577. *The Solvolysis of Arylmethyl Chlorides. Part III.* Further Demonstration of Retardation of Solvolysis Rates of* peri-*Compounds.*

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The rates of ethanolysis of several 2-aryl-2-chloropropanes have been measured at 0°. The retardation of the rates of solvolysis of the *peri*-compounds (*i.e.*, 1-naphthalene type), previously observed in the arylmethyl chloride series,[1,2] is here even more pronounced. This is interpreted as due to steric restriction in the transition state of the *peri*-compounds, which is more intense in the present series where the side-chains carry the more bulky methyl groups.

Experimental.—2-*Chloro*-2-2′-*naphthylpropane.* 2-2′-Naphthyl-propan-2-ol was prepared as described by Fieser and Chang[3] and had the recorded properties. This (9·3 g.), anhydrous benzene (15 ml.), and pyridine (1 drop) were stirred at 5° and thionyl chloride (3·9 ml.) was added. The mixture was warmed to 80° for 10 min. while a stream of nitrogen was passed through it. The solvent was distilled at reduced pressure and the residue *in vacuo*, yielding, at 132—134°/0·7 mm., 2-*iso*propenylnaphthalene (7·55 g., 90%), m. p. 54—54·5° (lit., 46—47°, 56°). Dry hydrogen chloride was bubbled slowly for 30 min. into a solution of 2-*iso*propenylnaphthalene (1·0 g.) in ether (80 ml.) at $-20°$ to $-10°$. After 18 hr. at 0° the solvent was distilled at room temperature, yielding a white crystalline residue, m. p. 34—36°, of crude 2-chloro-2-2′-naphthylpropane. The high solubility of this compound precluded its recrystallization from a number of solvents; from light petroleum (b. p. 40—60°) it formed poorly defined crystals whose m. p. was the same as that of the material first isolated. It decomposed on storage. It contained 95% of the theoretically required chlorine. Consequently, when required for kinetic measurements, the chloride was used immediately after removal of the solvent in which it was prepared.

2-*Chloro*-2-1′-*naphthylpropane.* 2-1′-Naphthylpropan-2-ol, obtained analogously to the 2-isomer, formed colourless needles, m. p. 83—85° (lit., 86°) from ether–light petroleum (b. p. 40—60°). Conversion of this material into the chloride was carried out in the same way as the conversion of 2-*iso*propenylnaphthalene.

2-Chloro-2-1′-naphthylpropane was also prepared from the alcohol *via* 1-*iso*propenylnaphthalene, as for the 2-isomer. The *iso*propenyl compound, obtained in excellent yield, had b. p. 100—102°/0·35 mm., n_D^{10} 1·6140.

The chlorides were both used for kinetic measurements immediately after preparation. The rate constants were not different by more than the experimental error (see Table).

The other chlorides were obtained in the same way from the corresponding alcohols, and

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* Part II, preceding paper.

[1] Dewar and Sampson, *J.*, 1956, 2789.

[2] Dewar and Sampson, preceding paper.

[3] Fieser and Chang, *J. Amer. Chem. Soc.*, 1942, **64**, 2043.

in one case also from the corresponding *iso*propenyl compound. In general the products contained 85—95% of the theoretically required chlorine.

2-2′-*Phenanthrylpropan*-2-*ol*. 2-Acetylphenanthrene[4] in benzene was added to methylmagnesium iodide (1·1 mol.) in ether, and refluxed for 30 min. Hydrolysis with aqueous ammonium chloride gave a good yield of 2-2′-phenanthrylpropan-2-ol, colourless needles, m. p. 108—109° (lit., 97—99°) from light petroleum (b. p. 80—100°) (Found : C, 86·5; H, 7·1. Calc. for $C_{17}H_{16}O$: C, 86·4; H, 6·8%).

In a preliminary experiment the Grignard complex was hydrolyzed with 0·5N-sulphuric acid, and the product (50%), obtained by chromatography on alumina from benzene, formed colourless plates, m. p. 183·5—184·5° (from dioxan–ethanol). This was probably 2-iso*propenylphenanthrene dimer* (Found : C, 93·3; H, 6·7%; *M*, 408. $C_{34}H_{28}$ requires C, 93·5; H, 6·5%; *M*, 437).

2-3′-*Phenanthrylpropan*-2-*ol*. This was made by the same method as the 2-phenanthryl isomer. It formed white needles, m. p. 100—101°, from light petroleum (b. p. 60—80°) (Found : C, 86·3; H, 7·0%). On distillation it yielded at 182—184°/0·1 mm. an extremely viscous syrup, probably 3-*iso*propenylphenanthrene. Both it and the alcohol were converted into the chloride for kinetic runs.

2-1′-*Phenanthrylpropan*-2-*ol*. Methyl 1-phenanthroate[1] in benzene was added to methylmagnesium iodide (4 mols.) in ether. After 30 minutes' refluxing the product was isolated as above and recrystallized repeatedly from 1 : 1 benzene–light petroleum (b. p. 80—100°), from which it formed colourless needles, m. p. 103—107° (decomp.). Its analysis was 1% low in carbon, so it was presumably contaminated with the starting material.

2-9′-*Phenanthrylpropan*-2-*ol*. This *alcohol* was obtained from methyl 9-phenanthroate[1] as for the 1-phenanthryl isomer. It recrystallized from benzene–light petroleum (b. p. 80—100°) in colourless needles, m. p. 86—89° (Found : C, 86·7; H, 7·2%).

Kinetics. The requisite amount of the chloride was prepared in the flask to be used for the kinetic work. After removal of the solvent, this flask was placed in a Dewar flask containing ice and water. Ethanol (105 ml.; dried by Lund and Bjerrum's method[5]) at 0° was added, and the flask swirled until the chloride had dissolved, giving a solution of concentration about 5×10^{-3}M. Samples (10 ml.) were removed and quenched in acetone (35 ml.) at −5°. The liberated hydrogen chloride was titrated with a solution of *ca.* 0·01N-triethylamine in toluene (lacmoid).

The reactions were followed for at least two half-lives, and a final reading, after at least ten half-lives, gave the initial concentration of chloride. The first-order rate constants, k_1, calculated by application of the simple law, remained constant throughout to within experimental error. The results are summarized in the Table.

Rates of ethanolysis at 0° *of* 2-*aryl*-2-*chloropropanes.*

Aryl group	10^5k_1 (sec.$^{-1}$) (individual runs)	10^5k_1 (sec.$^{-1}$) (mean values)	Aryl group	10^5k_1 (sec.$^{-1}$) (individual runs)	10^5k_1 (sec.$^{-1}$) (mean values)
Phenyl	—	1·47 *	2-Phenanthryl ...	12·5, 12·5	12·(5)
1-Naphthyl	6·86, 6·65	6·7(5)	3-Phenanthryl ...	22·9, 24·9	23·(5)
2-Naphthyl	11·0, 11·5	11·(2)	9-Phenanthryl ...	12·0	12·(0)
1-Phenanthryl ...	4·83, 4·83	4·8(3)			

* Taken from Baddeley, Chadwick, and Taylor, *J.*, 1956, 448.

Discussion.—Tertiary chlorides are well known to be susceptible to solvolysis by the limiting (S_N1) mechanism. Consequently it is likely that the highly reactive 2-aryl-2-chloropropanes studied in the present work will react by the limiting mechanism even in ethanol.

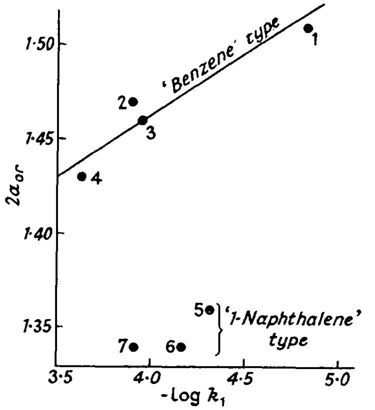
The relative retardation in the rates of the limiting solvolysis of arylmethyl chlorides of " 1-naphthalene " type was interpreted[1] as due to strain, imposed by *peri*-interaction, in some of the σ-bonds in the ions $Ar{\cdot}CH_2^+$. These ions tend to assume a planar configuration in order to enable maximum stability to be derived by conjugation. It appears in this case that full conjugation is achieved.[1] However, examination of molecular models

[4] Mosettig and Van de Kamp, *ibid.*, 1930, **52**, 3704.

[5] Lund and Bjerrum, *Ber.*, 1931, **64**, 210.

suggests that in the ions Ar·CMe$_2^+$ (Ar = " 1-naphthalene " type) *peri*-interaction will be even more serious, for to be completely free from σ-strain the plane of the aromatic portion must be almost perpendicular to the plane containing the two methyl groups and the extracyclic carbon atom. It seems likely, then, that the σ-energy increase necessary for planarity would be too great for compensation by the increased resonance energy. Consequently both the σ-energy and the resonance energy of the transition state would be unfavourably influenced by the *peri*-interaction.

The methyl groups of the ions Ar·CMe$_2^+$ are hyperconjugated with the remainder of the system. The hyperconjugation energy, which contributes to the total resonance energy, is a function of the group Ar· but no reliable estimate of the variation of its magnitude with the nature of Ar can be made. However, for the unhindered ions it is reasonably certain that the total resonance energies of the ions Ar·CMe$_2^+$ run parallel to those of the corresponding ions Ar·CH$_2^+$. Consequently in the Figure we have plotted $-\log k_1$ against $2a_{0r}$, a_{0r} being the coefficient at the extracyclic carbon atom of the non-bonding molecular orbital [1] of the corresponding ion Ar·CH$_2^+$. Because of the hyperconjugation a comparison of the value obtained for β_{eff} from the Figure with the values obtained for the solvolysis of arylmethyl chlorides [1, 2] will not yield useful information.



Solvolysis of 2-aryl-2-chloropropanes in ethanol at 0·0°.

1, Phenyl.
2, 2-Phenanthryl.
3, 2-Naphthyl.
4, 3-Phenanthryl.
5, 1-Phenanthryl.
6, 1-Naphthyl.
7, 9-Phenanthryl.

The Figure shows that the " 1-naphthalene " compounds are greatly retarded in comparison with the unhindered compounds. Unfortunately the " 1-naphthalene " compounds do not vary sufficiently in reactivity to permit an estimate of the fall in β_{eff} (*i.e.*, the fall in utilization of the potential conjugation) on passing to the " 1-naphthalene " compounds from the unhindered type. However, the order of magnitude of the retardation in the 2-aryl-2-chloropropane series compared with the arylmethyl chloride series (limiting conditions) [1] is made clear by the following ratios of rate-constants :

$$\frac{\textit{1-Chloromethylnaphthalene}}{\textit{2-Chloromethylnaphthalene}} = \frac{44 \times 10^{-6}}{2{\cdot}6 \times 10^{-6}} = 17$$

$$\frac{\textit{2-Chloro-2-1'-naphthylpropane}}{\textit{2-Chloro-2-2'-naphthylpropane}} = \frac{6{\cdot}75 \times 10^{-5}}{11{\cdot}2 \times 10^{-5}} = 0{\cdot}60$$

Thus the substitution of the methyl groups into the side-chain results in a reversed order of reactivity, and the 1-naphthyl compound suffers a 17/0·6 or 28-fold additional retardation.

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