

The heats evolved per mole of gas adsorbed, as obtained by the application of the Clausius-Clapeyron equation to pressure and temperature

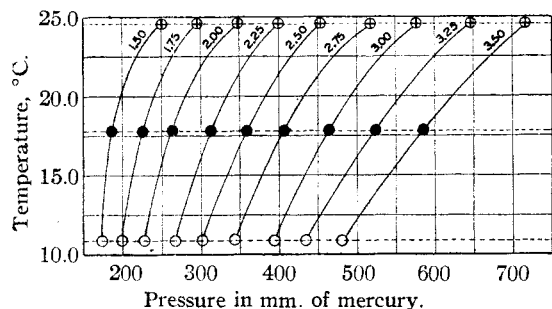


Fig. 6.—Adsorption isosteres.

readings taken from adsorption isosteres (Fig. 6), are plotted against amounts of gas adsorbed in Fig. 7.

Summary

1. It has been shown that an apparatus equipped with a variable volume unit offers an accurate means of checking adsorption equilibrium on both the adsorption and desorption side of the equilibrium point.

2. The maintenance of the total adsorption system at constant temperature has been found to offer advantages of accuracy of measurement and simplicity of calculation.

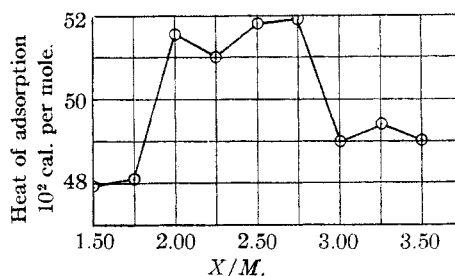


Fig. 7.—Heats of adsorption of methane on coal at 17.77°.

3. A successful application of the Freundlich equation, to data found for the adsorption of methane by coal, has been made.

4. The calculated heats of adsorption of methane on coal have been found to be between 4700 and 5200 calories per mole for x/m values between 1.5 and 3.5.

MORGANTOWN, W. VA.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHEASTERN UNIVERSITY]

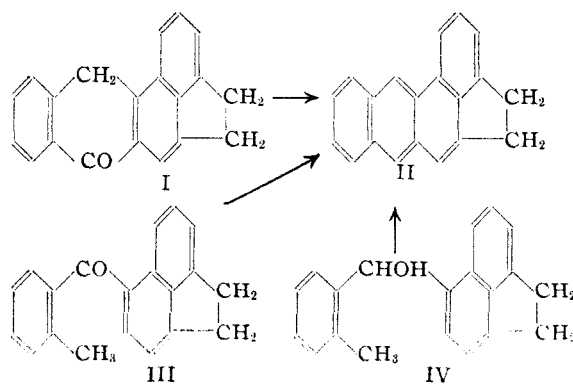
A Pyrolytic Synthesis of 2,3-(Naphtho-2',3')-acenaphthene¹

BY BRADFORD P. GEYER AND SAVERIO ZUFFANTI

2,3-(Naphtho-2',3')-acenaphthene (II) has been synthesized by Cook² by reduction of the anthrone (I), and, according to the statements in some patents,³ the hydrocarbon also can be obtained by the pyrolysis of 3-*o*-toluylacenaphthene (III) or 3-acenaphthyl-*o*-tolylcarbinol (IV) in the presence of a dehydrating catalyst. These intermediates have not been described in the literature, however, and there is no evidence to indicate that a catalyst is required in their pyrolysis. It appeared a matter of interest, therefore, to synthesize 3-*o*-toluylacenaphthene and then, by subjecting this ketone to the conditions ordinarily employed for effecting the Elbs reaction, to prepare the hydrocarbon II.

The ketone III was obtained from *o*-toluyl

chloride and acenaphthene by the Friedel-Crafts reaction. When pyrolyzed at 400–410°, it was converted smoothly into a hydrocarbon having the composition and the properties of the substance described by Cook.²



The authors are greatly indebted to Professor Louis F. Fieser of Harvard University for much helpful advice.

(1) A thesis submitted in June, 1935, by Bradford P. Geyer in partial fulfillment of the requirements for the degree of Bachelor of Science at Northeastern University.

(2) Cook, *J. Chem. Soc.*, 1087 (1930).

(3) O. Nicodemus, German Patent 481,819 (1929); O. Nicodemus and W. Berndt, U. S. Patent 1,776,925 (1930).

Experimental Part⁴

The *o*-toluyl chloride used in this work was made from the acid by the use of thionyl chloride; yield, 89%; b. p. 212°, corr.

3-*o*-Toluyacenaphthene (III).—Anhydrous aluminum chloride (30 g.) was added slowly, a little at a time, to an ice-cold mixture of 30 g. of pure acenaphthene and 30 g. of *o*-toluyl chloride in 75 cc. of carbon disulfide. After six hours at 0–5° the mixture was allowed to warm gradually to room temperature and then carefully treated with water and cracked ice. The solvent and some unchanged acenaphthene were removed from the crude, dark brown ketone by steam distillation, first in the presence of dilute hydrochloric acid, and then dilute sodium hydroxide, and the product was extracted with ethyl alcohol from a considerable amount of tarry residue. After three crystallizations from ethyl alcohol and a final recrystallization from methyl ethyl ketone, 3-*o*-toluyacenaphthene was obtained in the form of glistening, pale yellow, rhombic plates, m. p. 139–140°; yield, 12 g. (23%). The solution of the ketone in concentrated sulfuric acid is of a deep yellow-orange color.

Anal. Calcd. for C₂₀H₁₆O: C, 88.20; H, 5.92. Found: C, 88.11; H, 5.89.

2,3-(Naphtho-2',3')-acenaphthene (II) was prepared by the pyrolysis of 0.7 g. of 3-*o*-toluyacenaphthene under an

atmosphere of carbon dioxide in a two-bulb distilling flask at a bath temperature of 400–410° for forty minutes. At the conclusion of this time the elimination of water seemed to be complete. The crude product was then submitted to distillation in vacuum at a pressure of 2 mm., whereupon a golden-yellow crystalline solid was obtained. This material, when treated with an equal quantity of picric acid in benzene, formed a picrate which crystallized in clusters of slender, short, dark red-brown needles, m. p. 182.5–183.0°, corr. Decomposition of this picrate with ammonia and recrystallization of the regenerated hydrocarbon from ligroin (b. p. 90–120°) gave 2,3-(naphtho-2',3')-acenaphthene, very pale yellow leaflets, m. p. 192.5–193.5°, corr.; yield, 0.15 g. (23%). A benzene solution of this hydrocarbon possesses a yellow-green fluorescence, and the concentrated sulfuric acid solution has a red-violet color with an exceedingly strong, deep red fluorescence.

Anal. Calcd. for C₂₀H₁₄: C, 94.50; H, 5.50. Found: C, 94.37; H, 5.80. Calcd. for C₂₆H₁₇O₇N₃: N, 8.70. Found: N, 9.00.

Summary

2,3-(Naphtho-2',3')-acenaphthene has been synthesized by the Elbs condensation of 3-*o*-toluyacenaphthene.

BOSTON, MASSACHUSETTS

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(4) Microanalyses by Mrs. G. M. Wellwood.

[CONTRIBUTION FROM THE ORGANIC CHEMICAL LABORATORY OF THE UNIVERSITY OF FLORIDA]

Derivatives of Piperazine. VI. Alkylation by Means of Aldehydes

BY W. T. FORSEE, JR., AND C. B. POLLARD

Some secondary amines have been alkylated by using aldehydes in the presence of a reducing agent.^{1–5} However, the possibilities of the reaction seem to have attracted little attention.

Piperazine and N-monophenylpiperazine were quite readily alkylated by this method. In most cases products were obtained in better yields and were more easily purified than when prepared by other methods. N,N'-Dimethylpiperazine and N,N'-diethylpiperazine were prepared by the action of formaldehyde and acetaldehyde, respectively, on piperazine in the presence of powdered zinc and hydrochloric acid. N-Phenyl-N'-methylpiperazine and N-phenyl-N'-ethylpiperazine were prepared by the respective action of formaldehyde and acetaldehyde on N-monophenylpiperazine in the presence of zinc and

hydrochloric acid. With one exception, good yields were obtained and in some cases one distillation served to give a pure product. This method was not satisfactory for aldehydes which are insoluble in hydrochloric acid even when sufficient alcohol was added to keep them in solution.

Formic acid was used as the reducing agent for those aldehydes which are insoluble in hydrochloric acid. Where aliphatic aldehydes were involved the reaction required from one to three hours. With aromatic aldehydes the reaction velocities were very slow, requiring as much as five days of refluxing. All products were easily purified. The solid derivatives were crystallized from 60% alcohol.

The yields, properties and analyses of these compounds are shown in Table I.

Experimental

Using Zinc and Hydrochloric Acid as Reducing Agent.

To a water solution of the amine hydrochloride were added, for each equivalent of secondary nitrogen, one

(1) Wallach, *Ann.*, **343**, 54 (1905).

(2) Clarke, Gillespie and Weisshaus, *THIS JOURNAL*, **55**, 4571 (1933).

(3) Wagner, *ibid.*, p. 724.

(4) Skita and others, *Ber.*, **66B**, 1400 (1933).

(5) German Patents, 376,013 (1923), 491,856 and 503,113 (1930).