with the view that the overall elimination is well on the *E1cb* side of the spectrum of bimolecular eliminations.<sup>19</sup> The carbanion (10) must be stabilised by inductive electron-withdrawal by the adjacent groups as well as by the mesomeric distribution of the negative charge over the conjugated system.



The driving force for the overall loss of methanol is the formation of the second aromatic ring in 2,3-dichloro-

1-*p*-tolynaphthalene, just as that for the base-catalysed rearrangement of epoxides to allylic alcohols [equation (2)], which also can proceed under very mild conditions,<sup>20</sup> is the relief of strain in the 3-membered ring.

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