Nucleophilic Displacement in Polyhalogenoaromatic Compounds. Part 14.[1] Chloroazulenes

Roger Bolton,* Darren G. Hamilton and John P. B. Sandall
Department of Chemistry, Royal Holloway and Bedford New College, Egham Hill, Egham, Surrey TW20 0EX, UK

Methoxydechlorination of 5,6-dichloroazulene in NaOMe–MeOH shows second-order kinetics, apparently proceeding by the S_NAr mechanism in which the attack of the nucleophile, and not the loss of chloride ion, is rate-determining. No evidence of a Meisenheimer-type intermediate is found. The rate of the reaction is not affected by light, nor by the presence of nitrobenzene; radical contributions to the process are therefore unlikely. The corresponding reactions of 4,5,6,7- and 1,3,5,6-tetrachloroazulene, and of 1- and 3-nitro-5,6-dichloroazulene all show second-order kinetics and are all accelerated compared to the parent compound; 1,3,4,5,6,7-hexachloroazulene reacted too rapidly for measurement. As expected, the extent of such acceleration is conditioned not only by the nature of the substituent but also by its position. Unexpectedly, chlorine substituent effects are clearly greater from the five-membered ring than from the ring undergoing attack.

Semi-empirical all-valence-electron SCF–MO calculations are presented which rationalise the orientation of attack and describe the observed substituent effects.

The stability of the azulene system has often been rationalised in terms of resonance structures such as **1** in which the five-membered ring acquires cyclopentadienyl carbanionic character while the seven-membered ring loses an electron to become tropylium ionic in nature. Such contributions explain (*i*) the observed dipole moment[2] (*ii*) the ready electrophilic attack upon C-1 of the five-membered ring[3] and (*iii*) the similarly ready nucleophilic attack upon C-4 and C-6 by amide ion[4] and by carbanionic species generated from organometallic compounds.[5] The reports of amide-ion attack on azulene are confused, one claiming the 4-isomer[6] and the other the 6-isomer; in neither case is convincing evidence of isomeric identity presented, although later reports support the 4-aminoazulene.[5]

1

Some studies of electrophilic attack upon azulenes have been reported, such as hydrogen isotope exchange[7] and sulphonation reactions; in both cases, evidence is presented of σ-bonded intermediates (Wheland structures).[8] Studies of the spectral shifts of derivatives of 1-azulenol[9] and of pK_a measurements of some 2-, 3- and 6-substituted azulene-1-carboxylic acids[10] suggested that while groups at C-2 and C-3 showed similar interactions to those found with *ortho* and *meta*-substituted benzene systems, substituents at C-6 behaved substantially as though they were attenuated *para*-substituents. Under these conditions, and using σ_p values from the ionisation of benzoic acids, the dissociation constants of the four 6-substituted azulene-1-carboxylic acids (X = Me, MeO, Br, H) show ρ = *ca.* 1.2. The corresponding treatment of the pK_a values of the 3-substituted acids gives ρ = *ca.* 1.9, using σ_m as the substituent parameter. A study of the deuteriodeprotonation (CH_3CO_2D–CH_3OD, 100 °C) at C-1 of some 3-substituted azulenes showed $\rho = -4.35$, again using σ_m.[11] No kinetic studies of aromatic nucleophilic substitution of azulene systems have been reported. Indeed, while the putative displacement of chlorine from compounds such as 5,6-dichloroazulene was advanced[12] as a logical and preparatively desirable consequence of their synthesis, only the early work by Hafner[13] on the reaction of 6-chloro-4,8-dimethylazulene with methoxide ion and some amines stands as experimental support of this type of reaction at C-6, with similarly sparse reports of nucleophilic attack at C-2[14] and at C-4. In general, very few kinetic studies have been made upon azulene systems, and in particular there is little to suggest how variously positioned substituents might affect the rate of reaction at a site in such systems.

This paper reports a two-pronged approach upon this unaddressed problem; some of the results have already been published in a preliminary communication.[1b] A number of derivatives of 5,6-dichloroazulene have been prepared, and their rates of methoxydechlorination have been measured by following the changes seen in the visible spectrum of the azulene derivative. This allowed the mechanism and the substituent effects to be deduced. The second method of attack calculated the overall energy of formation, and the individual electron densities located upon each carbon atom of these derivatives so that an order of reactivity might be calculated and checked against experiment.

Discussion

Synthesis.—The reported preparation of 5,6-dichloroazulene **2**[6,15] by thermal decomposition of the adduct between 6-(dimethylamino)fulvene[16] and 3,4-dichlorothiophene 1,1-dioxide[17] is in principle a general synthetic method towards azulenes which has been used to obtain other chloroazulenes, although in very poor yield.[18] The formation of 2,3,4,5-tetrachlorothiophene 1,1-dioxide by the *m*-chloroperoxybenzoic acid oxidation of the tetrachlorothiophene is the basis of a report of the synthesis of a number of Diels–Alder adducts,[19] and this suggested a route to 4,5,6,7-tetrachloroazulene, which has been reported but without any experimental details.[20] The large-scale preparation of 2,3,4,5-tetrachlorothiophene 1,1-dioxide could not be repeated; only unchanged thiophene or 2,3,3a,4,5,6,7,7a-octachloro-3a,7a-dihydrobenzo[*b*]thiophene, the product of further reaction of the thiophene dioxide, could be isolated from such reaction mixtures, a problem encountered by other workers.[21] While the crude oxidation product contained sufficient of the thiophene dioxide to allow the isolation of 4,5,6,7-tetrachloroazulene (**3**) by the proposed

Table 1 Second-order rate constants for methoxydechlorination of some azulenes

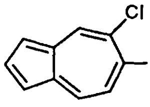
Substituents	[NaOMe]/ mol dm^{-3}	T/K	$k_2/10^{-3}$ dm^3 mol^{-1} s^{-1}
5,6-Cl$_2$	0.48	313	0.017
	0.48	323	0.060
	0.52	326	0.080^a
	0.17	328	0.097
	0.27	328	0.106
	0.40	328	0.130
	0.40	333	0.175
4,5,6,7-Cl$_4$	0.40	323	12.3
	0.40	328	16.5
	0.40	333	23.8
	0.20	328	18.0
	0.12	328	18.4
	0.08	293	4.1
	0.08	303	9.7
	0.08	313	13.5
	0.04	300	6.5
1,3,5,6-Cl$_4$	0.20	300	6.75
	0.40	300	5.75
1(3)-NO$_2$-5,6-Cl$_2$	0.02	288	375
	0.02	293	465
	0.02	303	650
	0.01	300	770
	0.02	300	465
	0.04	300	540
1,3,4,5,6,7-Cl$_6$	0.008	298	$>10^{5b}$

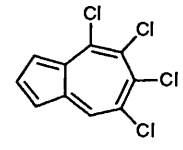
^{a} Irradiated by 100 W clear tungsten-filament lamp. ^{b} Immediate colour change on adding methoxide solution; after 5 s, no further detectable change in spectrum. Half-life estimated at *ca.* 1 s.

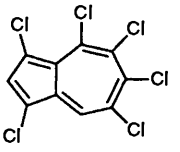
Table 2 Relative second-order rate constants ($k_{\rm rel}$) at 323 K

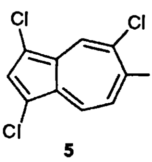
Azulene	$k_{\rm rel}$
5,6-Dichloro-	1
1,3,5,6-Tetrachloro-	400
4,5,6,7-Tetrachloro-	200
1(3)-Nitro-5,6-dichloro-	6×10^4
1,3,4,5,6,7-Hexachloro-	$>10^6$

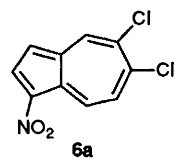
method the yields were poor and the crude mixture required repeated chromatography to free the azulene from unreacted tetrachlorothiophene. Pure 4,5,6,7-tetrachloroazulene could be obtained by crystallisation from ethanol; mass spectrometry showed (*i*) an exemplary spectrum for a tetrachloroazulene and (*ii*) the absence of tetrachlorothiophene, deductions which were confirmed by combustion analysis.

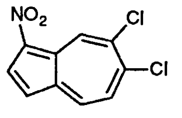

2


3


4

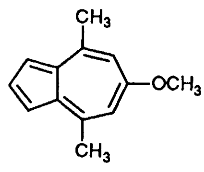

5

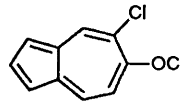

6a


6b

Substitution by *N*-chlorosuccinimide, which converts azulene into the 1,3-dihalogeno-derivative,[22] gave 1,3,5,6-tetrachloroazulene. With 4,5,6,7-tetrachloroazulene the corresponding compound was 1,3,4,5,6,7-hexachloroazulene (**4**) on the basis of mass spectrometry and ^{1}H NMR spectroscopy which showed peaks at δ 7.58 (2-H) and 8.36 (8-H) ppm. The calculated values were 7.54 and 8.41 ppm, respectively, based upon (*i*) the chemical shifts found in **3** and (*ii*) the incremental effect of 1,3-dichloro substitution upon **2** in **5**. Nitration of 5,6-dichloroazulene was achieved using copper(II) nitrate–acetic anhydride mixtures, as in the corresponding mono-nitration of azulene.[3] The reaction product, after purification by column chromatography, was a mixture of similar amounts of the 1- and 3-nitro derivatives which resisted separation. The isomeric mixture was used in the kinetic studies; it behaved as a single species in methoxydechlorination, suggesting that the two isomers showed similar rates of reaction.

Kinetics.—Methoxydechlorination follows second-order kinetics, *i.e.* rate = k_2[MeO$^-$][Chloroazulene] for the attack of 5,6-dichloroazulene, of 1,3,5,6-tetrachloroazulene (**5**) and its 4,5,6,7-isomer (**3**), and of the mixed 1- and 3-nitro-5,6-dichloroazulenes (**6a, b**) (Table 1). The spectral changes were entirely consistent with the formation of a single substance from the organic reagent although more than one product arose from 4,5,6,7-tetrachloroazulene. No intermediates analogous to the Meisenheimer complexes were detected, nor was the visible spectrum of 6-methoxy-4,8-dimethylazulene (**7**), or of 5-chloro-6-methoxyazulene (**8**), affected by the presence of sodium methoxide under our kinetic conditions. In such displacement reactions nucleophilic addition to the azulene, and not the loss of chloride ion from an intermediate, appears to be rate-limiting. Light did not increase the rate of displacement of chlorine by methoxide ion from 5,6-dichloroazulene, nor did the addition of nitrobenzene (1% by volume). While azulenes readily undergo oxidation in the presence of light, and are attacked by copper(II) derivatives such as CuCl$_2$ to give substitution products[23] no radical-induced mechanism of nucleophilic displacement analogous to the S$_{\rm RN}$1 process was found here.


7


8

Compounds **2** and **5** gave only the products of methoxydechlorination at C-6, while the mixed nitro-compounds **6a, b** gave a similarly intractible mixture of methoxydechlorination products which showed two OMe peaks, in similar quantity, in the ^{1}H NMR spectrum. 4,5,6,7-Tetrachlorazulene (**3**) on methoxydechlorination, afforded a mixture which could be interpreted, on the basis of the ^{1}H NMR spectrum, as containing 5,6,7-trichloro-4-methoxyazulene (δ 3.94 ppm; *J* 1 Hz), and 4,5,7-trichloro-6-methoxyazulene (δ 3.99 ppm) in equal amounts, together with 5,7-dichloro-4,6-dimethoxyazulene (δ 3.98 and 4.10 ppm). These tentative identifications are being further investigated.

The mechanism of the displacement appears to be the classic S$_{\rm N}$Ar reaction shown, for example, by the displacement of halogen from polyfluorinated arenes[24,25] or polynitrohalogenobenzenes.[26]

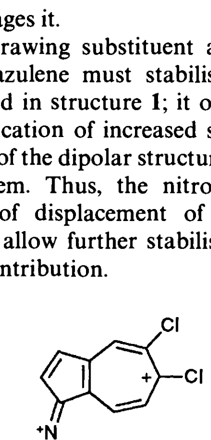
Substituent Effects.—Chlorine and nitro substituents clearly accelerate the displacement (Tables 1 and 2). Chlorine in the seven-membered ring, however, evidently has less effect than chlorine in the five-membered ring in assisting nucleophilic attack at C-6. For example, 1,3,5,6-tetrachloroazulene loses the 6-chlorine substituent more rapidly ($k_{\rm rel}$ 400; Table 2) than does

4,5,6,7-tetrachloroazulene (k_{rel} 200 at 323 K). This observation, that a more distant substituent has a greater effect, is at variance with experience in benzenoid systems, where the transmission of electronic effects across biphenyl,[24a] naphthalene,[24b] and other aromatic structures is markedly attenuated compared to the transmission of the same electronic effects across the benzene ring or across the same aromatic ring in a polybenzenoid system. Although σ-values obtained from benzene systems should not be applied to azulene, biphenyl or naphthalene systems the practice is common, and in the absence of any measurement of the effects of substituents upon the pK_a value of azulene-6-carboxylic acid we shall follow the earlier precedent.[9–11] Using σ_p to reflect the transmitted electronic effect from sites C-1 and C-3 to C-6 in the chloroazulene gives a value of ρ (6.0 at 323 K) much greater than that found in the methoxydefluorination of either polyfluorobiphenyls (ρ 1.7 at 323 K)[24a] or polyfluoronaphthalenes (ρ *ca.* 2 at 323 K),[24b] and comparable to those found in the analogous reaction of polyhalogenobenzenes. The magnitude of the transmission of effects in the azulene carboxylic acids is similarly comparable in value to that found in the benzene system, so that 2-, 3- and 6-substituted azulene-1-carboxylic acids all show ρ values of 1.0 or more.[10]

The explanation seems to rest upon a consideration of the azulene structure.

The dipolar contribution exemplified by **1** reflects the susceptibility of the two rings towards electrophiles and towards nucleophiles. A group contributing towards the nucleophilic displacement of chlorine from C-6 in an electron-poor ring system is in a different energetic situation from the same group acting upon a formally uncharged aromatic structure (as in chlorobenzene, for example). Specifically, electron-withdrawal must become more difficult from an electron-poor ring; and electron-donation must be encouraged in such a situation. The relative contributions of the −I and +M components of a halogen substituent might be different in a benzene system and in an azulene system and, by extension, the two contributions might be different when the group is attached to the electron-rich five-membered ring or to the electron-poor seven-membered ring. However, transmission across polybenzenoid systems[24,25] suggests that the total composite electronic substituent effect is passed across the π system. The formally deactivating component is not screened out in such transmission, and we therefore propose that the total electronic substituent effect of a group acts upon an aromatic system regardless of whether that system encourages this effect or discourages it.

An electron-withdrawing substituent attached to the five-membered ring of azulene must stabilise or encourage the polarisation described in structure **1**; it offers extra resonance forms with the implication of increased stability and hence a greater contribution of the dipolar structure to the ground state of the azulene system. Thus, the nitro substituent greatly enhances the rate of displacement of 5,6-dichloroazulene; structures such as **9** allow further stabilisation of the dipolar azulene resonance contribution.



9

Molecular Orbital Calculations.—Evidence has already been adduced for a typical S_NAr second order methoxydechlorination process with attack occurring at both positions C-4 and C-6. There are three possible approaches to a theoretical investigation of this kind of reaction: (*i*) simple determination of the electron densities, bond orders, *etc.* in the ground state (*ii*) calculations of the relative energies of Meisenheimer intermediates[27b] or (*iii*) a complete investigation of all possible reaction coordinates. Early investigations[28,29] of methoxydefluorination in polyfluorobenzenes using both semi-empirical and *ab initio* methods suggest that there is no great advantage in the more expensive and time-consuming approaches, and so ground-state structures only were considered in calculation. This approximation is also adequate in calculations which ignore solution energies.

All calculations showed the ground state to have a planar structure to within a few tenths of a degree. This also applied to the nitro-group when using the AM1 method; the early MNDO calculations twist this group out of the aromatic plane in nitrobenzene. Calculations of azulene itself showed the expected drift of electrons from the seven- to the five-membered ring; a dipole of 1.8 D (1.05 experimentally)[2] was obtained. The charge densities at carbon show positive values at C-4, C-6 and C-8 showing that it is these positions which are more likely to suffer nucleophilic attack when substituted with halogen, or even in the parent hydrocarbon, as experiment has shown. Thus the positive charge density at C-6 for 6-chloroazulene (+0.035 e) is greater than that at C-5 (−0.081 e) in the 5-isomer. These values suggest a very high degree of lability for chlorine at C-6, since values of positive charge density at C-1 of 4-nitrochlorobenzene (−0.03 e) and of 3,5-difluoro-4-nitrochlorobenzene (+0.03 e) are similar in magnitude. The charge density at C-4 in 4-chloroazulene is, however, still greater (+0.042 e) predicting even faster attack at this position in this compound.

This pattern of relative charge density remains in the 4,5,6,7-tetrachloroazulene system [charge densities are +0.045 (C-4) and +0.006 (C-6)] suggesting that in this compound two chlorine atoms will be replaced, as is indeed observed, but with C-4 reacting more rapidly than C-6.

In all these chloro compounds which have substituents in the seven-membered ring, the five-membered ring retains a large negative charge at C-1, C-2 and C-3. Even in 4,5,6,7-tetrachloroazulene these positions show charge densities of −0.16, −0.12 and −0.13 e, respectively, suggesting that electrophilic attack remains easy at all three positions, so that further chlorination of **3** proceeds fairly readily. Despite the reduction in charge density at C-3 to a level similar to that at C-2, attack appears to occur entirely at C-1 and C-3.

The validity of our suggestion concerning the dependence of substituent effects upon the nature of the ring to which they are bonded can be quantified by examination of the electron distribution in the various azulene derivatives. In 4,5,6,7-tetrachloroazulene the charge density at C-6 is +0.006 e, whereas in the 1,3,5,6-isomer this is increased markedly to +0.023 e. It seems probable that this effect is enhanced by the well-known mutual reduction in electronic effect in *ortho*-substituted chlorine groups.[30]

In the case of the two nitro-5,6-dichloroazulenes, the calculations correctly predict a similar reactivity at the C-6 position, independent of whether the nitro-group is at C-1 or C-3 relative to the second chlorine atom at C-5. The charge at C-6 (+0.012 e or **6a**; +0.0133 e for **6b**) is, however, smaller than that found at C-6 in 1,3,5,6-tetrachlorazulene (+0.023 e) suggesting that the latter should be more reactive, contrary to our experimental observations. Clearly these predictions based upon considerations of charge densities at carbon atoms should not be pressed too far.

Experimental

^1H and ^{13}C NMR spectra were obtained in $CDCl_3$ solution with TMS as standard, using a JEOL 270 MHz machine. All coupling contents are given in Hz. We thank Martyn Draper for these measurements, the University of London (ULIRS) facilities at the School of Pharmacy, Brunswick Square for measurement of low resolution mass spectra, and Medac (Brunel University) for combustion analyses. 5,6-Dichloroazulene[6,15] was obtained in 19% yield by the reaction of 6-(dimethylamino)fulvene[16] with 3,4-dichlorothiophene 1,1-dioxide.[17] Kinetically pure material was obtained by repeated column chromatography followed by recrystallisation from aqueous alcohol. 5,6-Dichloroazulene showed ^1H NMR absorbances at δ 8.51 (s, 4-H), 8.01 (d, $J_{7,8}$ 10, 8-H) and 7.39 (d, $J_{7,8}$ 11, 7-H). The proton 2-H appeared as an asymmetric triplet (δ 7.89, $J_{1,2}$ and $J_{2,3}$ 4) while those at 3-H (δ 7.36, d, $J_{2,3}$ 4) and 1-H (δ 7.33, d, $J_{1,2}$ 4) showed near equivalence.

4,5,6,7-Tetrachloroazulene [m.p. 137–138° C from ethanol (Found: C, 45.1; H, 1.5; Cl, 53.8. $C_{10}H_4Cl_4$ requires C, 45.16; H, 1.52; Cl, 53.37%); *m/z* 264, 266, 268, 270 (M^+), 229, 231, 233 ($M^+ - Cl$), 194, 196, 198 ($M^+ - 2Cl$), 158, 160 ($M^+ - 3Cl$), 122, 123 and 124 ($C_{10}H_4{}^{\cdot+}$–$C_{10}H_2{}^{\cdot+}$)] was prepared in 5–10% yield by the reaction of 2,3,4,5-tetrachlorothiophene 1,1-dioxide with 6-(dimethylamino)fulvene in tetrahydrofuran (THF) under carbon dioxide, initially at room temperature and later by warming to 40 °C for 1 h. Repeated chromatography upon alumina separated much of the unreacted tetrachlorothiophene and allowed pure tetrachloroazulene to be obtained by crystallisation. Hydrogen peroxide in a range of appropriate solvents was no more effective an oxidising agent of the thiophene; using 50–55% *m*-chloroperoxybenzoic acid gave even poorer yields, and magnesium monoperphthalate was ineffective.

1,3,5,6-Tetrachloroazulene [m.p. 140–141 °C; *m/z* 264, 266, 268, 270, 272 (M^+), 265, 267, 269, 271 ($M^+ + 1$, 11%), 229, 231, 233, 235 ($M^+ - Cl$), 194, 196, 198 ($M^+ - 2Cl$), 159, 161 ($M^+ - 3Cl$), and the corresponding M^{2+} ions] was obtained in 94% yield by the reaction of 5,6-dichloroazulene (2 mmol) with *N*-chlorosuccinimide (4.1 mmol) in benzene (15 cm^3) for 30 min at 80 °C. The corresponding reaction with 4,5,6,7-tetrachloroazulene gave 1,3,4,5,6,7-hexachloroazulene (58%); m.p. 138–139 °C (from ethanol); *m/z* 332, 334, 336, 338, 340, 342 (M^+), 333, 335, 337, 339 ($M^+ + 1$, 10%), 297, 299, 301, 303, 305 ($M^+ - Cl$), 262, 264, 266, 268, 270 ($M^+ - 2Cl$), 227, 229, 231 ($M^+ - 3Cl$), 192, 194, 196 ($M^+ - 4Cl$), 170–166 (M^{2+}), 157, 159 ($M^+ - 5Cl$) and 122 ($C_{10}H_2{}^{\cdot+}$).

Mononitro-5,6-dichloroazulene was prepared by the nitration [$Cu(NO_3)_2$–Ac_2O] of 5,6-dichloroazulene using the method by which Anderson and his colleagues nitrated azulene.[19] The reaction was followed by TLC, and the crude material from hydrolysis and solvent extraction was passed down a column of alumina to remove oxidation products and then chromatographed upon a second column of alumina to obtain 5,6-dichloro-X-nitroazulene; m.p. 148–150 °C; *m/z* 241, 243, 245 (M^+), 211, 213, 215 ($M^+ - NO$), 195, 197, 199 ($M^+ - NO_2$), 183, 185, 187 ($M^+ - NO - CO$), 160, 162 ($M^+ - NO_2 - Cl$), 148, 150 ($M^+ - NO - CO - Cl$) and 125 ($M^+ - NO_2 - 2Cl$). The ^1H NMR spectrum (270 MHz) showed this material to be approximately equal amounts of the two expected products, 5,6-dichloro-1-nitroazulene (**6a**) and the 3-nitro isomer (**6b**). These were most clearly distinguished by the behaviour of the protons near the nitro substituents, and by the readily identified 7-H and 8-H protons which showed the usual[20] 10–11 Hz coupling.

5,6-Dichloro-3-nitroazulene showed 4-H as a single peak at δ 9.83, a low-field shift of 1.4 ppm from the value found in 5,6-dichloroazulene itself, whereas 5,6-dichloro-1-nitroazulene was less perturbed at 4-H (δ 9.32). The doublet shown by 8-H in the 1-nitro isomer occured at δ 9.39 (expected, 9.25, $J_{7,8}$ 11.0), further downfield than that of 8-H in the 3-nitro isomer which appeared at δ 8.74 (expected, 8.75, $J_{7,8}$ 11.0). The proton 7-H occurred as a doublet of doublets in the spectrum of both isomers, that from 5,6-dichloro-3-nitroazulene (δ 8.29, $J_{7,8}$ 11.0, $J_{7,x}$ 1.5) occurring slightly upfield of its pair in the 1-nitro isomer (δ 8.39, $J_{7,8}$ 11.0, $J_{7,x}$ 1.5); this reflected the relative distances between the nitro-group and the proton under study in each case. The protons in the five-membered ring were more difficult to assign. 2-H appeared as a doublet of doublets in each system at δ 8.61 ($J_{1,2}$ 4.9, $J_{2,x} < 1$) and at δ 8.55 ($J_{1,2}$ 4.8, $J_{2,x}$ 1.5). They could be attributed to the 3-nitro compound and its 1-isomer, respectively, the slight differences in chemical shift reflecting long-range effects from the chlorine at C-5 (C-7) in the other ring. This effect was even smaller in the 1-H and 3-H protons, the two doublets at 7.59 and 7.57 ppm appearing as a triplet as a result of their similar chemical shifts ($J_{1,2}$ or $J_{2,3}$ 4.7).

5-Chloro-6-methoxyazulene (obtained as lavender needles from ethanol, m.p. 110–111 °C) showed a similar ^1H NMR spectrum to that of the parent dichloroazulene. The proton at 4-H was a singlet (δ 8.55) while those at 8-H (δ 8.20) and 7-H (δ 6.80) showed the usually observed interaction ($J_{7,8}$ 11). The proton at 2-H appeared as a slightly asymmetrically disposed triplet (δ 7.69; J 4 or 6) arising from interaction with the nearly-identical protons 1-H and 3-H, which showed a broad apparent triplet at δ 7.30–7.32. The methoxy peak appeared at δ 4.06.

1,3,5-Trichloro-6-methoxyazulene, m.p. 128–129 °C, was formed from 1,3,5,6-tetrachloroazulene by methoxydechlorination. The methoxy peak appeared at δ 3.88, the coupling protons 7-H and 8-H at δ 6.64 ($J_{7,8}$ 10) and 8.04 ($J_{7,8}$ 10) respectively, with 2-H (δ 7.40) and 4-H (δ 8.38) as singlets. The assignment of 7-H was confirmed in the methoxy compound since it alone suffered a considerable upfield shift as a result of exchanging Cl for OMe. Thus, 1,3,5,6-tetrachloroazulene shows peaks at δ 7.22 (7-H), 7.90 (8-H), 7.53 (2-H) and 8.38 (4-H); while the other peaks showed shifts of *ca.* 0.1 ppm upon methoxydechlorination, that of 7-H moved 0.58 ppm.

The product of methoxydechlorination of 4,5,6,7-tetrachloroazulene in sodium methoxide (0.5 mol dm^{-3} in methanol) at 330 K was a mixture showing a number of absorbances in the methoxy region of the 270 MHz ^1H NMR spectrum (δ 3.9–4.1); none of these could be identified positively, and TLC showed the presence of 4,5,6,7-tetrachloroazulene before red methoxydechlorination products.

Kinetics.—Solutions of cleaned sodium metal in purified, deoxygenated methanol were standardised by acid-base titration. Solutions of purified chloroazulenes were made by dissolving weighed amounts in known volumes of nitrogen-purged methanol. In the absence of oxygen, methoxydechlorination proceeds simply; the visible spectra (400–700 nm; Perkin-Elmer 551) showed the regular changes and isosbestic points expected, whereas solutions which were not both oxygen-free and maintained in a nitrogen atmosphere showed drift in the apparent isosbestic point.

5,6-Dichloroazulene showed peaks at λ 600 (ε/dm^3 mol^{-1} cm^{-1} 224) and 656 (195) nm with the isosbestic point at λ 572 nm; the maximum of 5-chloro-6-methoxyazulene occurred at 552 nm (ε 220). Corresponding values for the absorption maxima and extinction coefficients for **3** are 625 (330) and 679 (302); for **5**, 656 (279); and for **6**, 525 (835) with the isosbestic points occurring at 616 (**3**) and 488 nm (**6**).

Reactions were studied either by sampling from a thermostatted reaction mixture or by continuous analysis of a mixture in a thermostatted cell compartment of the spectrophotometer. All reactions were studied under pseudo first-order conditions, the bimolecular process being confirmed by the changes of k_1 with changes in the methoxide ion concentration. In each case, the plot of k_1 *vs.* [MeO^-] was linear except for the reaction at highest methoxide concentration. Methanolic solutions of chloroazulenes were stable, and so no solvolytic contribution was detected in the bimolecular process.

The Guggenheim treatment of the experimental points ensured that errors in the 'infinity' reading did not affect the accuracy of the rate constants; this treatment of the results confirmed and improved first-order rate constants obtained from the rate of change in the spectra of reaction mixtures, and was supported by an iterative fitting program in which the observed changes in the spectra with time were treated as a two-parameter equation in which neither the rate constant nor the absorbance at infinite time were known.

Calculations.—All-valence-electron SCF–LCAO–MO calculations were carried out on 5-chloro-, 6-chloro-, 5,6-dichloro-, 4,5,6,7-tetrachloro-, 1,3,5,6-tetrachloro-, 1- and 3-nitro-5,6-dichloro- and 1,3,4,5,6,7-hexachloro-azulenes (and some methoxy derivatives) using the MOPAC V package at Imperial College, University of London. The AM1 Hamiltonian[27] was used throughout, as doubts have been expressed as to the validity of the charge densities obtained by the PM3 method. Complete geometry optimisation was carried out on the ground states of the azulenes.

References

1 (*a* Part 13. R. K. Atwal and R. Bolton, *Aust. J. Chem.*, 1987, **40**, 241; (*b*) R. Bolton, D. G. Hamilton and J. P. B. Sandall, *J. Chem. Soc., Chem. Commun.*, 1990, 917.

2 G. W. Wheland and D. E. Mann, *J. Chem. Phys.*, 1949, **17**, 264.

3 A. G. Anderson, J. A. Nelson and J. J. Tazuma, *J. Am. Chem. Soc.*, 1953, **75**, 4980; A. G. Anderson, R. Scotoni, E. J. Cowles and C. G. Fritz, *J. Org. Chem.*, 1957, **22**, 1193.

4 C. A. Reece, quoted by W. Bauer and V. Mueller-Westerhoff, *Tetrahedron Lett.*, 1972, 1021.

5 R. N. McDonald, R. E. Petty, N. L. Wolfe and J. V. Paukstelis, *J. Org. Chem.*, 1974, **39**, 1887.

6 D. H. Reid, W. H. Stafford and J. P. Ward, *J. Chem. Soc.*, 1958, 1100.

7 (*a*) J. Schultze and F. A. Long, *J. Am. Chem. Soc.*, 1964, **86**, 331; (*b*) B. C. Challis and F. A. Long, *J. Am. Chem. Soc.*, 1965, **87**, 1196; B. C. Challis and F. A. Long, *Discuss. Faraday Soc.*, 1965, **39**, 67; (*c*) A. J. Kresge, Y. Chiang and R. A. More O'Ferrall, *J. Am. Chem. Soc.*, 1977, **99**, 2245.

8 F. G. Terrier, F. L. Debleds, J. F. Verchere and A. P. Chatrousse, *J. Am. Chem. Soc.*, 1985, **107**, 307; P. de Wit and H. Cerfontain, *Recl. Trav. Chim. Pays-Bas*, 1985, **104**, 25.

9 R. N. McDonald, *J. Org. Chem.*, 1976, **41**, 1811.

10 R. N. McDonald, R. R. Reitz and J. M. Richmond, *J. Org. Chem.*, 1976, **41**, 1822.

11 C. Weiss, W. Engelwald and H. Mueller, *Z. Chem.*, 1963, **3**, 307; *Tetrahedron*, 1966, **22**, 825.

12 D. Copland, D. Leaver and W. B. Menzies, *Tetrahedron Lett.*, 1977, 639.

13 K. Hafner, H. Patzelt and H. Kaiser, *Liebigs Ann. Chem.*, 1962, **656**, 24.

14 T. Nozoe, S. Seto and S. Matsumara, *Bull. Chem. Soc. Jpn.*, 1962, **35**, 1990.

15 S. E. Reiter, L. C. Dunn and K. N. Houk, *J. Am. Chem. Soc.*, 1977, **99**, 4199.

16 K. Hafner, K. H. Vogel, H. Ploss and C. Koenig, *Org. Synth.*, 1973, Coll. Vol. V, 431.

17 H. Bluestone, R. Bimber, R. Berkey and Z. Mandel, *J. Org. Chem.*, 1961, **26**, 346.

18 R. Bolton and H. Barker, unpublished results.

19 M. Raasch, *J. Org. Chem.*, 1980, **45**, 860.

20 K. Kanematsu, K. Harano and H. Dantsuji, *Heterocycles*, 1981, **16**, 1145; M. Raasch, *Chem. Heterocycl. Compd.* (*Engl. Trans.*), 1985, **44**, 571.

21 K. Mackenzie, G. Proctor and D. J. Woodnutt, *Tetrahedron*, 1987, **43**, 856.

22 A. G. Anderson and L. L. Replogle, *J. Org. Chem.*, 1963, **28**, 2578.

23 V. A. Nefedov, *Zh. Org. Khim.*, 1981, **17**, 570.

24 R. Bolton and J. P. B. Sandall, (*a*) *J. Fluorine Chem.*, 1978, **12**, 463; (*b*) *J. Chem. Soc., Perkin Trans. 2*, 1978, 746.

25 *e.g.* R. Bolton and J. P. B. Sandall, *J. Chem. Soc., Perkin Trans. 2*, 1978, 141 and refs. therein.

26 J. Miller, *Aromatic Nucleophilic Substitution*, Elsevier, Amsterdam, 1968.

27 (*a*) M. J. S. Dewar, E. G. Zoebisch, E. F. Healy and J. J. P. Stewart. *J. Am. Chem. Soc.*, 1985, **107**, 3902; (*b*) R. Bolton, D. B. Hibbert and S. Pirand, *J. Chem. Soc., Perkin Trans. 2*, 1986, 981.

28 J. Burdon and I. W. Parsons, *J. Am. Chem. Soc.*, 1977, **99**, 7445.

29 I. W. Parsons, *J. Fluorine Chem.*, 1982, **21**, 445.

30 R. Bolton, G. B. Carter and J. P. B. Sandall, *J. Chem. Soc., Perkin Trans. 2*, 1979, 388.

Paper 0/04594B
Received 12*th October* 1990
Accepted 23*rd November* 1990