3.26 g. (46%) of 1-guanylpiperidine picrate was obtained using 0.02 mole of S-methylisothiourea hydrochloride. Piperidine picrate could not be conveniently separated from a contaminant which was assumed to be S-methylisothiourea picrate.

(2) **3-Methylpiperidine at 25°.** (a) **Nitrosoguanidine.**—A yield of 2.29 g. (31%) of 1-guanyl-3-methylpiperidine picrate,[32] m.p. 227.5–228.5° was obtained.

Anal. Calcd. for $C_{13}H_{18}N_6O_7$: C, 42.16; H, 4.90; N, 22.70. Found: C, 42.37; H, 4.74; N, 22.73.

(b) **Cyanamide.**—A yield of 3.78 g. (51%) of 1-guanyl-3-methylpiperidine picrate, m.p. 227.5–228.5°, was obtained.

(c) **S-Methylisothiourea Hydrochloride.**—A yield of 4.10 g. (55%) of 1-guanyl-3-methylpiperidine picrate, m.p. 227.5–228.5°, was obtained.

(3) **2-Methylpiperidine at 25°.** (a)-**S-Methylisothiourea Hydrochloride.**—A solution of 2.56 g. (0.02 mole) of S-methylisothiourea hydrochloride and 1.98 g. of 2-methylpiperidine (0.02 mole) in 100 ml. of water was held at room temperature for 72 hours. The addition of 6.0 g. of ammonium picrate gave a yellow precipitate which was collected and fractionally crystallized from water to give 1.10 g. (15% yield) of 1-guanyl-2-methylpiperidine picrate, m.p. 227–229°. A second recrystallization from water provided an analytical sample, m.p. 227.5–229.5°.

Anal. Calcd. for $C_{13}H_{18}N_6O_7$: C, 42.16; H, 4.90; N, 22.70. Found: C, 42.48; H, 4.69; N, 22.62.

Concentration of the original filtrate gave 1.63 g. (25%) of S-methylisothiourea picrate, m.p. 220–221° (lit.[33] 221°) alone or when admixed with an authentic sample.

(b) **Cyanamide.**—A yield of 3.56 g. (41%) of 1-guanyl-2-methylpiperidine picrate, m.p. 227.5–229.5°, was obtained.

(c) **Nitrosoguanidine.**—A yield of 0.13 g. (2%) of 1-guanyl-2-methylpiperidine picrate, m.p. 227.5–229.5°, was obtained. In addition, 0.95 g. of unreacted substrate (54%), was recovered from the reaction mixture.

(4) ***cis*-2,6-Dimethylpiperidine at 25°.** (a) **Cyanamide.**—A solution of 0.84 g. (0.02 mole) of cyanamide and 2.26 g. of *cis*-2,6-dimethylpiperidine (0.02 mole) in 100 ml. of water was allowed to react for 72 hours at room temperature. The reaction mixture was acidified with picric acid and the solid precipitate collected. Crystallization from water gave 2.45 g. of *cis*-1-guanyl-2,6-dimethylpiperidine picrate, m.p. 213.5–216° (32% yield).

Anal. Calcd. for $C_{14}H_{20}N_6O_7$: C, 43.75; H, 5.25; N, 21.87. Found: C, 44.13; H, 5.01; N, 21.89.

(b) **S-Methylisothiourea Hydrochloride.**—No product could be detected from the reaction of this substrate with *cis*-2,6-dimethylpiperidine. Treatment of the reaction mixture with ammonium picrate (6.0 g.) afforded an insoluble mixture of picrate salts of the reagents.

(c) **Nitrosoguanidine.**—The reaction mixture afforded only a recovery of 1.06 g. (60%) of unreacted nitrosoguanidine and 5.64 g. (83%) of impure *cis*-2,6-dimethylpiperidine picrate, m.p. 156–161° (lit.[22] 163–165°).

(5) **Piperidine Hydrochloride at 100°.** (a) **Nitrosoguanidine.**—A suspension of 1.76 g. (0.02 mole) of nitrosoguanidine in a solution of 2.43 g. of piperidine hydrochloride (0.02 mole) and 100 ml. of water was refluxed for 40 hours. The reaction mixture now was neutralized by the dropwise addition of 6 *N* hydrochloric acid and then 4.92 g. of ammonium picrate (0.02 mole). The yellow solid was collected and after a single recrystallization from water it amounted to 3.28 g. (46%) of 1-guanylpiperidine picrate, m.p. 254–255°. The original filtrate, on concentration, yielded 0.53 g. (8%) of piperidine picrate, m.p. 153–155° (lit.[31] 147–149°).

(b) **Cyanamide.**—A yield of 3.50 g. (50%) of 1-guanylpiperidine picrate, m.p. 245.5–255.5°, was obtained. In addition, 0.45 g. (7%) of piperidine picrate was recovered.

(c) **S-Methylisothiourea Hydrochloride.**—A yield of 2.66 g. (36%) of 1-guanylpiperidine picrate, m.p. 255–255.5°, was obtained. From the mother liquors 1.38 g. (22%) of piperidine picrate, m.p. 154–155°, was recovered.

(6) **3-Methylpiperidine Hydrochloride at 100°.** (a) **Nitrosoguanidine.**—A yield of 3.44 g. (47%) of 1-guanyl-3-methylpiperidine picrate, m.p. 227–228.5°, was obtained.

(b) **Cyanamide.**—A yield of 3.55 g. (48%) of 1-guanyl-3-methylpiperidine picrate, m.p. 227.5–228.5°, was obtained.

(c) **S-Methylisothiourea Hydrochloride.**—A yield of 2.30 g. (31% yield) of 1-guanyl-3-methylpiperidine picrate, m.p. 227.5–228.5°, was obtained.

(7) **2-Methylpiperidine Hydrochloride at 100°.** (a) **S-Methylisothiourea hydrochloride.**—A solution of 2.56 g. (0.02 mole) of S-methylisothiourea hydrochloride and 1.98 g. of 2-methylpiperidine (0.02 mole) in 100 ml. of water was refluxed for 40 hours. The solution was acidified with 2 *N* hydrochloric acid and then 6.0 g. of ammonium picrate was introduced. The solid was collected and recrystallized from water to give 0.85 g. (11%) of 1-guanyl-2-methylpiperidine picrate, m.p. 227.5–229.5°.

(b) **Cyanamide.**—A yield of 1.65 g. (22%) of 1-guanyl-2-methylpiperidine picrate, m.p. 227.5–229.5°, was obtained.

(c) **Nitrosoguanidine.**—A yield 1.41 g. (19%) of 1-guanyl-2-methylpiperidine picrate, m.p. 227.5–229.5°, was obtained.

(8) ***cis*-2,6-Dimethylpiperidine Hydrochloride at 100°.** (a) **Cyanamide.**—A solution 0.84 g. (0.02 mole) of cyanamide and 2.99 g. (0.02 mole) of *cis*-2,6-dimethylpiperidine in 100 ml. of water was refluxed for 40 hours. To the clear solution was added 6.0 g. of ammonium picrate and the solid collected. Recrystallization from water gave 1.60 g. (21%) of 1-guanyl-2,6-dimethylpiperidine picrate, m.p. 214–216°.

(b) **Nitrosoguanidine.**—A yield at 1.58 g. (21%) of 1-guanyl-2,6-dimethylpiperidine picrate, m.p. 214–216°, was obtained.

(c) **S-Methylisothiourea.**—A yield of 0.96 g. (13%) of 1-guanyl-2,6-dimethylpiperidine picrate, m.p. 214–216°, was obtained.

(32) In this case, 0.55 g. of nitrosoguanidine (31%) was recovered at the end of 72 hours.

(33) E. A. Warner, *J. Chem. Soc.*, **99**, 1168 (1919).

[CONTRIBUTION FROM THE LABORATORIES OF THE PITTSBURGH PLATE GLASS COMPANY, THE ALDRICH CHEMICAL COMPANY AND HARVARD UNIVERSITY]

Unsaturated Aromatic Amines; A Novel Synthesis of Indoles

BY JOHN E. HYRE[1a] AND ALFRED R. BADER[1b]

RECEIVED JUNE 14, 1957

Convenient preparations of N-allyl-, N-crotyl- and N-pentenylaniline are described. N-Crotylaniline reacts with polyphosphoric acid to yield 2,3-dimethylindole and a 2,3-dimethylindoline.

Our recent studies of unsaturated phenols[2] prompted a study of the preparations and reactions of simple unsaturated anilines.

N-Allylaniline,[3a-c,d] which had previously been

(1) (a) Dept. of Chemistry, Harvard University; (b) Aldrich Chemical Company, Milwaukee, Wis.

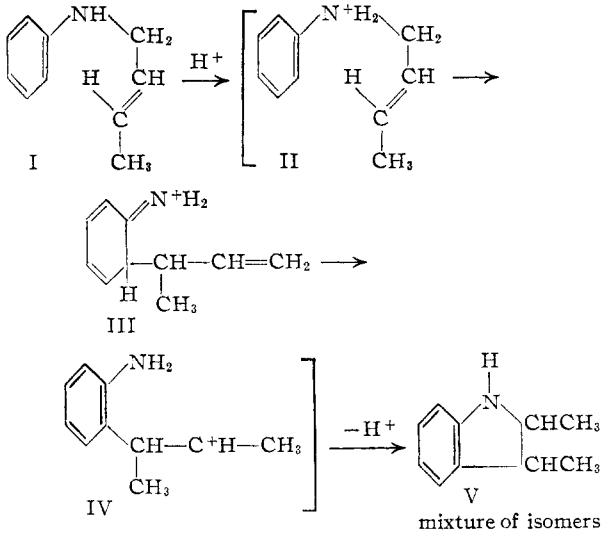
(2) A. R. Bader, THIS JOURNAL, **78**, 1709 (1956).

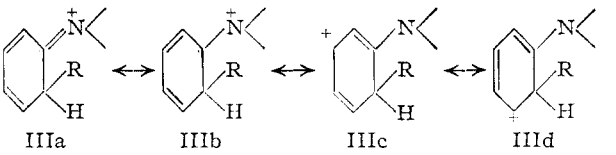
(3) (a) H. Schiff, *Ann. Suppl.*, **3**, 364 (1864); (b) F. B. Davis, R. Q. Brewster, J. S. Blair and W. C. Thompson, THIS JOURNAL, **44**, 2638 (1922); (c) F. L. Carnahan and C. D. Hurd, *ibid.*, **52**, 4586 (1930); (d) *cf.* also the paper by C. D. Hurd and W. W. Jenkins, *J. Org. Chem.*, **22**, 1418 (1957), which appeared while our paper was in press.

prepared only in low yields, is obtained conveniently and in 75–80% yields by the alkenylation of aniline with allyl chloride in non-polar solvents, under the conditions which favor C-alkenylation in phenols.[4] Hickinbottom[5] obtained *p*-crotylaniline, N-crotylaniline and less than 1% of 2,3-dimethylindole in the reaction of aniline with butadiene in the presence of aniline hydrochloride at 230–260°. N-Crotylaniline was prepared also by Arbuzov[6] in the reaction of 2-phenyl-3,6-dihydro-1,2,2H-oxazine with sodium in ethanol, and by Danforth[7] in the reaction of aniline with butadiene and sodium at 120°. Infrared spectra and hydrogenation to N-*n*-butylaniline indicate that the N-butenylaniline prepared by a modification of Danforth's method is predominantly N-crotylaniline. The analogous reaction of aniline with isoprene yields N-pentenylaniline.

When N-crotylaniline, I, was refluxed with polyphosphoric acid, 2,3-dimethylindole and a liquid amine, $C_{10}H_{13}N$, were isolated in *ca.* 32% yield each. The liquid amine was characterized by a benzenesulfonamide melting at 101–103° which differs from the benzenesulfonamide, m.p. 70–71°, of the 2,3-dimethylindoline prepared by the action of zinc dust and acid on dimethylindole.[8] The liquid amine contains two C-methyl groups, and is readily converted to 2,3-dimethylindole by the action of chloranil.[9] Thus, the liquid product is a 2,3-dimethylindoline which differs from the product of the zinc and acid reduction of 2,3-dimethylindole.

The formation of 2,3-dimethylindole and just one of the 2,3-dimethylindolines is of interest for at least two reasons. One is that we may be dealing with a *proton-catalyzed Claisen-type* rearrangement of N-crotylaniline,[10] the driving force being the resonance stabilization of the rearranged ion III; in the anilinium ion II





the charge cannot be distributed by resonance.

The second point of interest is the isolation of only one of the indolines, suggesting that the other isomer may have been selectively, stereospecifically dehydrogenated. If, as seems plausible, the *trans* isomer is the form obtained by metal–acid reduction,[8] and this is also the precursor of the 2,3-dimethylindole obtained here, then we are dealing with a *concerted, acid-catalyzed trans-elimination* of an α- and a β-hydrogen.[11]

This hypothesis explaining the isolation of only one 2,3-dimethylindoline postulates the dehydrogenation of the *trans*-2,3-dimethylindoline present in the reaction mixture. Because of electron availability, the salt would be more difficult to oxidize, and the conversion of the indoline cation to that of the indole would be thermodynamically more difficult because the indoline is a much stronger base than the indole.

Experimental

N-Allylaniline.—To a stirred and cooled mixture of 227 g. (10 moles) of sodium sand, 1000 cc. of toluene and 932 g. (10 moles) of aniline, a solution of 765 g. (10 moles) of allyl chloride in 500 cc. of toluene was added slowly. The reaction is somewhat exothermic and the reaction temperature was kept below 25°. The mixture was stirred at room temperature overnight and then refluxed for 7 hours. Methanol and water were then added, and the washed organic layer was fractionated through a 20″ Stedman column. The product (407 g., 77% based on unrecovered aniline) is a colorless oil, b.p. 68–70° (1.3 mm.), $n^{25}D$ 1.5614, d^{25}_{25} 0.9737.

Its toluenesulfonamide[3c] melts at 69°; the benzenesulfonamide forms needles from aqueous ethanol, m.p. 82–83°.

Anal. Calcd. for $C_{15}H_{15}NSO_2$: C, 65.94; H, 5.49. Found: C, 66.15; H, 5.42.

N-Allylacetanilide (acetic anhydride, sulfuric acid) forms needles from water, m.p. 46–47°.

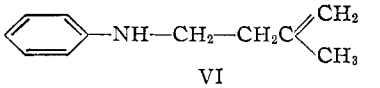
Anal. Calcd. for $C_{11}H_{13}NO$: C, 75.43; H, 7.43. Found: C, 75.31; H, 7.53.

N-Crotylaniline.—A mixture of 448 g. (4.7 moles) of aniline, 334 g. (6.2 moles) of butadiene and 20 g. (0.87 moles) of sodium was heated in an autoclave at 120° for 18 hours. Methanol and water were added, and the washed organic layer was distilled *in vacuo* to yield 370 g. (79% based on unrecovered aniline) of N-crotylaniline, b.p. 81–82° at 1.7 mm.; $n^{25}D$ 1.5553; d^{25}_{25} 0.9607; λ_{max}^{EtOH} 249 mμ (log ϵ 4.10); 295 mμ (log ϵ 3.30); λ_{min}^{EtOH} 273 mμ (log ϵ 3.0). The infrared spectrum in CS_2 shows a strong band at 10.4 μ indicative of a *trans* disubstituted double bond, RCH=CHR′.

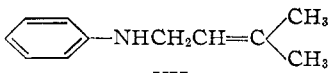
N-Butylaniline.—Hydrogenation of N-crotylaniline (methanol, Adams platinum oxide catalyst, 60 p.s.i.) quantitatively yielded N-*n*-butylaniline, b.p. 235–237°, $n^{25}D$ 1.5310, the infrared spectrum of which was identical with that of authentic N-*n*-butylaniline.

N-Pentenylaniline.—A mixture of 450 g. (4.7 moles) of aniline, 350 g. (5.1 moles) of isoprene and 20 g. of sodium similarly heated at 120° yielded N-pentenylaniline (216 g.), b.p. 94–95° at 1.7 mm., $n^{25}D$ 1.5502, d^{25}_{25} 0.9507. The product's infrared spectrum shows a pronounced band at 11.22 μ ($R_1R_2C{=}CH_2$) and weaker bands at 11.6 and 12.35 μ ($R_1CH{=}CR_2R_3$) suggesting that the product is largely VI perhaps accompanied by some VII.

(4) L. Claisen and E. Tietze, *Ber.*, **59B**, 2344 (1926).
(5) W. J. Hickinbottom, *J. Chem. Soc.*, 1981 (1934).
(6) Y. A. Arbuzov, *Doklady Akad. Nauk, S.S.S.R.*, **63**, 531 (1948).
(7) J. Danforth, U. S. Patent 2,495,890 (Jan. 1950).
(8) A. Steche, *Ann.*, **242**, 371 (1887).
(9) P. L. Julian and H. C. Printy, THIS JOURNAL, **71**, 3206 (1949).
(10) For acid catalysis of the Claisen rearrangement, see W. Gerrard, M. F. Lappert and H. B. Silver, *Proc. Chem. Soc.*, 19 (1957).
(11) For a stereospecific amine dehydrogenation involving however nitrogen and an α-hydrogen, *cf.* F. L. Weisenborn and P. A. Diassi, THIS JOURNAL, **78**, 2022 (1956).



VI



VII

Anal. Calcd. for $C_{11}H_{15}N$: C, 81.93; H, 9.38. Found: C, 82.20, 82.10; H, 9.37, 9.50.

Reaction of Aniline with Butadiene at Higher Temperatures.—When aniline, butadiene and sodium are heated to a higher temperature, small quantities of N,N'-diphenylformamidine surprisingly are formed also. Thus, when a mixture of aniline (448 g., 4.7 moles), butadiene (358 g., 6.63 moles) and sodium (20 g., 0.87 moles) was heated at 170–190° for 18 hours, 4.2 g. of diphenylformamidine, m.p. 136–137° after crystallization from aqueous ethanol, was isolated by fractional distillation. The material (λ_{max}^{EtOH} 282 mμ, log *e* 4.34; λ_{min} 240.5 mμ, log *e* 371) was identified by analysis and mixed melting point with authentic diphenylformamidine.[12]

Under similar conditions, (a) 100 g. of N-crotylaniline and 5 g. of sodium, (b) 29 g. of N-crotylaniline, 19 g. of aniline and 3 g. of sodium, (c) 19 g. of aniline, 15 g. of butadiene and 8 g. of sodium hydroxide, (d) 29 g. of N-crotylaniline, 19 g. of aniline and 8 g. of sodium hydroxide, and (e) 28 g. of N-crotylaniline, 18 g. of aniline, 4 g. of sodium hydroxide and 2 g. of sodium yielded no detectable diphenylformamidine.

The reaction of equimolar quantities of N-crotylaniline and potassium hydroxide at 220° for six hours yielded largely aniline, characterized through its benzenesulfonamide, and an insoluble black solid.

2,3-Dimethylindole and *cis*-2,3-Dimethylindoline.—A mixture of N-crotylaniline (100 g. 0.67 mole) and polyphosphoric acid (50 g.) was refluxed with stirring under inert gas for seven hours. The two phase mixture was hydrolyzed with 20% aqueous potassium hydroxide, and the product was extracted with ether, washed and fractionally distilled *in vacuo* to yield three fractions: A, b.p. 50–70° at 2 mm., 8 g.; B, b.p. 72–76° at 2 mm., 32 g., and C, b.p. 150–165° at 12 mm., 32 g. Fraction A, $n^{25}D$ 1.5802 consisted largely of aniline characterized by its benzenesulfonamide, m.p. 111–112°. Fraction B, $n^{25}D$ 1.5513, boiled sharply at 74° at 2 mm. on redistillation.

Anal. Calcd. for $C_{10}H_{13}N$: C, 81.63; H, 8.84. Found: C, 81.62, 81.76; H, 8.94, 9.04. Kuhn-Roth C-methyl, calcd. for one C-methyl group: 10.2%. Found: 12.0%. λ_{max}^{EtOH} 242.5 mμ (log *e* 3.80); 294 mμ (log *e* 3.36); λ_{min} 272 mμ (log *e* 3.05).

Fraction B, *cis*-2,3-dimethylindoline, was characterized by its benzenesulfonamide which crystallized in needles from aqueous ethanol, m.p. 101–103°.

Anal. Calcd. for $C_{16}H_{17}NSO_2$: C, 66.87; H, 5.96. Found: C, 66.93, 67.00; H, 5.88, 5.72.

The infrared spectrum of *trans*-2,3-dimethylindoline,[8] b.p. 107–109° at 12 mm., differs from that of the *cis* isomer, and the *trans* isomer was characterized by a benzenesulfonamide melting at 70–71°.

Anal. Calcd. for $C_{16}H_{17}NSO_2$: N, 4.88. Found: N, 5.31, 5.28.

cis-2,3-Dimethylindoline was recovered unchanged after refluxing with polyphosphoric acid for 4 hours. Fraction C crystallized in the receiver, m.p. 103–104° after recrystallization from heptane.

Anal. Calcd. for $C_{10}H_{11}N$: C, 82.71; H, 7.64; N, 9.65. Found: C, 82.76; H, 7.59; N, 9.65. λ_{max}^{EtOH} 228.5 mμ (log *e* 4.50); 284 mμ (log *e* 3.84); 292 mμ (inflection, log *e* 3.79); λ_{min} 248 mμ (log *e* 3.27).

Its picrate[13] forms red needles from ethanol, m.p. 156–157°; its addition compound with picryl chloride[14] crystallizes in brown needles from ethanol, m.p. 135–136°.

Reaction of *cis*-2,3-Dimethylindoline with Chloranil.[9]—A mixture of *cis*-2,3-dimethylindoline (1 g.), xylene (50 cc.) and chloranil (2 g.) was refluxed for 4 hours, filtered, freed of solvent and the residue dissolved in ether. The ethereal solution was dried after extraction with dilute aqueous hydrochloric acid to remove the more strongly basic indoline, and distilled to yield 0.37 g. (38%) of 2,3-dimethylindole.

Acknowledgment.—We wish to thank Professors M. G. Ettlinger and C. D. Hurd for valuable advice.

(12) W. Weith, *Ber.*, **9**, 457 (1876).

(13) L. Wolff, *ibid.*, **21**, 125 (1888).

(14) M. Padoa and C. Chiaves, *Gazz. chim. ital.*, **38I**, 236 (1908).

MILWAUKEE, WISCONSIN
CAMBRIDGE, MASSACHUSETTS

[CONTRIBUTION FROM THE CHEMISTRY DIVISION, U. S. NAVAL ORDNANCE TEST STATION]

The Alkaline Degradation of Some Polymethylenetrinitramines[1]

BY RUSSELL REED, JR.

RECEIVED JULY 22, 1957

The nature of the products formed when hydroxide ion, methoxide ion and benzylamine interact with certain esters of the 7-alkyl-2,4,6-trinitro-2,4,6-triazaheptanols-1 has been elucidated. Similar studies have been carried out with the bis-esters of the 2,4,6-trinitro-2,4,6-triazaheptandiol-1,7 and with the polymeric methylenenitramine $[CH_2N(NO_2)]_x$.

The alkaline decomposition of the simple nitramines has been studied extensively but little has been reported on compounds containing two or three nitramino groups. Compounds containing three nitramino groups which have been investigated are the trifluoroacetate esters of the 2,4,6-trinitro-2,4,6-triazaheptanol-1, $CH_3[N(NO_2)CH_2]_3OH$, and the 2,4,6-trinitro-2,4,6-triazaheptandiol-1,7, $HO[CH_2N(NO_2)]_3CH_2OH$.[2] The interesting and unusual behavior of these compounds prompted the present investigation of the alkaline degradation of compounds containing three methylenenitramine units.

Primary nitramines are acidic and readily form salts with alkalies and amines; the salts are not easily decomposed by bases except on prolonged boiling in concentrated aqueous alkali.[3] Van Erp[4] found that methylnitramine and potassium hydroxide yielded ammonia, hydrogen, formaldehyde and the salt of a nitrogen acid, perhaps hyponitrous. Lamberton and co-workers[5] found the mono- and diarylmethylnitramines to be cleaved easily by alkali with the formation of aldehydes or ketones,

(1) Presented in part before the Pacific Southwest Meeting of the American Chemical Society, San Diego, Calif., April 27, 1957.

(2) R. Reed, THIS JOURNAL, **78**, 801 (1956).

(3) H. J. Backer, *Sammlung Chem. und Chem. Tech. Vorträge*, **18**, 359 (1912).

(4) H. Van Erp, *Rec. trav. chim.*, **14**, 48 (1895); *Ber.*, **29**, 474 (1896).

(5) J. Barrott, M. I. Gillibrand and A. H. Lamberton, *J. Chem. Soc.*, 1282 (1951).