

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

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

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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[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.¹⁻³ 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).

TABLE I
YIELDS, PROPERTIES AND COMPOSITION OF ALKYLPIPERAZINES PREPARED

Compound	Yield, %	B. p., °C.	Mm.	M. p., °C.	N analyses, %	
					Found	Calcd.
1 N-Phenyl-N'-methylpiperazine ^b	42	109-110	5		15.95	15.91
2 N-Phenyl-N'-ethylpiperazine ^b	98	144-145	10		14.81	14.74
3 N,N'-Dimethylpiperazine ^b	88	130-135			24.51	24.56
4 N,N'-Dimethylpiperazine dihydrochloride ^a	74			263 (dec.)	14.83	14.97
5 N,N'-Diethylpiperazine ^b	92	174-177			19.69	19.70
6 N,N'-Dibutylpiperazine ^c	62	195-195.5	12		14.15	14.14
7 N,N'-Dibenzylpiperazine ^c	84			91.5-92.5	10.60	10.53
7 (From benzyl chloride)	75			92-93	10.83	10.53
8 N,N'-Di-(<i>p</i> -methylbenzyl)-piperazine ^c	31			101-102	9.54	9.53

^a Prepared from N,N'-dimethylpiperazine by passing dry hydrogen chloride into the anhydrous ether solution of the free base. ^b Prepared by using zinc and hydrochloric acid as the reducing agent. ^c Prepared by using formic acid as the reducing agent.

mole of the aldehyde and two moles (twice the calculated amount) of powdered zinc. A quantity of concentrated hydrochloric acid sufficient to react with the zinc was added gradually with stirring and cooling. After the zinc had all reacted, the mixture was made alkaline and the free base was extracted with ether. The ether solution was dried over anhydrous sodium carbonate, filtered and the ether evaporated. The free base was purified by distillation.

Using Formic Acid as Reducing Agent.—A mixture of 0.1 equivalent of the secondary amine and 0.1 mole of the aldehyde was refluxed with 40 cc. of formic acid (90%) until the evolution of carbon dioxide had ceased. The

excess formic acid was evaporated on a water-bath and the residue made alkaline. The free base was extracted with ether, dried, filtered and the ether evaporated. The derivative was purified by recrystallization or distillation.

Summary

Satisfactory methods are described for the preparation of alkyl piperazines by the condensation of piperazine or N-monophenylpiperazine with aldehydes in the presence of a reducing agent.

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The Free Energy Change that Accompanies Hydrogenation of Pyridine to Piperidine¹

BY GEORGE H. BURROWS AND LOUIS A. KING, JR.

That pyridine is readily hydrogenated to piperidine, and that the reaction is reversible, has been shown by Zelinski and Borisov.² The purpose of the present investigation is to determine the free energy change of the reaction, through direct determination in the vapor phase of the equilibrium involved at each of several temperatures.

Attempts to achieve this equilibrium through initial use of hydrogen and pure pyridine or of hydrogen and pure piperidine did not lead to the desired results, and substantiated the conclusion of Sadikov and Mikhailow³ that side products are extensively formed. It was also our experience that the active life of the platinum or nickel catalyst was short.

(1) Grateful acknowledgment is made to the Elizabeth Thompson Science Fund for aid in financing this research.

(2) Zelinski and Borisov, *Ber.*, **57**, 150 (1924).

(3) Sadikov and Mikhailow, *J. Russ. Phys.-Chem. Soc.*, **58**, 527 (1927).

On these accounts experiments were devised to apply the use of trial mixtures of the several components, that mixture being deemed of equilibrium composition which underwent no appreciable change on being passed over the active catalyst at the selected temperature.

Materials and Experimental Details

Pyridine and piperidine of high quality were obtained from the Eastman Kodak Company. The pyridine was refluxed over solid potassium hydroxide and distilled. Its boiling point was 115.2-115.4°, its index of refraction n_D^{25} was 1.50682. In some instances the piperidine was given this same treatment, in others no treatment was necessary, as shown by its refractive index. This had the value n_D^{25} 1.45036.

The hydrogen, a commercial electrolytic product of high purity, was freed from possible oxygen contamination by palladinized asbestos and thoroughly dried before use.

The compositions of pyridine-piperidine mixtures were determined through their refractive