minimum quantity of benzene and precipitated with ether. The solid obtained on filtration and washing with benzene–petroleum ether, on crystallization from the latter, gave 3.6 g (24%) of **4**, mp 113–115°, which was found to be identical with the sample of the same obtained in A (mixture melting point and tlc).

The filtrate from the above, on evaporation of the solvent, gave a semisolid product (4.2 g), which on alumina chromatography as described before, gave from the benzene–petroleum ether (1:1) eluate 0.72 g (5.6%) of the cyclic ketone **3**, mp and mmp 212–213.5° (benzene–petroleum ether).

C. **Intramolecular Cyclization of the Chloro Ketone 3.**—The chloro ketone **3** (0.6 g) was heated for 40 min with 20 ml of concentrated sulfuric acid on the water bath. After cooling, the reaction mixture was hydrolyzed with ice, neutralized with sodium carbonate, and worked up with benzene. The yield of **4** so obtained was 0.24 g (45.2%); after purification by alumina chromatography and crystallization from benzene–petroleum ether it melted at 212–213.5°. An attempt to cyclize **3** by using a 3 *M* proportion of aluminum chloride in nitrobenzene resulted in its recovery.

D. **9,10-Cyclopenteno-1,2,3,4-tetrahydrophenanthrene (5). Clemmensen Reduction of 3.**—A mixture of 0.45 g of **5**, 15.0 g of amalgamated zinc, 10 ml of concentrated hydrochloric acid, and 5 ml of toluene was refluxed for 24 hr and 3 ml of concentrated hydrochloric acid was added every 6 hr over this period. The toluene layer was separated and the aqueous layer was extracted with ether. The ether–toluene solution, worked up as usual, gave 0.31 g of an oily liquid which was purified by neutral alumina chromatography. The product obtained from the petroleum ether (bp 60–80°) eluate (0.12 g, mp 50–56°), on a second alumina chromatography, gave **5** as colorless crystals: mp 60–62° (acetone); ν_{CH} 13.25 μ; uv λ_{max} 322 mμ (ϵ 932), 293 (5239), 282 (4795), 270 (3330), 256 (2131), *237* (55,926), and 216 (25,885).

Anal. Calcd for $C_{17}H_{18}$: C, 91.85; H, 8.16. Found: C, 91.82; H, 8.24.

Huang-Minlon reduction of **3** (0.7 g), using 0.6 g of potassium hydroxide, 30 ml of diethylene glycol, and 1.5 ml of 85% hydrazine hydrate, by the usual procedure, gave 0.4 g (61.5%) of an oily product, which on purification by alumina chromatography, gave 0.3 g (46.1%) of the pure hydrocarbon **5**, mp 60–62° (acetone) (lit.[14] mp 65°), which was not depressed on admixture with the sample obtained by Clemmensen reduction. A thin layer chromatogram, using silica gel G as adsorbent, petroleum ether (bp 60–80°) as solvent, and 1% chloroform solution of $SbCl_3$ as spray reagent, gave an hR_f value of 55 for the hydrocarbon **5**.

E. **9,10-Cyclopentenphenanthrene (6).**—**5** (200 mg) was aromatized by heating with 48 mg of palladium black for 50 min at 260–70° under a nitrogen atmosphere. The reaction product, on working up in petroleum ether (bp 40–60°) gave 100 mg (52%) of **6**, which after neutral alumina chromatography melted at 134–139°. Repeated crystallization in ethanol raised the melting point to 136–140°. The pure product was obtained by the method of chromatographic decomposition[12] of the trinitrobenzolate, on basic alumina (Woelm): mp and mmp 147–149.5°; ir ν_{CH} 13.25 and 13.80 μ; uv λ_{max} 354 mμ (ϵ 610), 339 (741), 300 (5711), 289 (4817), 280 (5406), 270 (7608), *254* (22,672), 245 (18,617), 239 (15,805), 220 (11,406), and 213 (14,780).

Anal. Calcd for $C_{17}H_{14}$: C, 93.53; H, 6.46. Found: C, 93.21; H, 6.71.

The thin layer chromatogram gave an hR_f value of 46 for the sample of **6** obtained as above and for the authentic sample.[11]

F. **$\Delta^{1'}$-1′-Methyl-9,10-cyclopentadieno-1,2,3,4-tetrahydrophenanthrene (7).**—A benzene solution of 0.95 g of the cyclic ketone **3** was added, under cooling and mechanical stirring, to a solution of the Grignard reagent prepared from 0.42 g of magnesium and 1.2 ml of methyl iodide. The reaction mixture was heated under reflux for 2.5 hr, then decomposed with an ice–ammonium chloride mixture, and extracted with ether. The ethereal solution, on working up as usual, gave 0.9 g of the corresponding carbinol, which was directly dehydrated in 30 ml of pyridine by careful treatment with 0.3 ml of phosphorus oxychloride. The reaction mixture was heated on the steam bath for 20 min and finally hydrolyzed with ice and hydrochloric acid. The ethereal extract of the reaction product, on working up as usual, gave 0.74 g (78.9%) of **7** as an oily product, which was purified by neutral alumina chromatography. The product from the petroleum ether (bp 60–80°) eluate, on two crystallizations from the same solvent, gave **7**: mp 82–84°; ir ν_{CH} 13.32 μ (s); uv λ_{max} 331 mμ (ϵ 10,202), 326 (10,576), 314 (13,244), 247 (67,532), *241* (68,702), 220 (37,252), and 202 (35,053).

Anal. Calcd for $C_{18}H_{18}$: C, 92.26; H, 7.74. Found: C, 92.01; H, 7.82.

G. **1′-Methyl-1,2,3,4-tetrahydro-9,10-cyclopentenophenanthrene (8).**—A methanolic solution of 0.4 g of **7** was reduced catalytically employing 80 mg of palladium black at atmospheric pressure, obtaining thereby 0.245 g (61%) of **8** as a colorless liquid which, on purification by alumina chromatography, in which almost all the compound passed in the petroleum ether (bp 60–80°) eluate, was directly aromatized to **9**: ir ν_{CH} 13.25 μ (vs); uv λ_{max} 355 mμ (ϵ 2177), 329 (8558), 326 (7866), *237* (80,805), and 218 (36,815).

Anal. Calcd for $C_{18}H_{20}$: C, 91.47; H, 8.53. Found: C, 91.76; H, 8.34.

H. **1′-Methyl-9,10-cyclopentenophenanthrene (9).**—**8** (200 mg) was heated with 40 mg of platinum black, at 290–300° for about 40 min. The reaction product was taken up in dry petroleum ether (bp 40–60°) and directly passed through a column of neutral alumina (Woelm). The total petroleum ether eluate yielded 103 mg (52.2%) of **9** as a crystalline solid, which on repeated crystallization from ethanol gave mp and mmp 89–91° with an authentic sample[11] of 1′-methyl-9,10-cyclopentenophenanthrene: ir ν_{CH} 13.30 and 13.75 μ; uv λ_{max} 354 mμ (ϵ 1160), 338 (1113), 302 (12,156), 289 (10,115), 278 (11,368), 270 (17,075), *254* (52,195), 246 (42,734), 222 (21,576), and 212 (29,464).

Anal. Calcd for $C_{18}H_{16}$: C, 93.06; H, 6.94. Found: C, 92.97; H, 6.71.

Registry No.—**2**, 1013-08-7; **3**, 18910-39-9; **4**, 18910-40-2; **5**, 18910-41-3; **6**, 723-98-8; **7**, 18910-43-5; **8**, 18910-44-6; **9**, 18910-45-7.

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Trapping of 3,4-Pyridyne by Methylmercaptide Ion in Ammonia

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Compelling evidence for the intermediacy of 3,4-pyridyne (I) in the reactions of 3- and 4-halopyridines with nitrogen bases has been obtained.[1] Competition experiments involving the addition of pairs of nucleophiles to this intermediate generally have employed mixed nitrogen bases in an ether solvent.[2] There is also a report of a competition involving a nitrogen and a carbon nucleophile in ammonia but only the 4-

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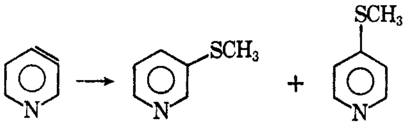
[1] For reviews of hetaryne chemistry, see (a) T. Kauffmann, *Angew. Chem. Intern. Ed. Engl.*, **4**, 543 (1965); (b) H. J. den Hertog and H. C. van der Plas, *Advan. Heterocycl. Chem.*, **4**, 121 (1965); (c) R. W. Hoffmann, "Dehydrobenzene and Cycloalkynes," Academic Press, New York, N. Y., 1967.

[2] Th. Kauffmann and R. Nürnberg, *Chem. Ber.*, **100**, 3427 (1967); Th. Kauffmann, H. Fischer, R. Nürnberg, M. Vestweber, and R. Wirthwein, *Tetrahedron Lett.*, 2911, 2917 (1967).

substituted pyridine products were recovered in low yield from the reaction of a 3-halopyridine.[3]

We report that methylmercaptide ion successfully adds to 3,4-pyridyne in the presence of amide ion in ammonia to give good yields of both 3- (II) and 4-methylthiopyridines (III). The design of our experiments was guided by the knowledge that thiophenoxide ion adds to arynes in the presence of nitrogen nucleophiles.[4]



I II III

3,4-Pyridyne was generated from 3-bromo- or 4-chloropyridine in the presence of $NaNH_2$ and $NaSCH_3$; the latter base was present in sixfold molar excess.[5] 3- and 4-methylthio- and 3- and 4-aminopyridine products were isolated. All products were characterized by comparisons with authentic materials.

In a separate experiment the stability of the methylthiopyridines toward amide ion was established. A mixture of 3- and 4-methylthiopyridines was exposed to $NaNH_2$ under conditions identical with those employed in the competition experiments, and 93% (nmr analysis) of the original mixture was recovered.

It is unlikely that direct nucleophilic substitution by methylmercaptide ion occurs concurrently with the generation of the pyridyne. If both direct substitution and pyridyne routes were being followed it is not likely that each of the two halopyridine reactants would give the same ratio of 4- to 3-methylthio products. Yet the observed ratio of products II and III formed from the two halopyridines is the same. Also, since this methylthio product ratio has a value of unity it indicates that methylmercaptide ion is not selective in its addition to 3,4-pyridyne. By contrast twice as much 4- as 3-aminopyridine is reported to form from the amination of 3,4-pyridyne.[6]

Our competition reaction probably can be used to trap other hetarynes formed in ammonia. Such experiments could be employed with advantage to determine the presence of hetaryne intermediates and to probe their reactivity.[7]

Experimental Section

Competitive Addition of Sodium Amide and Sodium Methylmercaptide. A. 3-Bromopyridine.—To 500 ml of ammonia in a 1-l. three-necked flask equipped with Dry Ice condenser, gas inlet tube, and stirrer were added 23.4 g (0.60 mol) of powdered sodium amide and a few crystals of triphenylmethane. When an equivalent amount of methylmercaptan was passed into the red mixture, the red color disappeared and the condenser, covered with solid ammonium methylmercaptide, was replaced. Small pieces of sodium (<0.5 g) were added to regenerate the red color. Following the addition of 3.9 g (0.10 mol) of sodium amide and 7.9 g (0.050 mol) of 3-bromopyridine, the reaction mixture was allowed to reflux for 3 hr. The reaction was quenched by the addition of 7.0 g of ammonium chloride followed by 250 ml of ether. After 5–7 hr the ammonia evaporated. The residue was washed with 100 ml of ether and the mixture was filtered. Washing was repeated three to five times. The ether extract was distilled. To the concentrate were added 10 ml of benzene and 0.290 g of *t*-butyl alcohol internal standard and the mixture was analyzed by nmr. The total yield (67%) of 3- and 4-methylthiopyridines was determined by comparison of the areas of the methylthio peaks (τ 8.0, 3-SCH_3, and τ 8.1, 4-SCH_3, in benzene) and the area of the standard. The reaction mixture then was distilled yielding 3.8 g (60%) of a mixture of 3- and 4-methylthiopyridines, bp 119–129° (33 mm).[8]

3- and 4-aminopyridines were isolated from another reaction mixture using established methods.[6]

B. 4-Chloropyridine.—Method A was employed except that an additional 1 equiv of sodium amide was added following the addition of methylmercaptan. In this way 4-chloropyridine was generated from its hydrochloride. Distillation of the reaction mixture afforded 69% of an equimolar mixture of 3- and 4-methylthiopyridines.

3-Methylthiopyridine.—Into a solution of 8 g (0.20 mol) of sodium hydroxide in 25 ml of water was bubbled 9.6 g (0.20 mol) of methylmercaptan. After 70 ml of dimethyl sulfoxide and 15.8 g (0.10 mol) of 3-bromopyridine were added the solution was heated at 110–120° in a metal bomb for 20 hr. The ethereal extracts of the reaction mixture were washed with several small portions of water and dried (K_2CO_3). Distillation gave 5.6 g (42%) of 3-methylthiopyridine, bp 110–115° (36 mm), lit.[10] bp 102° (17 mm).

Registry No.—I, 7129-66-0; methylmercaptide ion, 17302-63-5; ammonia, 7664-41-7.

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(4) J. F. Bunnett and T. K. Brotherton, *J. Org. Chem.*, **23**, 904 (1958); F. Scardiglia and J. D. Roberts, *Tetrahedron*, **3**, 197 (1958); R. Huisgen in "Organometallic Chemistry," H. Zeiss, Ed., Reinhold Publishing Corp., New York, N. Y., 1960, pp 36–87.

(5) Sodium mercaptide is soluble in ammonia under these conditions.

(6) M. J. Pieterse and H. J. den Hertog, *Rec. Trav. Chim.*, **80**, 1376 (1961).

(7) 2-Chloro- and 2-bromopyridines gave 2-aminopyridine as the major product under the conditions of the competition experiment.

(8) Authentic 4-methylthiopyridine[9] was prepared by methylating 4-mercaptopyridine.

(9) H. King and L. L. Ware, *J. Chem. Soc.*, 873 (1939).

(10) A. Albert and G. B. Barlin, *ibid.*, 2384 (1959).