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STUDIES OF DICHLORO- AND
TETRACHLORO- ADDUCTS OF NAPHTHALENE
AND SOME OF ITS SUBSTITUTED DERIVATIVES

A Thesis presented to the
University of Auckland
for the Degree of
Doctor of Philosophy

by

Graham William Burton

University of Auckland               December, 1973
To

H E D Y

and

M A T T H E W
trans-1,2-Dichloro-1,2-dihydronaphthalene has been obtained as the major product of the photochlorination of naphthalene at low temperature, and is the first authentically described naphthalene dichloride. Its further reaction with chlorine, under heterolytic conditions gives, in part, a new naphthalene tetrachloride, whose configuration has been assigned, by $^1$H n.m.r., as being that of the \( r-1, c-2, c-3, t-4 \)-isomer. The assigned configuration and conformation of the compound are confirmed by its behaviour on alkaline dehydrochlorination, which gives mainly trans-1,2,4-trichloro-1,2-dihydronaphthalene as an intermediate.

The naphthalene dichloride, and its 4-chloro-derivative, have been found to undergo solvolysis in methanol-acetone (4:1), and it is further found that heterolysis of the carbon-chlorine bond at C-2 is strongly favoured, leading largely to the 1-chloro-substituted elimination product. The former dichloride also gives a small amount of 1-methoxynaphthalene, which is possibly derived by unimolecular substitution at the 1-position. The presence of a chlorine atom at the 3-position of the structure is found to inhibit the solvolytic reaction. Bimolecular syn-elimination in these compounds is accelerated by the presence of additional chlorine substituents, and the increasing preference shown for attack at H-2, which is further accentuated by the use of the powerfully basic reagent, potassium t-butoxide in t-butanoldimethylsulphoxide (1:4), is interpreted as indicating a transition
state tending toward the E1cB-like side of the E2 spectrum of transition states.

The naphthalene tetrachlorides, and some derivatives, have been found to undergo aluminium trichloride-catalysed epimerization at the benzylic centres, which yields information on the relative thermodynamic stabilities of isomers with identical relative configurations at C-2 and C-3, and can also be of synthetic value.

The photochlorination of 1-chloronaphthalene in CCl₄ at room temperature proceeds analogously with the reaction of naphthalene under the same conditions, giving five new tetrachlorides, four of which have been thoroughly characterized.

The presence, in some tetrachlorides, of inter-ring non-bonded compressions between adjacent chlorines has been found to cause significant changes in the geometry of the alicyclic ring, causing a tendency for the half-boat conformation to be adopted, provided this does not lead to 1,4-diaxially related chlorines. The strain present in these compounds is manifested by their very marked tendency to undergo isomerization in the presence of aluminium trichloride, and greatly increased rates of alkaline dehydrochlorination.

The chlorination of 1,5-dichloronaphthalene in chloroform, or dichloromethane, has been studied and has been found to be markedly catalysed by traces of iodine. The products are almost wholly derived by addition of chlorine in the first stage, and this has been interpreted as arising from a steric inhibition of proton-loss by the adjacent peri-chlorine.
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