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HYDRIDE HYPERCONJUGATION IN 1(3)-METHYLAZULENES

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AN outstanding feature of the chemistry of azulene (I), dependent upon its considerable polarization and ready polarizability is the comparatively high degree to which electronic interaction prevails between substituents and the π-electron system of the nucleus.[1,2,3] This is especially reflected in the abnormal polarization of multiple bonds attached to, and conjugated with, the nucleus at $C_{(1)}$ [or $C_{(3)}$]. Consideration of these facts suggested that the methyl group of 1(3)-methylazulenes may interact with the nucleus to an important degree by <u>hydride hyperconjugation</u>. Polar structures [exemplified by (IIb) and (IIc) in the case of 1-methylazulene (II)] should then contribute significantly to the ground state of 1(3)-methylazulenes, with consequent lengthening of the C-H bonds of the 1(3)-methyl group, and in a suitable environment hydrogen might be capable of ready removal from the methyl group as hydride ion. We present now results of experiments on

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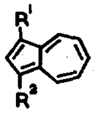
[1] D.H. Reid, <u>Azulene and Related Substances</u> p. 69. Special Publication No. 12 of the Chemical Society, London (1958).

[2] E.C. Kirby and D.H. Reid, <u>J. Chem. Soc.</u> 494 (1960).

[3] D.H. Reid, W.H. Stafford and W.L. Stafford, <u>J. Chem. Soc.</u> 1118 (1958).

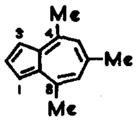


I $R^1 = R^2 = H$

II $R^1 = Me$, $R^2 = H$

III $R^1 = Ph_3C$, $R^2 = H$

IV $R^1 = R^2 = Ph_3C$



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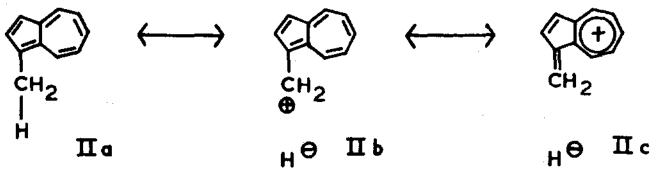
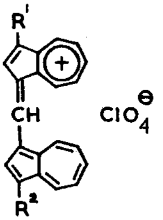
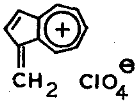


IIa IIb IIc

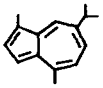


VI $R^1 = Me$, $R^2 = H$

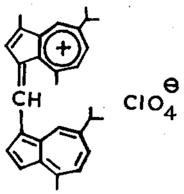
VII $R^1 = R^2 = Me$



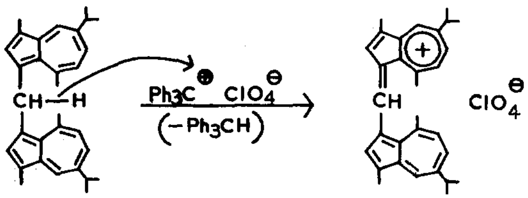
VIII



IX



X



XI XII

the reactions of azulenes with triphenylmethyl perchlorate, which are satisfactorily interpreted on the basis of these ideas.

Azulene (I) underwent electrophilic substitution by triphenylmethyl perchlorate in boiling acetic acid to give a mixture of the dimorphic 1-triphenylmethylazulene (III) (Found: C, 93.6; H, 6.2. $C_{29}H_{22}$ requires C, 93.9; H, 6.1%), blue prisms which melt at 110-120° with subsequent resolidification ($>135°$) to blue needles, m.p. 175-177° [λ_{max} (in benzene) 602 mμ; log ε 2.49], and 1,3-bis triphenylmethylazulene (IV) (Found: C, 94.1; H, 5.9. $C_{48}H_{36}$ requires C, 94.3; H, 5.5%), blue crystals, m.p. 289-291° [λ_{max} (in benzene) 622 mμ; log ε 2.54]. Notably, 4,6,8-trimethylazulene (V) failed to react. The 4- and 8-methyl substituents evidently screen effectively the 3- and 1-positions of the nucleus against electrophilic attack by the bulky triphenylmethyl cation, and are themselves unattacked.

In contrast, triphenylmethyl perchlorate reacted with an excess (400%) of 1-methylazulene (II) under identical conditions to give in 80% yield a dye-salt, green needles (from acetonitrile), m.p. 350°(decomp.) (on block preheated to $\not< 350°$) [λ_{max} (in acetic acid) 652 mμ; log ε 5.02]. Triphenylmethane was formed concomitantly, being isolated in comparable yield. The dye-salt (Found: C, 70.0; H, 4.9; Cl, 9.1%), at first believed to be 1-(azulen-1-yl methylene)-3-methylazulenium perchlorate (VI), is now known to be identical with 1-(3-methylazulen-1-yl)methylene-3-methylazulenium perchlorate (VII)[4] ($C_{23}H_{19}ClO_4$ requires C, 70.0; H, 4.9; Cl, 9.0%) on the basis of a comparison of the visible and infra-red spectra and X-ray powder diagrams of the three salts. These results demonstrate that in the primary step the triphenylmethyl cation attacks the 1-methyl substituent, abstracting

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[4] E.C. Kirby and D.H. Reid, J. Chem. Soc. In press.

a hydride ion with formation of the reactive methyleneazulenium perchlorate (VIII) which, in an as yet unclarified manner, reacts further with the excess of 1-methylazulene to give eventually (VII).

Guaiazulene (IX) with triphenylmethyl perchlorate likewise gave a dye-salt (48% yield), green needles (from acetic acid), m.p. 260-262.5° (block preheated to 250°) [λ_{max} (in acetic acid) 632 mμ; log ε 5.03], which is believed to possess structure (X) (Found: C, 73.2; H, 6.7; Cl, 7.4. $C_{30}H_{33}ClO_4$ requires C, 73.1; H, 6.8; Cl, 7.2%). Triphenylmethane (71%) was isolated from the mother liquors.

3,3'-Diguaiazulenylmethane (XI)[5] reacted similarly, as depicted, to give a complex mixture from which 5-isopropyl-1-(5-isopropyl-3,8-dimethylazulen-1-yl)methylene-3,8-dimethylazulenium perchlorate (XII) was isolated in low yield, black crystals (from acetic acid), m.p. 243-248° (decomp.), identical (m.p. mixed m.p., and visible spectrum) with an authentic specimen[6] prepared by condensation of guaiazulene with 3-ethoxymethyleneguaiazulenium perchlorate. Triphenylmethane was isolated from the mother liquors.

Full details of these and related experiments will be published later. Thanks are expressed to the Department of Scientific and Industrial Research for the award of a Research Studentship (to E.C.K.), the Royal Society for a Research Grant, and Dr. D. G. Watson for comparisons of the X-ray powder diagrams.

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[5] H. Arnold and K. Pahls, Ber. **89**, 121 (1956).

[6] E.C. Kirby and D.H. Reid. Unpublished results.