Communications TO THE EDITOR

Electrophilic Substitution of 1,3-Dichloroazulene

Sir:

The electrophilic substitution of azulene in the 1-position and disubstitution in the 3-position were shown to occur several years ago[1] and are now well-known. Further substitution of 1,3-disubstituted azulenes has, however, not been reported.

The ground state electron density calculations by Julg[2] (Fig. 1) using the self-consistent field method show the 5-position to have the next highest value after the 1- and 3-positions.[3] The localization energies[4] (Fig. 1, β-values) show essential equivalence of the 2- and 5-positions in regard to ease of electrophilic substitution.[5]

We have now achieved the acetylation of 1,3-dichloroazulene (I) by means of acetyl chloride in carbon tetrachloride with stannic chloride as the catalyst. The principal product was isolated as green needles in 16% actual (36% net) yield. The major part of these needles melted at 92–95°, with the remainder melting at 101–103°. The resolidified sample then melted at 101–103°. An analytical sample partially melted and underwent a transition at *ca.* 95°, resolidified, and then melted at 103–104°.

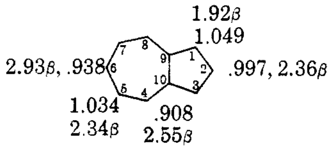
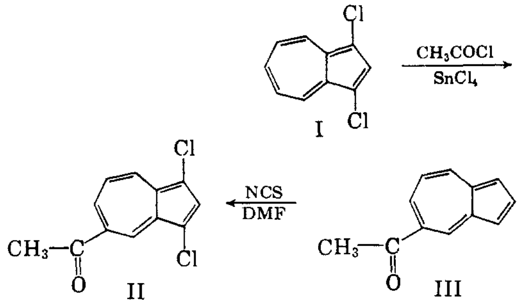


Fig. 1. Theoretical localization energies (in β) and ground state electron densities

Anal. Calcd. for $C_{12}H_8OCl_2$: C, 60.28%; H, 3.37%. Found: C, 60.55%; H, 3.29%. The infrared spectrum showed a carbonyl band at 5.97μ. A cyclohexane solution exhibited maxima in mμ ($\epsilon \times 10^{-4}$) in the ultraviolet at 227 (1.55), 242 (1.82), 296 (3.17), 306 (3.40), 322 (1.11), 379 (0.94), and 400 (1.62) and in the visible (ϵ) with a shoulder at 578 (323), shoulder at 606 (410), 627 (467), 655 (410), 664 (415), 687 (428), shoulder at 738 (183) and 769 (165).

The position (627 mμ) of the principal maximum in the visible suggested that the compound was 5-acetyl-1,3-dichloroazulene (II) on the basis of assumed additivity of the spectral shifts due to the substituents[6] (638 mμ for 1,3-dichloroazulene and -12 mμ for a 5-acetyl group[7] gives a calculated λ_{max} = 626 mμ). Proof of this structure was provided by the dichlorination of 5-acetylazulene (III)[7] in 40% yield with *N*-chlorosuccinimide in dimethylformamide. The products obtained *via* the two routes were identical (melting point; ultraviolet, visible and infrared spectra).



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

(2) A. Julg, *J. Chim. phys.*, **52**, 377 (1955).

(3) These values differ from other calculated electron densities which show the 2-position to have the next highest electron density. (*cf.* E. Heilbronner, Non-Benzenoid Aromatic Compounds, D. Ginsburg, ed., Interscience Publishers, Inc., New York, 1959, p. 196).

(4) R. D. Brown, private communication to D. Peters, *J. Chem. Soc.*, 1028 (1958).

(5) These considerations do not include any possible effect of substituents in the 1,3-positions.

(6) A. G. Anderson, Jr., C. G. Fritz and R. Scotoni, Jr., *J. Am. Chem. Soc.*, **79**, 6511 (1957); E. J. Cowles, **79**, 1093 (1957); A. G. Anderson, Jr., R. Scotoni, Jr., E. J. Cowles, and C. G. Fritz, *J. Org. Chem.*, **22**, 1193 (1957).

(7) W. Treibs and M. Quarg, *Ann.*, **598**, 38 (1955).

(8) National Science Foundation Predoctoral Fellow, 1959–1960.

Oxidative Coupling of Acetylenes

Sir:

The oxidative coupling of acetylenes has generally been effected with air or oxygen in an ammonia-