12-Pyridylbenz[a]anthracenes[1,2]

FRANK A. VINGIELLO AND THOMAS J. DELIA[3,4]

Department of Chemistry, Virginia Polytechnic Institute, Blacksburg, Virginia

Received March 17, 1964

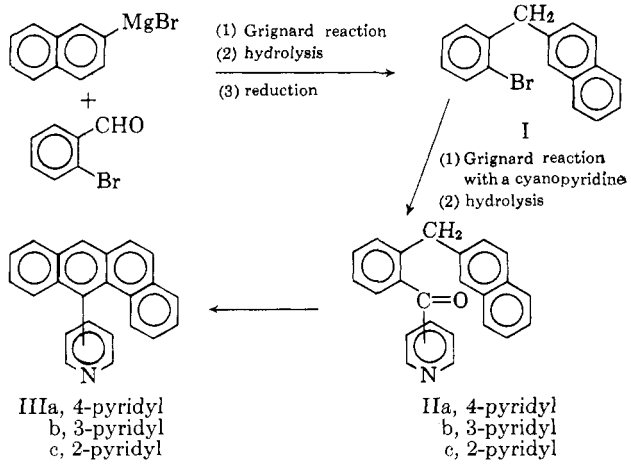
Five new ketones and one ketimine have been prepared and ring closed to their corresponding 12-pyridylbenz[a]anthracenes which were then studied in dehydrogenation reactions.

As part of our continuing effort to aid in the study of air pollution problems, we recently published a synthesis of alkyl dibenzopyrenes[5] which utilized the dehydrogenation of 12-phenylbenz[a]anthracenes as the last step in the synthetic route. In view of the known carcinogenicity of polynuclear aromatic compounds containing ring nitrogen, it appeared useful to attempt to extend the dehydrogenation reaction to the 12-pyridylbenz[a]anthracenes and thus have azadibenzopyrenes available for testing purposes. In order to make the desired compounds using a reaction route similar to the one which was successful in the hydrocarbon series,[6] it was necessary to prepare the three isomeric 2-(2-naphthylmethyl)phenyl pyridyl ketones and/or the three isomeric 1-(2-benzyl)naphthyl pyridyl ketones. Either of these series of ketones should, on aromatic cyclodehydration,[7] lead to the desired 12-pyridylbenz[a]anthracenes. The cyclodehydrogenation of these new structures was also studied and led to rather unusual results.

The synthetic route shown in Chart I was first adopted as the most feasible approach to the 12-pyridylbenz[a]anthracenes.

When 2-naphthylmagnesium bromide[8] was allowed to react with 2-bromobenzaldehyde[9] and the resulting adduct was hydrolyzed, a mixture of 2-naphthyl-2-bromophenylmethane and 2-naphthyl-2-bromophenyl ketone was obtained instead of the expected secondary alcohol, 2-naphthyl-2-bromophenylcarbinol. We are currently investigating this reaction further. The mixture was reduced in excellent yield with lithium aluminum hydride and aluminum chloride according to the method of Blackwell and Hickinbottom.[10]

CHART I



IIIa, 4-pyridyl
b, 3-pyridyl
c, 2-pyridyl

IIa, 4-pyridyl
b, 3-pyridyl
c, 2-pyridyl

The three isomeric 2-(2-naphthylmethyl)phenyl pyridyl ketones (IIa–IIc) were prepared from the Grignard reagent of I and the appropriate cyanopyridine. The yields were as follows: the 4-isomer (IIa), 50%; the 2-isomer (IIc), 45%; and the 3-isomer (IIb), 35%). That the 3-isomer gives the lowest per cent yield has also been observed in related work in the preparation of 2-benzylphenyl pyridyl ketones[11] and 2-(1-naphthylmethyl)phenyl pyridyl ketones.[12] The ketones were isolated as very viscous oils which distilled above 200° (0.20 mm.) and which gave satisfactory carbon, hydrogen, and nitrogen analyses. The ketones exhibited strong absorption at 5.9–6.0 μ, which is consistent with a diaryl ketone and is further evidence for the structures assigned (IIa–IIc).

In view of the difficulties encountered in preparing the 2-(2-naphthylmethyl)phenyl pyridyl ketones and since the isomeric 1-(2-benzyl)naphthyl pyridyl ketones (VIa–VIc) would presumably give the desired 12-pyridylbenz[a]anthracenes when subjected to an aromatic cyclodehydration reaction,[7] we sought to prepare these compounds using the reactions shown in Chart II.

The nuclear bromination of 2-methylnaphthalene was effected in 80% yield according to the improved method of Hall and Mitchell,[13] and the side-chain bromination to give 1-bromo-2-bromomethylnaphthalene (IV) was achieved in 70% yield according to the method of Newman and Kosak.[14] A recently devised Grignard reagent cross-coupling procedure[15] was used to cross couple 1-bromo-2-bromonaphthalene with phenylmagnesium bromide to give a 71% yield of 1-bromo-2-benzylnaphthalene. An interesting side product, tentatively designated as 1,2-bis-2,2′-(1-bromonaphthyl)ethane, was isolated in 13% yield.

The Grignard reagent of V was prepared in ether. When the Grignard reagent was formed, the ether was replaced with benzene and the cyanopyridines were added, dissolved in benzene. From these reactions after the usual hydrolysis, there was obtained a 65% yield of the 4-isomer (VIa) and a 63% yield of the 3-

(1) Presented in part before a joint meeting of the Division of Water and Waste Chemistry and the Division of Analytical Chemistry at the 140th National Meeting of the American Chemical Society, Chicago, Ill. Sept., 1961.

(2) This investigation was supported by a research grant (AP-0008-06) from the Division of Air Pollution, Bureau of State Services, U. S. Public Health Service.

(3) Allied Chemical Corp. Fellow, 1960–1961.

(4) This paper has been taken from the Doctorate Thesis of T. J. Delia presented to the Virginia Polytechnic Institute in 1961.

(5) F. A. Vingiello and W. W. Zajac, *J. Org. Chem.*, **26**, 2228 (1961).

(6) F. A. Vingiello and A. Borkovec, *J. Am. Chem. Soc.*, **78**, 1240 (1956).

(7) C. K. Bradsher, *ibid.*, **62**, 486 (1940).

(8) Prepared by the method of F. A. Vingiello, T. J. Delia, P. Polss, and D. Farrier [*J. Chem. Educ.*, **40**, 544 (1963)].

(9) Prepared by the general method of H. G. Hass and M. L. Bender [*Org. Syn.*, **30**, 99 (1950)].

(10) J. Blackwell and W. J. Hickinbottom, *J. Chem. Soc.*, 1405 (1961).

(11) F. A. Vingiello and M. M. Schlechter, *J. Org. Chem.*, **28**, 2448 (1963).

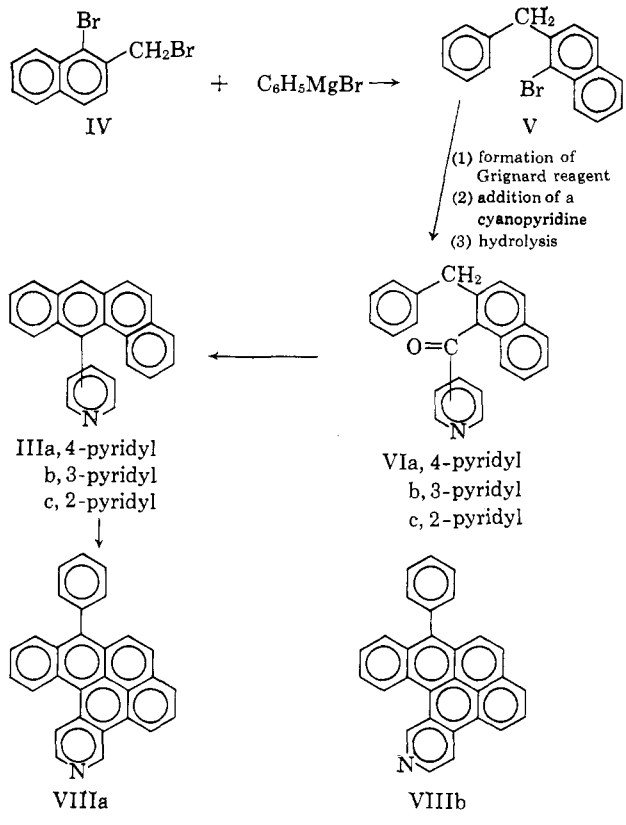
(12) F. A. Vingiello, E. B. Ellerbe, T. J. Delia, and J. Yanez, *J. Med. Chem.*, **7**, 121 (1964).

(13) D. M. Hall and R. K. Mitchell, *J. Chem. Soc.*, 1375 (1951).

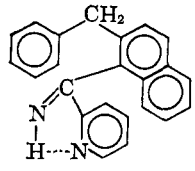
(14) M. S. Newman and A. I. Kosak, *J. Org. Chem.*, **14**, 375 (1949).

(15) F. A. Vingiello, S-G. Quo, and J. Sheridan, *ibid.*, **26**, 3202 (1961).

CHART II



isomer (VIb). However, none of the 2-isomer (VIc) was ever isolated. There was obtained instead a 94% yield of the corresponding ketimine (VII). Several attempts to hydrolyze this to the ketone failed and finally, under quite vigorous conditions, it was cyclized to 12-(2-pyridyl)benz[*a*]anthracene. This resistance to hydrolysis may be understood by examining the



VII

structure of VII. Two factors are at once clear: first, a five-membered hydrogen-bonded structure is favored; second, the back side of the ketimine group is well protected by the adjacent naphthyl group. It is interesting to note that the infrared spectrum of VII shows no N–H peak. The ketones VIa and VIb exhibited strong absorption at 6.0 μ and formed 1:1 adducts with picric acid.

All three isomeric 2-(2-naphthylmethyl)phenyl pyridyl ketones (IIa–IIc) were converted to their corresponding 12-pyridylbenz[*a*]anthracenes (IIIa–IIIc) using an acid-catalyzed aromatic cyclodehydration reaction.[7] In a similar way the two isomeric 1-(2-benzyl)-naphthyl pyridyl ketones VIa and VIb and the ketimine VII were converted to IIIa–IIIc. As expected, more vigorous conditions were needed to cyclize VIa, VIb, and VII than were needed to cyclize IIa, IIb, and IIc, since ring closure is effected into the less reactive phenyl ring rather than a naphthyl ring. The products obtained by either route were identical as shown by melting points and ultraviolet spectral patterns, and subsequent dehydrogenation reactions.

Attempts to convert the pyridylbenz[*a*]anthracenes (IIIa–IIIc) to their corresponding N-oxides using the method of Boekelheide and Linn[16] met with success only in the case of the 4-isomer, IIIa.

A study of the cyclodehydrogenation of the 12-pyridylbenz[*a*]anthracenes was undertaken using known dehydrogenation catalysts.[5,17] Thirty-seven reactions were run using various catalysts and reaction conditions. Under none of the conditions tried could simple dehydrogenation to an azadibenzopyrene be accomplished. Only when benzene was used as a solvent was dehydrogenation observed, and in each case it was accompanied by phenylation. In the best examples, the 4-isomer (IIIa) gave 14% of a compound tentatively considered to be 3-aza-10-phenyldibenzo[*def,p*]chrysene (VIIIa); the 3-isomer (IIIb) gave 6% of a compound tentatively considered to be 2-aza-10-phenyldibenzo[*def,p*]chrysene (VIIIb); the 2-isomer (IIIc) did not give a dibenzochrysene. The assigned structures are consistent with ultraviolet absorption data, elemental analysis, and molecular weight determinations.

The yields of dehydrogenation products may be rationalized if one looks carefully at the respective molecular models. Addition of $AlCl_3$ to the nitrogen atom of IIIc gives a structure which cannot assume a planar configuration. It seems reasonable that this would prevent dehydrogenation. The analogous salt of IIIb can assume a planar structure when the nitrogen atom is away from the "a" ring of the benz[*a*]anthracene moiety but not when it is adjacent to it. The analogous salt of IIIa poses no steric interference between the attached $AlCl_3$ and the benz[*a*]anthracene moiety. It should be mentioned that a yield of 14% for this type of reaction is not low.

Dual dehydrogenation–phenylation reactions have been reported by Zander.[18] In the present series it appears that the nitrogen atom favors phenylation since it does not occur in the similar carbocyclic series.[5] The conditions under which the reactions were run suggest the possibility of a free-radical reaction. The phenylation might then be expected to occur at the deactivated 10-position since it is known that other deactivating groups (*e.g.*, nitro) facilitate phenylation.[19] The suggestion that phenylation occurs at the 10-position is further supported by the work of Roitt and Waters.[20] In studying the attack of free radicals on polynuclear aromatic hydrocarbons, they find that only the *meso* positions of anthracene, benz[*a*]anthracene, and benz[*a*]pyrene are attacked. They also report that the 12-position of benz[*a*]anthracene is not attacked because attack of the radical occurs by approaching in the same plane as the polynuclear system and only a completely exposed position would undergo such an attack.

(16) V. Boekelheide and W. J. Linn, *J. Am. Chem. Soc.*, **76**, 1286 (1954).
(17) E. Clar, *Ber.*, **63**, 112 (1930).
(18) M. Zander, *ibid.*, **92**, 2749 (1959).
(19) E. S. Gould, "Mechanism and Structure in Organic Chemistry," Henry Holt and Co., New York, N. Y., 1959, p. 722.
(20) I. N. Roitt and W. A. Waters, *J. Chem. Soc.*, 2695 (1952).

Experimental[21-24]

2-Bromobenzaldehyde.—A solution of 18 g. (0.80 g.-atom) of sodium dissolved in 800 ml. of absolute ethanol was added to a 2-l. three-necked, round-bottomed flask equipped with a stirrer, reflux condenser, and separatory funnel. To this solution was added 74 g. (0.83 mole) of 2-nitropropane followed by 300 g. (0.80 mole) of 2-bromobenzyl bromide.[25] The mixture was stirred for 15 hr., filtered, and the filtrate was concentrated. The residue was dissolved in a solution of 320 ml. of ether and 480 ml. of water. The two layers were separated and the water layer was extracted with ether. The combined ether layers were washed twice with 75-ml. portions of 10% sodium hydroxide, once with an equal volume of water, dried over magnesium sulfate, concentrated, and distilled at 12 mm. The fraction distilling at 115–118°, lit.[26] b.p. 118–119° (12 mm.), weighed 97 g. (66%).

2-(2-Naphthylmethyl)bromobenzene (I).—A Grignard reagent was prepared, in ether, from 103 g. (0.50 mole) of 2-bromonaphthalene[8] and 12 g. (0.50 g.-atom) of magnesium. A solution of 80.2 g. (0.430 mole) of 2-bromobenzaldehyde in ether was added to the Grignard reagent. The solution was heated under reflux for 2 hr. and hydrolyzed with concentrated hydrochloric acid. The usual work-up produced a yellow, viscous oil which distilled at 188–193° (0.50 mm.), yield 64 g. An infrared spectrum of the mixture revealed a carbonyl function having a peak at 6 μ but no hydroxyl function.

This mixture was not purified further. A solution of 148 g. of the mixture in ether was added slowly to a slurry of 222 g. of aluminum chloride and 31 g. of lithium aluminum hydride in ether. The mixture was heated under reflux for 2 hr., decomposed with ethyl acetate, and worked up in the usual way. The product was collected as a colorless oil at 155–175° (0.15 mm.), yield 120 g. The product solidified on standing, m.p. 49.0–50.5°.

Anal. Calcd. for $C_{17}H_{13}Br$: C, 68.70; H, 4.41; Br, 26.89. Found: C, 68.72; H, 4.59; Br, 26.68.

2-(2-Naphthylmethyl)phenyl 4-Pyridyl Ketone (IIa).—A Grignard reagent was prepared from 18.2 g. (0.06 mole) of 2-(2-naphthylmethyl)bromobenzene and 1.50 g. (0.06 g.-atom) of magnesium turnings in 75 ml. of dry ether. When almost all of the magnesium had reacted, 6.40 g. (0.06 mole) of 4-cyanopyridine dissolved in 75 ml. of dry ether and 25 ml. of dry benzene was added over a period of 1 hr. The complex precipitated and the mixture was heated under reflux for 12 hr. After cooling, the mixture was decomposed with 40 ml. of 20% ammonium chloride solution and 10 ml. of concentrated hydrochloric acid and heated under reflux for 10 hr. The mixture was cooled, the organic layer was separated, and the aqueous layer was neutralized with sodium carbonate solution. The neutral solution was extracted with an ether–benzene mixture, the organic solutions were combined, dried, and concentrated. The residual oil was distilled under reduced pressure and the product was collected as an extremely viscous, dark red oil, b.p. 229–256° (0.90 mm.), 10.3 g. (52%). Redistillation gave an analytical sample, b.p. 207–209° (0.20 mm.).

Anal. Calcd. for $C_{23}H_{17}NO$: C, 85.42; H, 5.30; N, 4.33. Found: C, 85.15; H, 5.15; N, 4.20.

2-(2-Naphthylmethyl)phenyl 3-Pyridyl Ketone (IIb).—This compound was prepared essentially as the 4-isomer. Using 30.0 g. (0.10 mole) of 2-(2-naphthylmethyl)bromobenzene, 2.40 g. (0.10 g.-atom) of magnesium, and 15.0 g. (0.14 mole) of 3-cyanopyridine dissolved in dry benzene, there was obtained an extremely viscous, dark red oil, b.p. 237–247° (0.60 mm.), 12.8 g. (40%). Redistillation gave an analytical sample, b.p. 207–208° (0.10 mm.).

Anal. Calcd. for $C_{23}H_{17}NO$: C, 85.42; H, 5.30; N, 4.33. Found: C, 85.74; H, 5.36; N, 4.61.

2-(2-Naphthylmethyl)phenyl 2-Pyridyl Ketone (IIc).—This compound was prepared essentially as the 4-isomer. Using 28.0 g. (0.09 mole) of 2-(2-naphthylmethyl)bromobenzene, 2.30 g. (0.09 g.-atom) of magnesium, and 9.40 g. (0.09 mole) of 2-cyanopyridine in dry ether, there was obtained an extremely viscous, dark red oil, b.p. 230–298° (1.5 mm.), 13.8 g. (48%). Redistillation gave an analytical sample, b.p. 212–214° (0.12 mm.).

Anal. Calcd. for $C_{23}H_{17}NO$: C, 85.42; H, 5.30; N, 4.33. Found: C, 85.39; H, 5.38; N, 4.50.

1-Bromo-2-benzylnaphthalene (V) and 1,2-Bis-2,2′-(1-bromonaphthyl)ethane.—A Grignard reagent was prepared from 157 g. (1.0 mole) of bromobenzene and 24.3 g. (1.0 g.-atom) of magnesium turnings in 400 ml. of dry ether. When most of the magnesium had reacted, the ether was replaced with benzene and 150 g. (0.50 mole) of 1-bromo-2-bromomethylnaphthalene in 400 ml. of benzene was added. The mixture was refluxed for 12 hr. and worked up essentially as was described for IIa above. The product distilled at 150–179° (0.14 mm.), lit.[27] b.p. 136–138° (10^{-4} mm.), 104.5 g. (71%).

The residue on trituration with acetone gave 13.2 g. of tan solid assumed to be a dimerization product, m.p. 173–184°. Recrystallization from benzene gave white prisms, m.p. 190.5–191°.

Anal. Calcd. for $C_{22}H_{16}Br_2$: C, 60.03; H, 3.66. Found: C, 60.25; H, 4.21.

1-(2-Benzyl)naphthyl 4-Pyridyl Ketone (VIa).—A Grignard reagent was prepared from 29.7 g. (0.10 mole) of 1-bromo-2-benzylnaphthalene and 2.43 g. (0.10 g.-atom) of magnesium turnings in dry ether. Most of the ether was replaced with benzene so that the boiling point of the solution was 72°. A solution of 10.0 g. (0.096 mole) of 4-cyanopyridine in dry benzene was added during 30 min. The mixture was heated for 10 hr. and worked up essentially as has been described for IIa. The product, a viscous, red oil, distilled at 234–250° (0.8 mm.), 20 g. (65%). The oil crystallized on standing and was recrystallized from ethanol to give near-white, plate-like crystals, m.p. 106–107°.

Anal. Calcd. for $C_{23}H_{17}NO$: C, 85.42; H, 5.30; N, 4.33. Found: C, 85.42; H, 5.33; N, 4.23.

A picrate was prepared in ethanol and had m.p. 193–195°.

Anal. Calcd. for $C_{29}H_{20}N_4O_8$: C, 63.04; H, 3.65; N, 10.14. Found: C, 62.90; H, 4.13; N, 9.66.

1-(2-Benzyl)naphthyl 3-Pyridyl Ketone (VIb).—This compound was prepared essentially as the 4-isomer. Using 29.7 g. (0.10 mole) of 1-bromo-2-benzylnaphthalene, and 2.43 g. (0.10 g.-atom) of magnesium turnings, and 9.8 g. (0.094 mole) of 3-cyanopyridine, there was obtained an extremely viscous, red oil, b.p. 227–247° (0.70 mm.), 19.3 g. (64%). Redistillation gave an analytical sample, b.p. 212–219° (0.60 mm.).

Anal. Calcd. for $C_{23}H_{17}NO$: C, 85.42; H, 5.30; N, 4.33. Found: C, 85.21; H, 5.57; N, 4.42.

A picrate was prepared in ethanol and had m.p. 145–147°.

Anal. Calcd. for $C_{29}H_{20}N_4O_8$: C, 63.04; H, 3.65; N, 10.14. Found: C, 62.46; H, 3.72; N, 10.24.

1-(2-Benzyl)naphthyl 2-Pyridyl Ketimine (VII).—A Grignard reagent was prepared from 29.7 g. (0.10 mole) of 1-bromo-2-benzylnaphthalene and 2.43 g. (0.10 g.-atom) of magnesium turnings in dry ether. When most of the magnesium had reacted, 9.00 g. (0.086 mole) of 2-cyanopyridine dissolved in dry benzene was added, and the mixture was refluxed for 30 min. It was then decomposed with 100 ml. of 10% sodium hydroxide, refluxed for 1 hr., and made acidic with dilute hydrochloric acid. The organic layer was separated and, on standing, large, light green, cubic crystals formed, 17.2 g., m.p. 59–68°. Concentration of the filtrate gave an additional 9.00 g.; total yield, 26.2 g. (94%). Recrystallization from benzene gave large, white cubic crystals, m.p. 61–68°.

Anal. Calcd. for $C_{23}H_{18}N_2$: C, 85.68; H, 5.63; N, 8.69. Found: D, 85.06; H, 5.63; N, 9.35.

12-(4-Pyridyl)benz[*a*]anthracene (IIIa). A. From 2-(2-Naphthylmethyl)phenyl 4-Pyridyl Ketone (IIa).—A mixture of 6.1 g. of IIa, 20 ml. of 48% hydrobromic acid, and 40 ml. of glacial acetic acid was heated under reflux for 18 hr. The mixture was poured onto ice, the solution was neutralized with sodium carbonate solution, and the product was extracted with benzene. The solution was concentrated and cooled, yielding crystals, m.p. 215–216.5°, 4.8 g. (83%). Recrystallization from benzene gave fine, white needles, m.p. 220–221°.

(21) All boiling points are uncorrected. All melting points were taken on a Fisher-Johns melting apparatus and are corrected.

(22) All analyses were carried out by Geller Laboratories, Bardonia, N. Y.

(23) The infrared data were taken on a Beckman Model IR-5 spectrophotometer in CCl_4 solution. The ultraviolet data were taken on a Model 3000 Perkin-Elmer Spectracord using a 1-cm quartz cell and ethanol as the solvent.

(24) The chromatography column used in this investigation was 18 mm. × 370 mm. packed with Fisher's basic alumina, Brockman activity I, 80–200 mesh. The petroleum ether had a 30–60° boiling range.

(25) R. L. Letsinger and I. H. Skoog, *J. Am. Chem. Soc.*, **77**, 5176 (1955).

(26) I. Heilbrons, "Dictionary of Organic Compounds," Vol. I., Oxford University Press, New York, N. Y., 1946, p. 273.

(27) E. A. Evans, *J. Chem. Soc.*, 2790 (1957).

Anal. Calcd. for $C_{23}H_{15}N$: C, 90.46; H, 4.95; N, 4.59. Found: C, 90.36; H, 5.13; N, 4.69.

The wave-length maxima for IIIa are λ 368, 358, 350, 342, 335, 329, 288, 277, 267, 256, and 232 mμ.

B. From 1-(2-benzyl)naphthyl 4-Pyridyl Ketone (VIa).—A mixture of 3.85 g. of VIa, 50 ml. of 48% hydrobromic acid, and 100 ml. of glacial acetic acid was heated under reflux for 47 hr. and then worked up as was IIa in A. The product weighed 3.15 g. (87%), m.p. 218–221°.

12-(3-Pyridyl)benz[*a*]anthracene (IIIb). A. From 2-(2-Naphthylmethylphenyl 3-Pyridyl Ketone (IIb).—A mixture of 4.4 g. of IIb, 20 ml. of 48% hydrobromic acid, and 40 ml. of glacial acetic acid was heated under reflux for 18 hr. and then worked up as was IIIa in A. The product, 2.0 g. (48%), was recrystallized from ethanol giving pale yellow needles, m.p. 169–170°.

Anal. Calcd. for $C_{23}H_{15}N$: C, 90.46; H, 4.95; N, 4.59. Found: C, 90.14; H, 4.93; N, 4.78.

The wave-length maxima for IIIb are λ 366, 360, 350, 343, 335, 289, 278, 269, 253, and 232 mμ.

B. From 1-(2-Benzyl)naphthyl 3-Pyridyl Ketone (VIb).—A mixture of 2.7 g. of VIb, 25 ml. of 48% hydrobromic acid, and 50 ml. of glacial acetic acid was sealed in a Carius tube and heated for 9 hr. at 180° and then worked up as was IIIa in A. The product, 1.7 g. (67%), on recrystallization from ethanol gave pale yellow needles, m.p. 169–170°. The same reaction conducted at reflux temperature for 48 hr. gave only 42% of IIIb.

12-(2-Pyridyl)benz[*a*]anthracene (IIIc). A. From 2-(2-Naphthylmethyl)phenyl 2-Pyridyl Ketone (IIc).—A mixture of 0.40 g. of IIc, 20 ml. of 48% hydrobromic acid, and 40 ml. of glacial acetic acid was heated under reflux for 13 hr. and worked up as was IIIa in A. The product, 0.17 g. (45%), was recrystallized from absolute ethanol giving white plate-like crystals, m.p. 131.5–132.5°.

Anal. Calcd. for $C_{23}H_{15}N$: C, 90.46; H, 4.95; N, 4.59. Found: C, 90.30; H, 4.93; N, 4.69.

The wave-length maxima for IIIc are λ 366, 368, 349, 342, 335, 288, 278, 268, 254, and 232 mμ.

B. From 1-(2-Benzyl)naphthyl 2-Pyridyl Ketimine (VII).—A mixture of 1.0 g. of VII, 15 ml. of 48% hydrobromic acid, and 30 ml. of glacial acetic acid was placed in a Carius tube and heated for 24 hr. at 180°. The product was chromatographed[24] giving 0.13 g. (14%) of IIIc.

12-(4-Pyridine N-oxide)benz[*a*]anthracene.—A solution of 1.0 g. of 12-(4-pyridyl)benz[*a*]anthracene in glacial acetic acid was oxidized with 30% hydrogen peroxide using the method of Boekelheide and Linn.[16] The product, 0.60 g. (57%), was recrystallized from ethanol giving white needles, m.p. 276.0–278.5° dec.

Anal. Calcd. for $C_{23}H_{15}NO$: C, 85.96; H, 4.70; N, 4.36. Found: C, 86.31; H, 4.77; N, 4.28.

The wave-length maxima for the N-oxide are λ 370, 360, 351, 343, 336, 288, 277, 268, 254, and 233 mμ.

3-Aza-10-Phenyldibenzo[*def*,*p*]chrysene (VIIIa).[28]—A solution of 0.50 g. of 12-(4-pyridyl)benz[*a*]anthracene in 75 ml. of benzene was heated under reflux, 1 g. of $AlCl_3$ was added, and the mixture was heated for 5 min. The mixture was cooled, decomposed with dilute hydrochloric acid, and neutralized. The aqueous layer was separated and extracted with benzene–acetone, and the organic solutions were combined, washed with water, and dried over calcium sulfate. The solution was concentrated to *ca.* 5 ml. and chromatographed on alumina using a mixture of benzene and petroleum ether (1:1) as the eluent. A colorless, blue fluorescent band was removed from which no pure material could be obtained. The remaining yellow band was removed using benzene as the eluant. Upon concentration and cooling there was obtained a yellow solid, m.p. 281–282°, yield 0.87 g. (14%).

The analytical sample was obtained by recrystallization from benzene as fine, yellow needles, m.p. 282–283°.

Anal. Calcd. for $C_{29}H_{17}N$: C, 91.79; H, 4.52; N, 3.69; mol. wt., 379. Found: C, 91.51; H, 4.42; N, 3.91. mol. wt. (Rast), 399 and 400.

The wave-length maxima for VIIIa are λ 331, 316, 300, 289, 265, 255, and 248 mμ.

2-Aza-10-phenyldibenzo[*def*,*p*]chrysene (VIIIb).—This product was obtained essentially as was compound VIIIa. One-half gram of 12-(3-pyridyl)benz[*a*]anthracene yielded 0.039 g. (6%) of fine, yellow needles, m.p. 258.0–259.5°.

Anal. Calcd. for $C_{29}H_{17}N$: C, 91.79; H, 4.52; N, 3.69. Found: C, 91.92; H, 4.78; N, 3.74.

The wave-length maxima for VIIIb are λ 331, 316, 300, 289, 258, 243, and 232 mμ.

(28) This is the best of 37 experiments.

The Chemistry of Pyridine. III. Substitution of 1-Alkoxy, 1-Acyloxy-, and 1-Sulfonyloxypyridinium Salts by Mercaptans

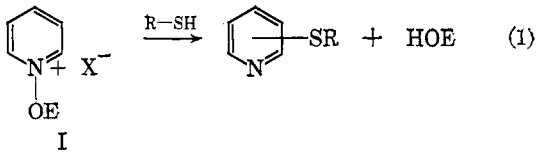
LUDWIG BAUER AND THOMAS E. DICKERHOFE

Department of Chemistry, College of Pharmacy, University of Illinois at the Medical Center, Chicago 12, Illinois

Received March 18, 1964

The substitution of pyridine N-oxide *via* N-alkoxy-, N-alkoxy-, N-acyloxy-, and N-sulfonyloxypyridinium salts with 1-butanethiol produced mixtures of 2-, 3-, and 4-butylmercaptopyridine. The yield of these sulfides and the distribution of the isomers depended on the reaction conditions and the nature of the departing substituent from the ring nitrogen of the pyridinium moiety. The mode of formation of the diverse products is discussed.

It had previously been shown[1,2] that N-alkoxypyridinium salts were substituted by mercaptans to form a mixture of alkylmercaptopyridines according to eq. 1.



I (1)

It was of interest to ascertain the course of this reaction when groups of different electronic disposition were attached to the ring nitrogen of I. This paper describes the reaction expressed by eq. 1 when E was ethyl, acetyl, benzoyl, and arenesulfonyl. It was found that a change of E from alkyl to acyl or sulfonyl resulted in different mixtures of alkylmercaptopyridines.

Before studying the substitution of the various pyridinium salts it was essential to establish if pyridine N-oxide itself would be substituted by mercaptide ion. When the N-oxide was treated with 1-butanethiol in the presence of sodium *n*-butylmercaptide, it was recovered partly, and no alkyl pyridyl sulfides could be detected.[3] Therefore it seemed essential to convert pyridine N-oxide first to a salt of type I before substitution by mercaptans could take place. The most available salts are the crystalline N-alkoxypyridinium salts (I, E is alkyl), which are readily formed when

(1) L. Bauer and L. A. Gardella, *J. Org. Chem.*, **28**, 1320 (1963).

(2) L. Bauer and L. A. Gardella, *ibid.*, **28**, 1323 (1963).

(3) In conducting this experiment, cognizance was taken of the reduction of N-oxides with mercaptans described by D. I. Relyea, P. O. Tawney, and A. R. Williams [*ibid.*, **27**, 477 (1962)]. However, our experiment was performed in the presence of the sodium mercaptide.