

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.<sup>2,3</sup>

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

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

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

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### 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-nitroben-

zene<sup>1</sup> 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.

(1) Borsche and Rantschiff, *Ann.*, **379**, 163 (1910).

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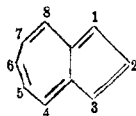
RECEIVED FEBRUARY 9, 1950

## 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<sup>1</sup> 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<sup>2</sup> of polarization energies and  $\pi$ -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 ( $\lambda_{\max}$  in  $m\mu$  at 240,  $\log \epsilon$  4.28; 279,  $\log \epsilon$  4.61; 338,  $\log \epsilon$  3.62; 346,  $\log \epsilon$  3.68; 364,  $\log \epsilon$  3.50; 607, 658 and 732)<sup>3</sup> 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;  $\lambda_{\max}$  in  $m\mu$  at 240,  $\log \epsilon$  4.51; 289,  $\log \epsilon$  4.69; 308,  $\log \epsilon$  4.49; 382,  $\log \epsilon$  4.00; 498,  $\log \epsilon$  2.85).

Reaction of azulene with copper nitrate and acetic anhydride at room temperature yielded red needles (51%), m. p. 98–99° ( $\lambda_{\max}$  in  $m\mu$  at 219,  $\log \epsilon$  4.32; 269,  $\log \epsilon$  4.23; 309,  $\log \epsilon$  4.32; 382,  $\log \epsilon$  4.03; 532,  $\log \epsilon$  2.77; 572,  $\log \epsilon$  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-

(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).

diate reaction and yielded an amorphous, gray-blue solid which was not obtained sufficiently pure for analysis.

The mild conditions found to be necessary and the short reaction times observed in these experiments indicate azulene to be markedly more reactive with respect to electrophilic substitution than the isomeric naphthalene. The rapid reaction of mercuric chloride with azulene is noteworthy as the chloromercuration of thiophene requires several days.<sup>4</sup>

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(4) F. C. Whitmore, "Organic Compounds of Mercury," Am. Chem. Soc. Monograph No. 3, Chemical Catalog Co., New York, N. Y., 1921.

(5) Shell Oil Fellow, 1949-1950.

### BACTERIAL DESOXYPENTOSE NUCLEIC ACIDS OF UNUSUAL COMPOSITION

Sirs:

Previous work in this laboratory<sup>1</sup> has shown that the desoxypentose nucleic acids (DNA) of different species differ in composition. All specimens examined so far, however, were, with one exception, considerably richer in adenine and thymine than in guanine and cytosine. Only in the DNA of avian tubercle bacilli<sup>2</sup> were the molar ratios of adenine to guanine or to cytosine and of thymine to cytosine lower than 1.

Two other instances of microbial DNA of unusual composition have now been found, namely in preparations from *Serratia marcescens* and from a facultatively autotrophic hydrogen organism, *Bacillus Schatz*, kindly given us by Drs. van Niel and Schatz.

Because of the strong DNA depolymerase activity of *Serratia marcescens* cultures a modification of a previously described procedure<sup>3</sup> was used. Washed cells from a 48-hr. culture on nutrient agar at room temperature were ground in 3.5 M aqueous NaCl with pyrex powder. The supernatants (20,000 x g, 0.5 hr.) from repeated extracts of the ground material (0°, 3.5 M NaCl) were injected into cold alcohol, the precipitated fibers deproteinized and processed as described before<sup>3</sup>; yield 0.08% of wet cells, 92-97% DNA, 1.1-2.6% RNA.

Similar procedures led to the isolation of DNA from the hydrogen organism, *Bacillus Schatz*. The fibrous preparations were freed of tenaciously held RNA (9%) by dialysis of their solution against dilute NaOH of pH 13.5 for 18 hr. at 30°; yield, 0.1%, 100-108% DNA, 0.5-3% RNA.

Three independently prepared samples from each of the organisms were analyzed for purines

(1) Chargaff, *Experientia*, **6**, 201 (1950).

(2) Vischer, Zamenhof and Chargaff, *J. Biol. Chem.*, **177**, 429 (1949).

(3) Chargaff and Zamenhof, *J. Biol. Chem.*, **173**, 327 (1948).

and pyrimidines by a modification<sup>4</sup> of previously published procedures.<sup>5</sup> The molar ratios reproduced in Table I represent averages for these preparations.

TABLE I  
MOLAR RATIOS IN TWO BACTERIAL DNA

	<i>Serratia marcescens</i>	Hydrogen organism, <i>Bacillus Schatz</i>
Adenine/guanine	0.76	0.68
Thymine/cytosine	.63	.59
Adenine/cytosine	.64	.63
Purines/pyrimidines	.92	.98

Several generalizations can be made. DNA, apart from smaller differences in composition characteristic of the species, appears to occur in two main groups: the "AT type" (DNA from animal tissues, yeast, etc.) in which adenine and thymine preponderate, and the "GC type" (DNA of tubercle bacilli and compounds discussed here) in which guanine and cytosine are the major constituents. Adenine and thymine occur mostly in almost equimolar quantities, as do guanine and cytosine and also total purines and pyrimidines.

This work was supported by a research grant from the U. S. Public Health Service.

(4) Chargaff, Green and Lipshitz, unpublished experiments; Zamenhof and Chargaff, *J. Biol. Chem.*, in press.

(5) Vischer and Chargaff, *J. Biol. Chem.*, **176**, 703, 715 (1948).

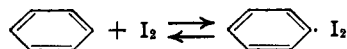
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### THE HEAT OF FORMATION OF THE BENZENE- IODINE COMPLEX

Sir:

Benesi and Hildebrand<sup>1</sup> have recently reported the existence of an intense ultraviolet absorption peak for solutions of iodine in benzene with a maximum at  $\lambda = 297 \text{ m}\mu$ . This characteristic absorption serves as part of the evidence for the formation of a 1:1 complex:



The absorption by this complex for various concentrations of iodine and benzene in a non-complexing solvent, such as carbon tetrachloride or *n*-heptane, has been used by Benesi and Hildebrand for determining equilibrium constants for the above reaction. They assumed that the equilibrium constant is the same for all concentrations of the benzene, and evaluated  $K$  and the extinction coefficient of the complex  $\epsilon_c$  by a linear extrapolation. This led to radically different values of  $\epsilon_c$  in carbon tetrachloride and *n*-heptane and involved extrapolation of two curves through a single point (pure benzene,  $x_a = 1$ ).

(1) H. A. Benesi and J. H. Hildebrand, *THIS JOURNAL*, **71**, 2703 (1949).