Naphthalene Tetrachlorides and Related Compounds. Part 6.[1] Alkaline Dehydrochlorination of Some 1-Arylnaphthalene Tetrachlorides

By **Keith R. Bedford** and **Peter B. D. de la Mare**,* Chemistry Department, University of Auckland, Private Bag, Auckland, New Zealand

By heterolytic chlorination of 1-(*p*-nitrophenyl)-, 1-(*p*-chlorophenyl)-, 1-phenyl-, and 1-(*p*-methylphenyl)-naphthalene, the corresponding 1-aryl-*r*-1,*c*-2,*t*-3,*t*-4-tetrachlorotetralins have been prepared. Alkaline dehydrochlorination of each of these tetrachlorides gives the corresponding 1-aryl-2,3-dichloronaphthalene, with its 1-aryl-2,4-dichloro-isomer as an accompanying minor component. The observed rate coefficients have been dissected to derive rates for the two competing processes of bimolecular elimination, both of which are modestly favoured by electron withdrawal in the aryl group. The implications of these findings in relation to the mechanisms and transition states for these eliminations are discussed.

PATHWAYS in the alkaline dehydrochlorination of the isomeric naphthalene tetrachlorides are reasonably well understood,[2,3] and the relative rates of these processes have proved to be helpful in the assignment of structure to some of their derivatives.[4,5] Difficulties arise, however, because in this system the competing modes of elimination can have very similar rates. Furthermore, even the directions in which changes in substituents will influence the rate are difficult to predict unambiguously and so cannot be disentangled directly from positional and stereochemical factors. For this reason we have sought to analyse the polar effects of 1-substituents through study of the bimolecular dehydrochlorination of a series of 1-arylnaphthalene tetrachlorides. Results for 1-chloronaphthalene tetrachloride[6] and for 1-phenylnaphthalene tetrachloride[7] have already been reported.

EXPERIMENTAL

Some of the materials and methods are described in earlier papers.[1-3,5-7] A full experimental account, including a description of the preparation of the required 1-arylnaphthalenes, is given in Supplementary Publication No. SUP 22303 (35 pp.)†

Chlorinations of the arylnaphthalenes were carried out in dry purified chloroform; a solution of chlorine was slowly added to a solution of the 1-arylnaphthalene, and the mixture was allowed to stand overnight at room temperature in the dark. The solvent was then removed *in vacuo*, and the oily product was shaken with n-pentane or a suitable light petroleum fraction and allowed to stand at 0°. The solid material was filtered off and the required 1-arylnaphthalene tetrachloride was obtained by column chromatography or by recrystallisation of the crude product. Separations of the required tetrachlorides from unchanged starting material and products of substitution were easy, but it was often difficult to remove minor products of addition. The formation of more highly chlorinated products gave particular difficulty in the preparation of the required 1-(*p*-methylphenyl)naphthalene tetrachloride; it was essential in this case to use the starting material in excess over the added chlorine. 1-(*p*-Methoxyphenyl)naphthalene gave no significant amount of product of addition; presumably it underwent substitution preferentially *ortho* to the methoxy-group.

Pure samples of the new tetrachlorides listed below were obtained in 8—10% yield based on 1-arylnaphthalene consumed in the reaction.

1-(p-*Nitrophenyl*)-r-1,c-2,t-3,t-4-*tetrachlorotetralin* had m.p. 202—205° (Found: C, 49.3; H, 2.9; N, 3.7; Cl, 36.5. $C_{16}H_{11}Cl_4NO_2$ requires C, 49.1; H, 2.8; N, 3.6; Cl, 36.3%).

1-(p-*Chlorophenyl*)-r-1,c-2,t-3,t-4-*tetrachlorotetralin* had m.p. 177.5—179° (Found: C, 50.5; H, 2.8; Cl, 46.7. $C_6H_{11}Cl_5$ requires C, 50.5; H, 2.9; Cl, 46.6%). 1-(*p*-*Methylphenyl*)-r-1,c-2,t-3,t-4-*tetrachlorotetralin* had m.p. 147—148.5° (Found: C, 57.0; H, 3.8; Cl, 39.3. $C_{17}H_{14}Cl_4$ requires C, 56.7; H, 3.9; Cl, 39.4%). The i.r. and ^{1}H n.m.r. spectra of these compounds are given in SUP 22303 along with results of computer simulation of the spectra, which are not amenable to first-order analysis, particularly for solutions in $CDCl_3$. The related information relating to 1-phenyl-*r*-1,*c*-2,*t*-3,*t*-4-tetrachlorotetralin has already been presented.[7]

To prepare reference samples of the products of dehydrochlorination, of which the properties of the new compounds are listed below, the appropriate 1-arylnaphthalene tetrachloride was heated with aluminium trichloride in CS_2 at reflux temperature. The mixture of products was recovered and separated by chromatography, normally on alumina with n-hexane as the eluant. Column fractions were monitored by ^{1}H n.m.r. spectroscopy and were combined appropriately for recrystallisation. New compounds were obtained as follows. 2,3-*Dichloro*-1-(p-*nitrophenyl*)*naphthalene* had m.p. 224° (Found: C, 60.4; H, 3.0; N, 4.5; Cl, 21.9. $C_{16}H_9Cl_2NO_2$ requires C, 60.4; H, 2.9; N, 4.4; Cl, 22.3%). 2,4-*Dichloro*-1-(p-*nitrophenyl*)*naphthalene* had m.p. 121.5—124.5° (Found: C, 60.7; H, 2.9; N, 4.2; Cl, 22.0%). 2,3-*Dichloro*-1-(p-*chlorophenyl*)*naphthalene* had m.p. 161° (Found: C, 62.7; H, 3.0; Cl, 34.3. $C_{16}H_9Cl_3$ requires C, 62.5; H, 3.0; Cl, 34.6%). 2,4-*Dichloro*-1-(p-*chlorophenyl*)*naphthalene* had m.p. 69—71.5° (Found: C, 62.3; H, 3.1; Cl, 34.6%). 2,3-*Dichloro*-1-(p-*methylphenyl*)*naphthalene* had m.p. 141—143° (Found: C, 71.1; H, 4.2; Cl, 24.5. $C_{17}H_{12}Cl_2$ requires C, 71.1; H, 4.2; Cl, 24.7%). 2,4-*Dichloro*-1-(p-*methylphenyl*)*naphthalene* had m.p. 107—108° (Found: C, 71.1; H, 4.4; Cl, 24.4%).

---

† For details of Supplementary Publications see Notice to Authors No. 7 in *J.C.S. Perkin II*, 1977, Index issue.

[1] Part 5, G. W. Burton, P. B. D. de la Mare, and H. Suzuki, *J.C.S. Perkin II*, 1974, 1914.

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

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

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

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

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

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

Details of the i.r. and ^1H n.m.r. spectra of these compounds are given in SUP 22303. The ^1H n.m.r. spectra of the 1-aryl-2,3-dichloronaphthalenes were distinguished from those of their 2,4-dichloro-isomers through the fact that the signal for 4-H appeared (as expected) as a singlet, δ 8.0—8.1, downfield from the multiplet provided by the other naphthalenoid and most of the benzenoid protons. Only for the 1-*p*-nitrophenyl-substituted compound did any of these protons provide signals still further downfield.

Rates of Alkaline Dehydrochlorination.—These were determined as in earlier investigations,[2,3] using the solvent systems 80% methanol–20% acetone (v/v) and 75% benzene–25% methanol (v/v) to facilitate comparison with earlier results. Further details are given in SUP 22303. The rate coefficients are summarised in Table 1.

TABLE 1

Rate-coefficients for alkaline dehydrochlorination of 1-aryl-*r*-1,*c*-2,*t*-3,*t*-4-tetrachlorotetralins (initially 6 × 10^{-4}M) at 25°

Aryl substituent	[NaOMe]/M	k_2/l mol^{-1} s^{-1} Solvent 80 : 20 MeOH–$(CH_3)_2CO$	Solvent 75 : 25 C_6H_6–MeOH
p-$O_2NC_6H_4$	0.06	0.0235	0.006 72
p-ClC_6H_4	0.06	0.0116	0.002 34
C_6H_5	0.06	0.006 81	0.001 28
p-MeC_6H_4	0.26—0.29	0.006 74	0.001 11 [a]

[a] [NaOMe]/M = 0.06.

Products of Alkaline Dehydrochlorination.—Dehydrochlorinations were carried out by using conditions as close as possible to those used for the kinetic measurements. The recovered 1-aryldichloronaphthalene mixtures were analysed by g.l.c., with the results given in Table 2. Further details are given in SUP 22303.

TABLE 2

Products of alkaline dehydrochlorination of 1-aryl-*r*-1,*c*-2,*t*-3,*t*-4-tetrachlorotetralins (initially 6 × 10^{-4}M) at 25°

Aryl substituent	[NaOMe]/M	Solvent [a]	1-Aryl-2,4-dichloronaphthalene in product (%) [b]
p-$O_2NC_6H_4$	0.06	A	3.6, 3.9
	0.012	A	3.3
	0.06	B	3.4, 3.7
	0.012	B	2.1
	0.012	C	4.4
p-ClC_6H_4	0.06	A	1.6, 1.5
	0.012	A	1.2
	0.06	B	1.0, 1.2
	0.012	B	1.0
	0.012	C	1.8
C_6H_5	0.29	A	0.6
	0.06	A	0.7, 0.7
	0.012	A	0.8
	0.06	B	0.9, 0.9
	0.012	B	0.6
	0.012	C	1.6
p-MeC_6H_4	0.27	A	0.7, 0.7
	0.06	A	1.2, 1.1
	0.012	A	2.5
	0.06	B	0.9, 0.9
	0.012	B	1.1
	0.012	C	1.0

[a] Solvents: A, 80 : 20 MeOH–$(CH_3)_2CO$; B, 75 : 25 C_6H_6–MeOH; C, 95 : 5 C_6H_6–MeOH. [b] Peak area of the 1-aryl-2,4-dichloronaphthalene as a percentage of the total peak areas of the 1-aryl-2,3- and -2,4-dichloronaphthalenes.

The formation of dichloronaphthalenes from a naphthalene tetrachloride involves two consecutive processes of elimination. The possibility exists, therefore, that an intermediate chlorodichloride could build up in concentration during the course of the reaction, if the first process were sufficiently faster than the second. Attempts to detect such an intermediate by examining the product of partial reaction by isolation, or by carrying out the dehydrochlorination in an n.m.r. tube and examining the spectrum after extracting the reaction mixture with deuterium oxide [8] were unsuccessful. It is highly probable, therefore, that the second stage of dehydrochlorination is faster than the first, so that the intermediate dichloride does not build up to detectable concentration.

DISCUSSION

In an earlier paper,[7] the structure and predominant conformation of 1-phenylnaphthalene tetrachloride was deduced from the products of alkaline dehydrochlorination and from details of its ^1H n.m.r. spectrum. By using *X*-ray crystallography, Godfrey and Waters [9] have confirmed this result. The additional 1-arylnaphthalene tetrachlorides examined in this work all have similar ^1H n.m.r. spectra, with one large vicinal coupling constant clearly identifiable with $J_{2,3}$ (mean value, 11.1 Hz in $CDCl_3$; 11.4 Hz in C_6D_6) and one small value (mean, 3.6 Hz in both solvents) identifiable with $J_{3,4}$. It seems clear that they are all 1-aryl-*r*-1,*c*-2,*t*-3,*t*-4 isomers analogous in structure to naphthalene α-tetrachloride and existing almost exclusively (>93%) [8] in conformation (1) (Scheme).

The major products of alkaline dehydrochlorination of all these compounds are the appropriate 1-aryl-2,3-dichloronaphthalenes. These are distinguishable from their 2,4- and 3,4-isomers by the fact that the ^1H n.m.r. signals, appearing as a singlet and hence attributable to the single proton in the substituted ring, lie downfield from the main aromatic multiplets, and hence clearly represent 4-protons. In the minor products, on the other hand, the corresponding singlets are overlapped by the remaining aromatic signals. The latter compounds are considered not to be 1-aryl-3,4-dichloronaphthalenes for three reasons: first, because such compounds could only be formed by *syn*-elimination of 3-H, 2-Cl from (1) or (2) in the first stage of dehydrochlorination and this is not expected, since *anti*-elimination (of 3-H,4-Cl or 4-H,3-Cl respectively) would surely prevail; secondly, because no 1,2-dichloronaphthalene is obtained by dehydrochlorination of naphthalene α-, γ-, or δ-tetrachloride;[2,3] and thirdly, because 2,4-dichloro-1-phenylnaphthalene was prepared independently from 1-amino-2,4-dichloronaphthalene and was found to be identical with the minor product from the dehydrochlorination of 1-phenylnaphthalene tetrachloride.[7]

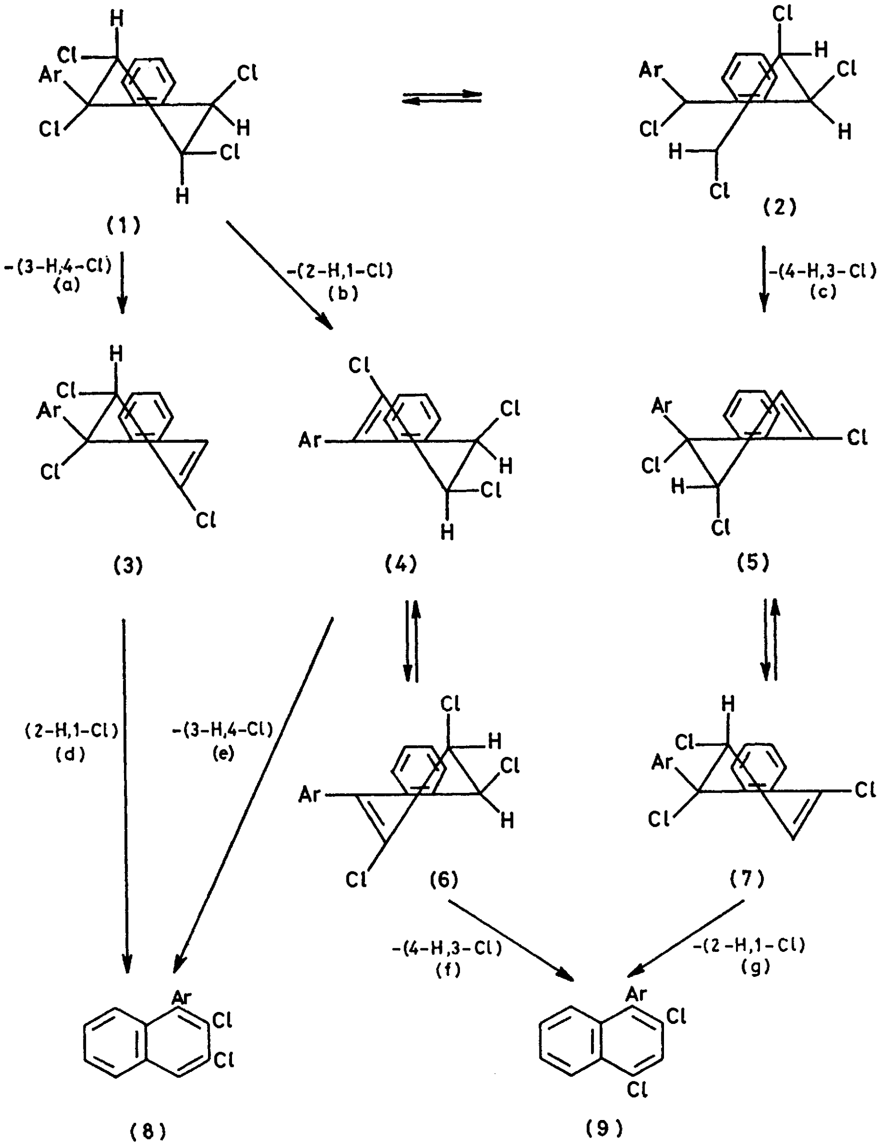
The rates and products of dehydrochlorination of the naphthalene tetrachlorides and of those substituted derivatives which we have examined can be interpreted if we accept the generalisations from our earlier [2,3] discussions of the reactions of related compounds, namely

---

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

[9] J. E. Godfrey and J. M. Waters, *Cryst. Struct. Comm.*, 1975, **4**, 45.

that *anti*-eliminations involving the 1,2- or 3,4-positions will prevail over those involving the 2,3-positions; that the latter in turn will prevail over reactions involving *syn*-eliminations from the 3,4-positions, which then prevail over *syn*-eliminations from the 2,3-positions. On this basis we can use the sequences shown in the Scheme for discussion of the reactions of the 1-arylnaphthalene tetrachlorides.



SCHEME Possible pathways in the dehydrochlorination of the 1-aryl-*r*-1, *c*-2, *t*-3, *t*-4-tetrachlorides

The main (perhaps the exclusive) conformation in which these compounds exist in solution is (1), as is shown by the results of ^{1}H n.m.r. spectroscopy. Conformation (2) is theoretically available; its analogue contributes to the course of elimination from the α-isomer of naphthalene tetrachloride. Elimination with *anti*-stereochemistry from (2) could, however, lead only to the 1-aryl-2,4-dichloronaphthalene (9) through the chlorodichloride (5) $\rightleftarrows$ (7). In discussing the rates of dehydrochlorination in connection with the formation of the major product, therefore, we can to a good approximation neglect this route; we shall return to a consideration of it later, and will present evidence which makes it unlikely that it is adopted at all.

Two modes of *anti*-elimination are in principle available for the tetrachloride (1); they would give the intermediates (3) and (4) respectively. Both these are *cis*-dichlorides and would be expected to undergo rapid further elimination; (3) can give only the 1-aryl-2,3-dichloronaphthalene, whereas (4) [by conformational change to (6) expected to be very rapid] could give also the 2,4-dichloro-derivative (9). For sensible discussion of the variation in rate coefficient for the slow first stage of elimination, however, it is necessary to make assumptions concerning the partitioning of (1) between (3) [step (a)] and (4) [step (b)]. This could be done if we knew the ratio in which (4) partitions between (8) [step (e)] and (9) [step (f), and its pre-equilibrium]. No *cis*-

1,2-dichlorides have been isolated in the naphthalene series; but they are known to be intermediates in the alkaline dehydrochlorination of naphthalene α-tetrachloride and of its analogue 1,1,*r*-2,*t*-3,*t*-4-pentachlorotetralin derived from 1-chloronaphthalene. In each case the product ratios for the total dehydrochlorination are best interpreted on the assumption that the chloro-dichlorides analogues in structure to (4) $\rightleftharpoons$ (6) give both possible dichloronaphthalenes, with the 2,4-isomer analogous to (9) if anything in excess over the 2,3-isomer analogous to (8).

If this conclusion can be applied to the aryl derivative (4) $\rightleftharpoons$ (6), the fact that very little 2,4-dichloro-derivative (9) is formed means also that very little 1-aryl-2,3-dichloronaphthalene is derived by the sequence (1) $\longrightarrow$ (4) $\longrightarrow$ (8). We have assumed that this is so, and have analysed the results given in Table 1 in terms of various assumptions as to the partition ratio between steps (e) and (f). The effects of structure on the rate-coefficients for loss of 3-H,4-Cl [process (a), Scheme], are fitted well by the classical single-parameter Hammett equation, the σ constants *p*-NO_2 0.778; *p*-Cl 0.238; H 0.000; *p*-Me −0.129 being used.[10] The values of ρ derived thus are given in Table 3.

TABLE 3

Variation of calculated Hammett ρ values for elimination of 3-H,4-Cl from 1-aryl-*r*-1,*c*-2,*t*-3,*t*-4-tetrachlorotetralins with assumed partition ratio for intermediate (4)

Assumed partition ratio, step (e)/ step (f)/Scheme	Derived Hammett ρ for solvent MeOH–Me_2CO (80 : 20)	C_6H_6–MeOH (75 : 25)
9	0.44	0.71
4	0.55	0.81
1	0.60	0.85
0.54	0.61	0.86
0.1	0.61	0.86

It can be seen that only a very extreme assumption concerning the behaviour of the intermediate (4) would alter significantly the magnitude of ρ, and its sign is clearly in the direction that electron withdrawal favours the reaction. The potential development of carbanionic character at the 3-carbon atom, γ to the aryl group, in the transition state is therefore helpful for the reaction.

A number of Hammett correlations of rates of *E*2 eliminations have been recorded; the most relevant ones for comparison with our results involve reactants with the aryl substituent on the carbon atom from which the proton is being removed.[11-14] Some of these are recorded in Table 4.

The transmission factor for the insertion of a CH_2CH_2 group into a side chain between the aryl group and the site of the reaction is usually[15] *ca.* 0.2. It may be estimated, therefore, that the insertion of such a group would reduce the ρ value for elimination from 2-phenylethyl chloride with ethoxide ion in ethanol from 2.58 to *ca.* 0.5. This is close to our results for the methanol–acetone solvent system, where the hydrogen atom being attacked is γ- rather than α- to the varying aryl group.

TABLE 4

Reaction constants (Hammett ρ values) for some bimolecular eliminations

Substrate	Solvent, base	$T/°C$	ρ	Ref.
$RC_6H_4·CH_2·CH_2Cl$	EtOH, EtO^-	60	2.58	11
$RC_6H_4·CH_2·CMe_2Cl$	MeOH, MeO^-	66	1.00	12
$RC_6H_4·CH_2·CHPhCl$	EtOH, EtO^-	50	1.98	13
$(RC_6H_4)_2CH·CHCl_2$	MeOH, MeO^-	30	1.93	14

It has been suggested,[6] on the basis of the observation of a large kinetic isotope effect, that the alkaline dehydrochlorination of 1-chloronaphthalene tetrachloride involves a ' central ' transition state, with the C–H bond approximately half broken. The major elimination pathway studied in the present work also involves loss of 3-H,4-Cl, so it is likely that a central transition state is involved also in the major pathway (1) $\longrightarrow$ (3) $\longrightarrow$ (8) for elimination from the 1-arylnaphthalene tetrachlorides. This is consistent with the magnitude of ρ, which indicates that in the transition state there is moderately large charge separation in the C–H bond, the distance of the substituent from this bond being borne in mind.

Hammett[16] predicted that ρ should vary inversely with the dielectric constant of the solvent, and a general tendency in this direction has often been observed.[17] The present results (Table 3) indicate that ρ is somewhat larger in the solvent (75 : 25 benzene–methanol) of lower dielectric constant, and this is probably to be attributed to an increase in carbanionic character at the 3-carbon atom in the transition state. We are unable to evaluate, however, whether this or other effects associated with the change in solvent system make the greatest contribution to the increased value of ρ.

The rate coefficient for elimination of (3-H,4-Cl) from 1-phenyl-*r*-1,*c*-2,*t*-3,*t*-4-tetrachlorotetralin, dissected from the total rate by assuming a partition ratio of one between steps (e) and (f) of the Scheme (0.006 7 l mol^{-1} s^{-1}) can be compared with that of the corresponding reaction of the stereochemically analogous 1,1,*r*-2,*t*-3,*t*-4-tetrachlorotetralin.[6] For this compound, a detailed dissection of the rate coefficients was made possible by study of deuterium isotope effects on rates and product ratios. The appropriate rate coefficient is $k_2 = 0.074\ 5$ l mol^{-1} s^{-1}. The chlorine substituent (σ_I 0.46) is more electron-withdrawing than the phenyl group (σ_I 0.10),[15] and the above difference in rate coefficients is consistent with a reaction pathway facilitated quite markedly by inductive electron withdrawal.

---

[10] H. van Bekkum, P. E. Verkade, and B. M. Wepster, *Rec. Trav. chim.*, 1959, **78**, 815.

[11] C. H. De Puy and C. A. Bishop, *J. Amer. Chem. Soc.*, 1960, **82**, 2535.

[12] L. F. Blackwell, A. Fischer, and J. Vaughan, *J. Chem. Soc.* (*B*), 1967, 1084.

[13] J. V. Griepenbury, Ph.D. Thesis, University of Rochester, 1970; through W. H. Saunders and A. F. Cockerill, ' Mechanisms of Elimination Reactions,' Wiley–Interscience, New York, 1973.

[14] A. B. N. Gray and D. J. McLennan, *J.C.S. Perkin II*, 1974, 1377.

[15] O. Exner, in 'Advances in Linear Free Energy Relationships,' eds. N. B. Chapman and J. Shorter, Plenum, London, 1972, pp. 1*ff.*

[16] L. P. Hammett, *J. Amer. Chem. Soc.*, 1937, **59**, 96.

[17] H. H. Jaffé, *Chem. Rev.*, 1953, **53**, 191.

The reaction pathway which leads to the formation of 1-aryl-2,4-dichloronaphthalene (9) (Scheme 1) is increased in relative importance by electron withdrawal in the 1-aryl group. Its ρ value must, therefore, be positive and greater than that for the formation of the major product. The most direct interpretation is that (9) is formed by path (b), for which ρ is *ca.* 1.5 in methanol–acetone and *ca.* 1.6 in benzene–methanol. This result is consistent with published results in other related systems. Thus Baciocchi *et al.*[18] give the relative rates of elimination from $ArCH(Cl){\cdot}CH_2Ph$, which are compared in Table 5 with the relative proportions of the minor product (9) obtained from the dehydrochlorination of (1) (Scheme), and for the moment attributed to reaction by way of path (b) (Scheme). The results run nicely parallel, even to the extent that if comparison is made under standard conditions the position of the methyl group is slightly anomalous.

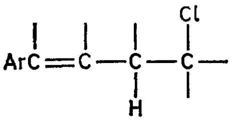
TABLE 5

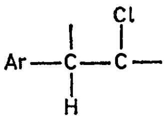
Relative rates and relative proportions of some bimolecular eliminations

	Substituent R in aryl group			
	p-NO_2	*p*-Cl	*p*-H	*p*-Me
Relative rate of reaction of $RC_6H_4CHCl{\cdot}CH_2Ph$ with EtONa in EtOH at 50 °C [18]	6.5	2.1	1.0	1.6
Reactions of 1-arylnaphthalene tetrachloride with MeONa at 25 °C; relative proportion of minor product				
in 80 : 20 $MeOH–Me_2CO$	5.4	2.2	1.0	1.7
in 75 : 25 C_6H_6–MeOH	4.0	1.1	1.0	1.0

It is clear from the Scheme, however, that two other possible interpretations of the change in proportion of (9) with structure need consideration. The first is that we are observing a change in the proportion of reaction through the alternative conformation (2) of the starting material. It is highly unlikely that the proportion of (2) in equilibrium with (1) changes with the structure of the aryl group, so it would need to be assumed that bimolecular elimination from (2) with varying Ar has a ρ value of *ca.* 1.5 in methanol–acetone, or of *ca.* 1.6 in benzene–methanol. Such a value would be very high in view of the distance of the aryl group from the 4-hydrogen atom. Even given two pathways for the transmission of an inductive effect, neither of these involves a conjugative relationship between the varying substituent and the position being affected. Thus we think it very unlikely that the ρ value for removal of (4-H,3-Cl) in (2) could be greater than that for removal of (3-H,4-Cl) from (1). We conclude that the pathway *via* (2) is unlikely to be a major contributor, probably because of the conformational rigidity encouraged by the presence of the 1-aryl group.

A third possible explanation of change in the proportion of (9) with change in structure is that the partitioning of (4) $\rightleftharpoons$ (6) between paths (e) and (f) (Scheme) changes as the aryl substituent is changed. Under these circumstances the partitioning would be considered not to occur in the rate-determining stage (1) → (3)—(5) of the reaction, so the difference in ρ values that would be under consideration would not include the contribution provided by this stage, which would be approximately that of the main reaction (1) → (3). It would, therefore, take a value of *ca.* $(1.5 - 0.6) = 0.9$ for the solvent methanol–acetone and of *ca.* $(1.6 - 0.85) = 0.75$ for the solvent benzene–methanol. This would then represent the difference between the structural influences on elimination of (3-H,4-Cl) from (4) and of (4-H,3-Cl) from (6). Both are likely to be of small magnitude, and will almost certainly be more positive in (4), where we have the system (A) vinylogous with (B), than in (6), where the conjugation between the aryl group and the developing double bond requires interaction with a carbocationic rather than with a carbanionic centre. If the proportion of (9) were determined by partitioning through this route, therefore, electron withdrawal in the aryl group would be expected to favour (8), rather than (9); the latter is observed.


(A)


(B)

We conclude, therefore, that our first interpretation of the effect of structure on the minor pathway for reaction is to be preferred, and that a modestly large positive value of ρ can be ascribed to the effect of change in the aryl group on elimination of (α-H,β-Cl) in these cyclic analogues of β-arylethyl chlorides.

We thank the University Grants Committee for a Postgraduate Scholarship (to K. R. B.), and for the provision of equipment.

[7/2045 *Received, 21st November,* 1977]

---

[18] E. Baciocchi, P. Perucci, and C. Rol, *J.C.S. Perkin II*, 1975, 329.