

LEWIS ACIDS AS CATALYSTS FOR REGIOSPECIFIC ISOMERISATIONS AND ELIMINATIONS INVOLVING
REACTIONS INITIATED AT BENZYLIC CENTRES

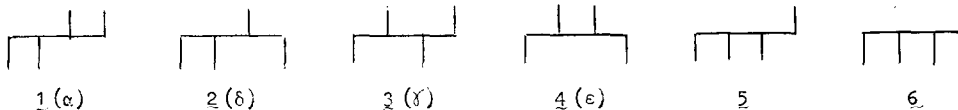
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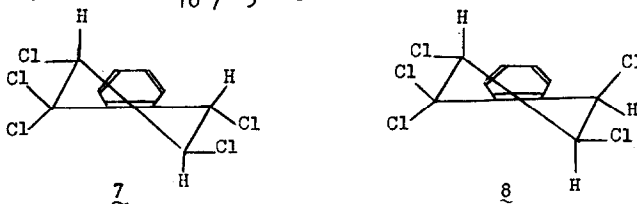
Aluminium chloride, like other Lewis acids, can initiate ionisation from organic chlorides, RCl , in suitable aprotic solvents. Subsequent reactions of the resulting carbonium ion-pair, $[\text{R}^+\text{AlCl}_4^-]$ can include reaction with a nucleophile to give products of electrophilic substitution by R^+ ; ¹ proton-loss, to give products of elimination; ^{2,3} ionic recombination to give racemised RCl ; ⁴ and rearrangements of various kinds. ^{1,3} Well known as these reactions are, their potential for selective promotion of particular reaction paths does not seem to have been documented extensively. We now report three examples from our studies of the naphthalene tetrachlorides and their derivatives to illustrate this feature.

First, of the six possible naphthalene tetrachlorides having the geometrical configurations indicated below, four are known. ⁵ With excess of aluminium chloride in carbon disulphide at ca. 20° the ϵ -isomer is unaffected, but any one of the first three isomers (α, γ, δ) isomerises smoothly over 6 h to an equilibrium mixture having the approximate composition-ratio $\delta:\alpha:\gamma = 20:10:1$. None of the ϵ -isomer is formed; nor are either of the two as yet unknown isomers present in the reaction mixture, as judged by ¹H n.m.r. spectroscopy, gas-liquid chromatography (g.l.c., which can be carried out at 170°C on either 5% SE-30 or 5% OV-17 with little decomposition of the tetrachlorides), or by thin-layer chromatography (t.l.c.). No decomposition of the tetrachlorides is noted, but the solid AlCl_3 is blackened after some time. By using nitromethane or nitrobenzene as solvents either alone or diluted with chloroform or methylene chloride, the speed of the reactions is greatly increased, presumably because of the increased solubility of aluminium chloride. Isomerisation is complete within a few minutes; some subsequent decomposition occurs. Antimony pentachloride also catalyses the isomerisations and the subsequent decompositions; stannic chloride is very much slower in its action.



The equilibrium mixture formed in this reaction is that which would be expected if isomerisation involved ionisation specifically at benzylic centres. The unknown isomers 5 and 6 should consequently give a mixture of 4, 5, and 6, in which 4 would probably predominate since we found that it did not isomerise when treated similarly.

Secondly, the 1-chloronaphthalene tetrachloride 7, m.p. 137°, when treated with aluminium chloride in nitrobenzene, gives an equilibrium mixture containing ca. 80% of the isomer 6 8, m.p. 131-132.5°. A similar equilibrium is reached from 8 under the same conditions. Both of these compounds undergo subsequent eliminations more readily than do the naphthalene tetrachlorides. The structure of 7, which is one of the products of photolytic chlorination of 1-chloronaphthalene follows from its ¹H n.m.r. spectrum, which is deceptively simple in CDCl₃, but in (CD₃)₂CO is sufficiently resolved to be treated by first-order analysis and to show clearly the existence of two large alicyclic coupling constants; τ 4.71 (d, 1H, J_{2,3} 11.6 Hz, 2-H), 5.34 (q, 1H, J_{2,3} 11.6, J_{3,4} 9.1 Hz, 3-H), 4.26 (d, 1H, J_{3,4} 9.1 Hz, 4-H), 1.8-2.1 and 2.2-2.6 (m, 4H, Aromatic H). (Found: C, 39.3; H, 2.4; Cl, 58.6; C₁₀H₇Cl₅ requires C, 39.4; H, 2.3; Cl, 58.2%).



Thirdly, more vigorous treatment of 8 with aluminium chloride (e.g., under reflux in carbon disulphide) gives 1,2,4-trichloronaphthalene (70%) and 1,2,3-trichloronaphthalene (30%). In the alkaline dehydrochlorination of 8, however, the direction of preponderant elimination is reversed (1,2,4-trichloronaphthalene, 20%; 1,2,3-trichloronaphthalene, 80%, for reaction in 80% methanol-20% acetone at 25°C), ⁶ thus illustrating the dichotomy between reaction paths taken in eliminations catalysed by nucleophiles on the one hand and electrophiles on the other.

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