

Nucleophilic Displacement in Chloroazulenes

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Methoxydechlorination of 5,6-dichloroazulene and of some chlorinated derivatives apparently proceeds by the S_NAr mechanism in methanol, and shows some unusually long-ranged substituent effects.

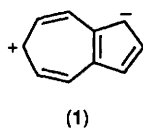
The observed dipole moment of azulene (1.0 D),¹ its nucleophilic attack at C-4 and C-6,² and its ready electrophilic substitution at C-1 and C-3³ are all rationalised in terms of resonance contributions such as structure (1). The nucleophilic displacement of halogen from the seven-membered ring has been demonstrated by Hafner⁴ for 6-chloro-4,8-dimethylazulene, and was advocated⁵ as a route to new azulenes following the synthesis of 5,6-dichloroazulene^{5,6} although no such reactions have been reported.

We now report the first kinetic studies of nucleophilic substitution in the azulene system, using methoxydechlorination of derivatives of 5,6-dichloroazulene in methanol. The reaction shows the bimolecular kinetics in equation (1) expected of the S_NAr mechanism,⁷ and is also unaffected by irradiation by light; both this behaviour and the kinetic form

argue against the $S_{RN}1$ mechanism.⁸ Although σ -bonded intermediates were found in the sulphonation⁹ and carb-anionic attack² of azulene, we found no suggestion of the formation of stable Meisenheimer complexes in these reac-

Table 1. Rate constants for methoxydechlorination of polychloroazulenes.

| Azulene | $k_2/\text{mol}^{-1} \text{dm}^3 \text{s}^{-1}$ (323 K) | k_{rel} |
|---------------------|--|------------------|
| 5,6-Dichloro | 6.0×10^{-5} | 1 |
| 1,3,5,6-Tetrachloro | 2.4×10^{-2} | 400 |
| 4,5,6,7-Tetrachloro | 1.2×10^{-2} | 200 |



tions of 5,6-dichloroazulene, the only detectable organic products being those of methoxydechlorination (visible, ^1H and ^{13}C NMR, and mass spectroscopy).

$$-d[\text{ArX}]/dt = k_2[\text{ArX}][\text{MeO}^-] \quad (1)$$

Attack occurred at C-6 and, where possible, concurrently at C-4; the sites observed to undergo displacement are shown in bold type in Table 1. In contrast with the methoxydefluorination of polyfluoronaphthalenes¹⁰ or of polyfluorobiphenyls¹¹ substituents were slightly more effective at the more distant 1- and 3-positions than at C-4 and C-7; 4,5,6,7-tetrachloroazulene reacted more slowly than the 1,3,5,6-isomer even though attack took place at similar rates (NMR analysis of the product mixture) at C-4 and C-6. In the former isomer activating electron-withdrawal is resisted by the tropylium-like charged aromatic system, while in the 1,3,5,6-tetrachloro

compound electron-withdrawal encourages polarisation as in (1) and in this manner facilitates reaction.

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