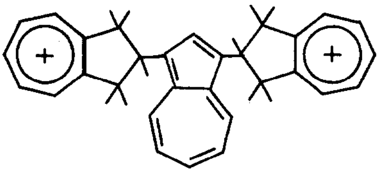
Tetrahedron Letters No.20, pp. 1497-1502, 1965. Pergamon Press Ltd.
Printed in Great Britain.

ELECTROPHILIC SUBSTITUTION OF AZULENE BY AZULENIUM ION

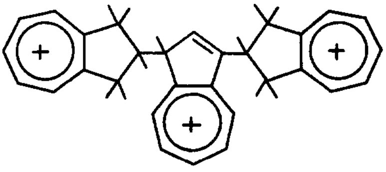
Philip C. Myhre and Robert D. Andersen[1]
Department of Chemistry, Harvey Mudd College
Claremont, California

(Received 15 March 1965)

Although several detailed investigations of protonation equilibria of azulenes have been reported,[2,3] the early report of Plattner and Pfau[4] indicating that azulene undergoes irreversible transformation in acid solution to products of unspecified structure has apparently received little direct attention.[5] In view of the susceptibility of azulene to electrophilic attack by very weak electrophiles,[3] a possible initial step of this transformation could be an electrophilic substitution of azulene by azulenium ion. We report here the isolation of crystalline dicarbonium ion salts from solutions of azulene in aqueous acid and present data which strongly indicates that the dicarbonium ion is 1,3-di-2-(2,3-dihydroazulenium)-azulene, I. We suggest that the formation of I is substantive support of the proposed reaction path.



I



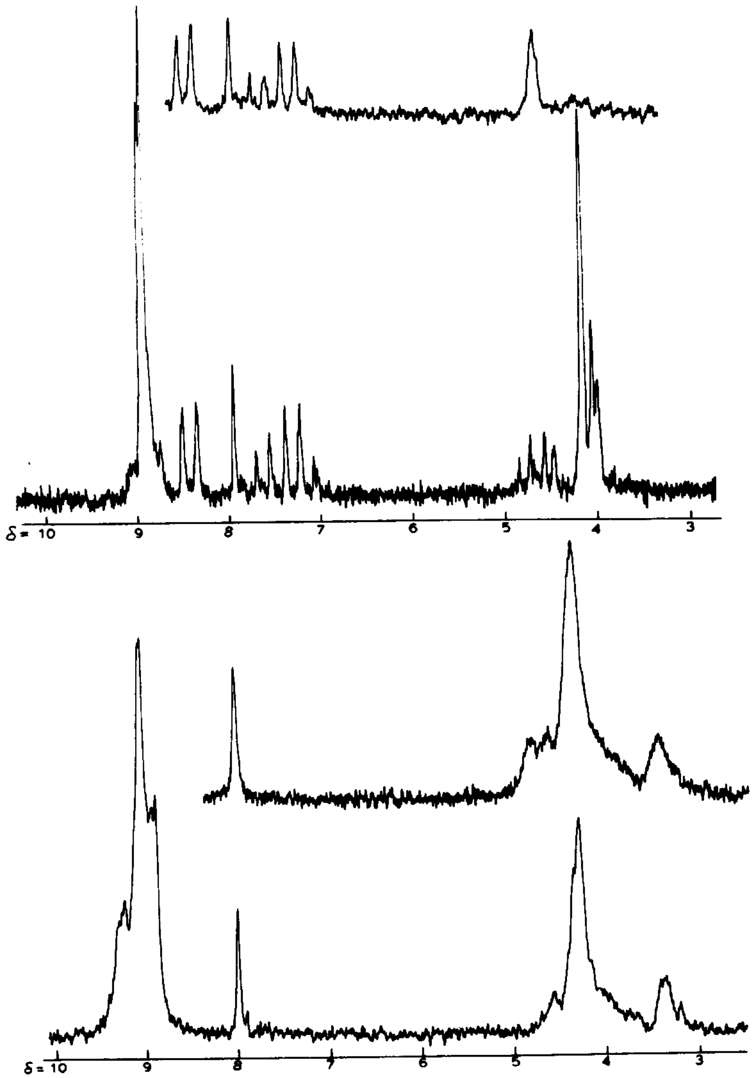
II

Microcrystalline precipitates deposit from spectral solutions of azulene (ca. 10^{-4}M) in 20 to 50% perchloric or fluoroboric acid during a one or two week period. Kinetic studies of the rate of disappearance of azulene from perchloric acid solutions show a clear second-order dependence on added azulene. The apparent second-order rate constant is maximum at about 22% perchloric acid, the acidity at which azulene and azulenium ion are in equal concentration.[2] The corrected second-order rate constant is impressive, 3×10^{-1} liters $mole^{-1}sec.^{-1}$

A convenient preparative reaction can be conducted by allowing a nearly saturated solution of azulene in purified n-heptane to remain in contact with 40% perchloric or fluoroboric acid for about 24 hours. Well formed crystals of the perchlorate (red-black dendroids, m.p. 219°, evacuated sealed tube, explodes 221°) and the fluoroborate salt (black needles with no definite m.p.) can be isolated in 90-95% yield by filtration.[5]

Anal. Calcd. for $C_{30}H_{26}(ClO_4)_2$: C, 61.55; H, 4.48; Cl, 12.1; mol. wt., 585.4; equiv. wt., 292.7. Found: C, 61.23; H, 4.68; Cl, 12.2; mol. wt., 600 (3 X 200, osmometer); equiv. wt., 291 (potentiometric titration in acetonitrile with tetrabutylammonium hydroxide). Ultraviolet spectral data showed: $\lambda_{max}^{H_2SO_4}$ 234, 268, 302, 360 mu (ϵ 99,300, 27,200, 11,600, 13,400). The fluoroborate salt gave carbon-hydrogen analyses within 0.3% of theory.[7] Infrared spectra of the two salts were identical except for the bands attributable to the perchlorate and fluoroborate anions.

The n.m.r. spectrum of the perchlorate salt in sulfur dioxide (Fig. 1) shows an absorption pattern indicative of two substituted tropylium rings (8.9 δ, 10 H), a 1,3-disubstituted azulene (lines from 8.5 to 7.1 δ, 6 H), and deshielded methine protons (multuplet centered at 4.6 δ, 2 H) spin coupled with methylene protons (multuplet centered



FIGS. 1 and 2

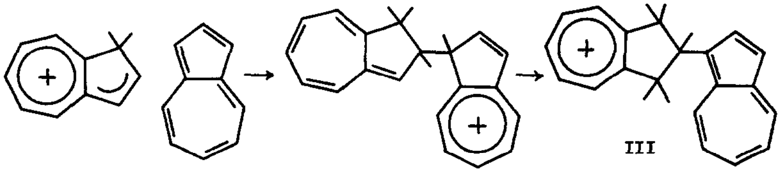
N.m.r. spectra of I in liquid sulfur dioxide, trifluoroacetic acid, and trifluoroacetic acid-$\underline{d}_1$. Top insert shows a spectrum of I prepared from azulene-1,3-$\underline{d}_2$ and perchloric acid-$\underline{d}_1$.

at 4.1 δ, 8 H).[8,9] The perchlorate salt prepared from azulene-1,3-$\underline{d}_2$ and perchloric acid-$\underline{d}_1$ gives a spectrum which is identical in the lower field region, but which shows only a broadened singlet at 4.6 δ (2 H) in the upper field region.

In trifluoroacetic acid solvent, the n.m.r. spectrum of the perchlorate salt (Fig. 2) is notably different. The multuplet at 9.1 δ (15 H) is indicative of two tropylium rings and the seven-membered ring protons of an azulenium ion. One absorption line at 7.9 δ (1 H) attributable to a proton on C-2 of an azulenium ion remains.[8] In the upper field region two broadened bands at 4.7 δ (1 H) and 4.6 δ (1 H) are discernable as well as a broad multuplet with maximum at 4.3 δ (9 H). The spectrum of the salt in trifluoroacetic acid-$\underline{d}_1$ is identical except for the absence of the band at 4.7 δ. Spectra of the salt prepared from azulene-1,3-$\underline{d}_2$ and perchloric acid-$\underline{d}_1$ taken in trifluoroacetic acid show three bands at 4.7 δ (1 H), 4.6 δ (1 H) and 4.1 δ (1 H).

The analytical data and the n.m.r. spectral data imply that the salt is a dicarbonium ion composed of three azulene units, two of which contain saturated carbon atoms in the five-membered ring. The coupling pattern and the deuterium labelling evidence indicates that bonding occurs between C-1 and C-3 of the azulene ring and C-2 of the azulene units containing saturated carbons in the five-membered ring. Finally, the spectrum in trifluoroacetic acid ($-H_o = 3.5$) indicates that the central azulene ring undergoes protonation in strong acid, as would be expected, to give a tricarbonium ion, II. The absence of exchange in <u>deuterio</u>-acid clearly shows that the position of protonation is on carbon bearing no other proton.

The mode of formation of I seems most rationally formulated as an electrophilic substitution of azulene by azulenium ion followed by proton loss from C-1 of the attacked azulene and proton addition to C-3 of the attacking species. The resulting intermediate carbonium ion, III, must suffer attack by azulenium ion to yield product. The available kinetic data is consistent with this interpretation.


III

Spectral evidence and titrimetric data indicate that I suffers proton loss in basic media affording, presumably, a heptafulvene derivative. However, we have been able to isolate only polymeric material from treatment of I with base. The polymer appears to be similar to that reported by Plattner[4] and those isolated from abortive electrophilic substitution reactions of azulene.

Kinetic studies of the formation of I are continuing and the chemistry of the salt is being explored. The present results offer a rational explanation for the sensitivity of azulene to strong acids and clearly imply that valid protonation equilibrium studies can only be carried out in very dilute solution. Finally, this reaction offers a very convenient route to an unusual class of stable polycarbonium ion salts of potential interest.

ACKNOWLEDGEMENT

Acknowledgement is made to the donors of The Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

REFERENCES AND FOOTNOTES

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2. J. Schulze and F. A. Long, *J. Am. Chem. Soc.*, **86**, 322, 327, 333 (1964).
3. E. Heilbronner, "Azulenes", Chap. V in *Nonbenzenoid Aromatic Compounds*, D. Ginsburg, ed., Interscience, New York, 1959.
4. P. A. Plattner and A. S. Pfau, *Helv. Chim. Acta*, **20**, 224 (1937).
5. It should be noted that a number of elegant methods of substitution of azulene (A. G. Anderson, J. A. Nelson and J. J. Tazuma, *J. Am. Chem. Soc.*, **75**, 4980 (1953) and related papers) have been developed due, in part, to the decomposition of azulene in acidic media.
6. Product isolated from kinetic studies was shown to be identical with that prepared by the preparative method described.
7. Acceptable carbon-hydrogen analyses were obtained independently by Mr. C. F. Geiger, Ontario, California, and Dr. R. R. Jay, Aerojet-General Corp., Azusa, California. Molecular weight and equivalent weight determinations were obtained by Dr. Jay.
8. D. Meuche, B. B. Malloy, D. H. Ried, and E. Heilbronner, *Helv. Chim. Acta*, **46**, 2483 (1963).
9. An AB_2C_2 would be anticipated for the methine and methylene protons. The spectrum has not been analyzed, but we note that the theoretical AB_4 pattern where $\Delta\nu/J$ is about 3 (K. B. Wiberg and B. J. Nist, *Interpretation of NMR Spectra*, Benjamin, (1962) fits the observed spectrum fairly well.