solid. This was separated and hydrolyzed by boiling for seven hours with 30 ml. of 70% ethanol and 10 ml. of 45% potassium hydroxide. The product was cooled, neutralized with hydrochloric acid and treated with Darco. The acid was obtained by acidification. It was recrystallized from acetic acid; yield 1.5 g.; recrystallized from ether, m. p. 135–137°.

Anal. Calcd. for $C_{14}H_{12}O_2$: C, 79.2; H, 5.7. Found: C, 79.2; H, 5.6.

This completes a series of these acids since the *o*- and *p*-phenyl isomers have been described.[2,3]

I am grateful to Dr. David T. Mowry of the Monsanto Chemical Co. who provided the *m*-acetylbiphenyl.

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[2] von Braun and Manz, *Ann.*, **468**, 258 (1929).

[3] Schwenk and Papa, *J. Org. Chem.*, **11**, 798 (1946).

JEFFERSON MEDICAL COLLEGE
PHILADELPHIA, PENNA. D. L. TURNER

RECEIVED MARCH 17, 1950

5-Nitroquinoxaline

A solution of 5.0 g. (0.019 mole) of glyoxal sodium bisulfite and 2.5 g. (0.016 mole) of 1,2-diamino-3-nitrobenzene[1] in 30 ml. of water was heated at 90° for one hour. The dark red solution was filtered, cooled to 10° and made basic with 10 ml. of 30% potassium hydroxide solution. The yellow precipitate was filtered by suction, rinsed with cold water and dissolved in 25 ml. of warm (50°) 95% ethanol. The ethanol solution was treated with charcoal and filter-aid, and filtered into 75 ml. of warm water. After cooling, 2.0 g. (70% yield) of matted yellow needles came down, m. p. 93–94°.

For analysis the material was sublimed at 100° (1 mm.), recrystallized from ethanol–water and again sublimed to give yellow-white needles, m. p. 96–97°.

5-Nitroquinoxaline was insoluble in water and 10% hydrochloric acid, soluble in cold ethanol, soluble with decomposition in warm alkali solution.

Anal. Calcd. for $C_8H_5N_3O_2$: N, 24.0. Found: N, 23.9.

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[1] Borsche and Rantscheff, *Ann.*, **379**, 163 (1910).

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF MIAMI
CORAL GABLES, FLORIDA HARRY P. SCHULTZ

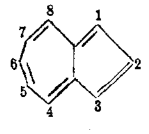
RECEIVED FEBRUARY 9, 1950

COMMUNICATIONS TO THE EDITOR

ELECTROPHILIC SUBSTITUTION OF AZULENE

Sir:

Since the elucidation of the azulene structure there has been considerable interest in the existence and properties of non-benzoid aromatic hydrocarbons. Although several different hypothetical structures (*i.e.*, pentalene and heptalene) have been proposed, azulene is the only known compound of this type and has, therefore, been the subject of numerous theoretical considerations. As previous chemical experiments[1] had shown only the strongly unsaturated character of the molecule, it seemed of importance in our study of azulene to investigate its behavior with aromatic substitution reagents.



Approximate quantum mechanical calculations according to Brown[2] of polarization energies and π-electron densities indicated that electrophilic substitution would take place in the 1-position. In the course of work in progress azulene has been allowed to react with certain electrophilic reagents. The results of one of these experiments support the prediction of Brown and current studies are designed to characterize the products and establish the position or positions of substitution in the other cases.

A minute amount of 1-methylazulene (λ_{max} in mμ at 240, log ε 4.28; 279, log ε 4.61; 338, log ε 3.62; 346, log ε 3.68; 364, log ε 3.50; 607, 658 and 732)[3] was obtained from the reaction of azulene with methyl chloride or iodide below room temperature and in the presence of aluminum chloride.

Azulene reacted readily with acetic anhydride in the presence of aluminum chloride. The principal product (62%), which is probably a diacetylazulene, was isolated as bright red needles, m. p. 189–190° (Calcd. for $C_{14}H_{12}O_2$: C, 79.2; H, 5.7. Found: C, 78.9; H, 5.6; λ_{max} in mμ at 240, log ε 4.51; 289, log ε 4.69; 308, log ε 4.49; 382, log ε 4.00; 498, log ε 2.85).

Reaction of azulene with copper nitrate and acetic anhydride at room temperature yielded red needles (51%), m. p. 98–99° (λ_{max} in mμ at 219, log ε 4.32; 269, log ε 4.23; 309, log ε 4.32; 382, log ε 4.03; 532, log ε 2.77; 572, log ε 2.69). The analysis most nearly corresponded to that calculated for a mononitroazulene (Calcd. for $C_{10}H_7O_2N$: C, 69.36; H, 4.08. Found: C, 68.71; H, 4.11).

Treatment of a solution of azulene in ethanol and aqueous sodium acetate with an aqueous solution of mercuric chloride resulted in an imme-

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[1] For a recent review article see A. J. Haagen-Smit, "Fortschritte der Chemie organischer Naturstoffe," Vol. V, Julius Springer, Wien, 1948, pp. 40–71.

[2] R. D. Brown, *Trans. Faraday Soc.*, **44**, 984 (1948).

[3] The absorption spectra for the various mono- and the known dialkylazulenes are characteristic; *cf.* Pl. A. Plattner and E. Heilbronner, *Helv. Chim. Acta*, **30**, 910 (1947); **31**, 804 (1948); T. Wagner-Jauregg, H. Arnold, F. Hüter and J. Schmidt, *Ber.*, **74B**, 1522 (1941).