ethanol, showed m.p. 150–151° and $[\alpha]^{25}D$ −7.4° in chloroform, *c* 5.2.

Anal. Calcd. for $C_{19}H_{27}O_{14}N$ (493.4): C, 46.2; H, 5.52. Found: C, 46.1; H, 5.34.

D-Manno-pentaacetoxy-1-nitroheptene-1.—Two grams of the above nitroalcohol hexaacetate in 25 cc. of benzene was refluxed for 90 minutes with 2 g. of sodium bicarbonate. Filtration and concentration then produced 1.59 g. (90%) of D-manno-pentaacetoxy-1-nitroheptene-1. After recrystallization from ethanol, the acetylated nitroölefin melted at 111–113° and showed $[\alpha]^{25}D$ 37.3° in chloroform, *c* 4.

The acetylation of 1-nitro-1-desoxy-D-manno-D-*talo*-heptitol with acetic anhydride and sulfuric acid produced a sirupy hexaacetate. The latter, on refluxing in benzene solution with sodium bicarbonate, yielded 58% of D-manno-pentaacetoxy-1-nitroheptene-1, m.p. 111–113°, and $[\alpha]^{25}D$ 38.1 in chloroform, *c* 3.2.

Anal. Calcd. for $C_{17}H_{23}O_{12}N$ (433.4): C, 47.1; H, 5.35. Found: C, 47.1; H, 5.25.

1-Amino-1-desoxy-D-manno-D-*gala*-heptitol Oxalate.—Two grams of 1-nitro-1-desoxy-D-manno-D-*gala*-heptitol in 50 cc. of water was shaken with hydrogen in the presence of 1 g. of Raney nickel at room temperature and atmospheric pressure. The reduction was complete in one and three-quarters hours with the absorption of 3 mole-equivalents of hydrogen. After filtration onto 0.53 g. of oxalic acid dihydrate, concentration of the solution to dryness produced a crystalline residue. Filtration with ethanol then yielded 1.9 g. (90%) of the amine oxalate. After recrystallization from water by the addition of ethanol, the pure salt melted at 193–195°, with decomposition, and showed $[\alpha]^{25}D$ 13.2° in water, *c* 3.4.

Anal. Calcd. for $C_8H_{18}O_8N$ (256.2): C, 37.5; H, 7.08. Found: C, 37.8; H, 7.05.

Reduction of 1-nitro-1-desoxy-D-manno-D-*talo*-heptitol also proceeded smoothly to the amine but the latter failed to yield a crystalline salt with either oxalic acid or *p*-toluenesulfonic acid.

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

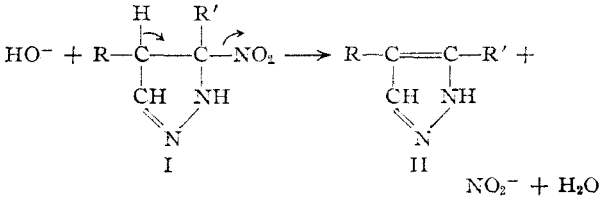
The Condensation of Diazo Compounds with Nitroölefins. II. 3-Bromo- and 3-Nitropyrazoles

BY WILLIAM E. PARHAM AND JAMES L. BLEASDALE[1]

Mechanisms for the decomposition of 3-nitropyrazolines into pyrazoles in acidic and basic media are discussed. The condensation of 1-bromo-1-nitro-2-phenylethylene with diazomethane was effected and the decomposition of the resulting pyrazoline with acid and base was studied. The results were found to follow essentially those anticipated by the mechanisms postulated. The decomposition of 3-bromo-3-nitro-4-phenylpyrazoline with hydrogen chloride was observed to give a 66% yield of 3-bromo-4-phenylpyrazole. The decomposition of the same pyrazoline with sodium carbonate was observed to give a 73% yield of 3-nitro-4-phenylpyrazole. The structure of 3-nitro-4-phenylpyrazole was established by reduction to the corresponding amine and synthesis of the latter from 3-carbethoxy-4-phenylpyrazole by means of a Curtius reaction. The availability of bromonitroölefins suggests that the reaction described might represent a general synthesis for the otherwise difficultly accessible 3-bromo- and 3-nitropyrazoles.

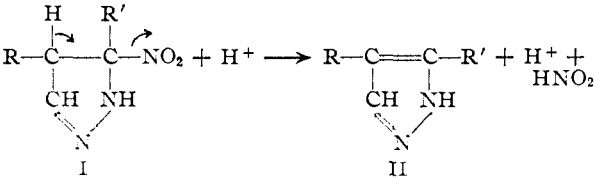
The condensation of diazocompounds with nitroolefins and the decomposition of the resulting nitropyrazolines to give pyrazoles was recently described.[2] The observation that nitropyrazolines could be converted into pyrazoles by the action of either acids or bases prompted us to investigate the decomposition of 3-bromo-3-nitro-4-phenylpyrazoline (IV) with the intention of gaining additional information concerning the mechanism for this elimination reaction.

The decomposition of 3-nitropyrazolines (I)[3a] by alkali probably takes place by the removal of a proton from C_4 followed by a shift of the C_4 electrons into the ring and the simultaneous elimination of the nitro group as an anion[3b] (E_2-mechanism).



The hydrogen atom at C_4 is attached to a carbon–carbon–nitrogen system similar to that found in α-picoline and the increased acidity observed in such systems is usually explained by resonance stabilization[4] of the resulting ion (—C̄—C=N ↔ —C=C—N̈—).

The decomposition of 3-nitropyrazolines (I) by treatment with strong mineral acids may take place by an acid-catalyzed ionization of the nitro group facilitated by the coördination of a proton with subsequent or simultaneous expulsion of a proton at C_4.



A study of the decomposition of 3-bromo-3-nitro-4-phenylpyrazoline (IV) in acidic and basic media was considered of interest to this problem since it was recognized that the decomposition of this pyrazoline could follow a different course depending upon the mechanism of elimination involved. In the presence of base the reaction could proceed by means of an E_1 or E_2 elimination mechanism,[5] and the product would depend upon whether a bromide or nitrite ion is preferentially eliminated from the pyrazoline IV. If the control-

(1) From the Ph.D. Thesis of James L. Bleasdale, July, 1950.

(2) W. E. Parham and J. L. Bleasdale, THIS JOURNAL, **72**, 3843 (1950).

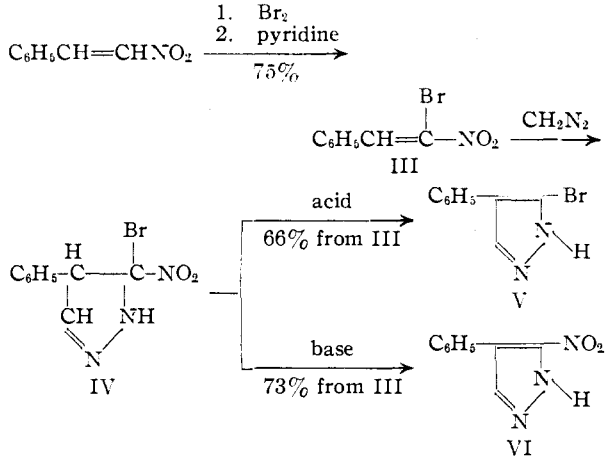
(3) (a) The well established tautomerization of pyrazolines and pyrazoles is assumed during this discussion. (b) *Cf.* M. Kloetzel, *ibid.*, **70**, 3571 (1948), for a similar type of β-elimination in β-nitro esters.

(4) E. Alexander, "Principles of Ionic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1950, p. 130.

(5) *Cf.* ref. 4, p. 104.

ling factor in this case is the relative strength of the base being eliminated one might anticipate the loss of the less basic bromide ion[6] resulting in the formation of the nitropyrazole (VI). On the other hand if the mechanism presented above for the acid-catalyzed elimination in nitropyrazolines is essentially correct one might anticipate the preferential elimination of nitrous acid in acidic media resulting in the formation of the bromopyrazole (V). That the nitro group would be more susceptible to electrophilic attack by hydrogen ion than the bromine atom was suggested by the increased solubility of nitroalkanes relative to bromoalkanes in sulfuric acid.

The products of decomposition of IV were observed to be essentially those anticipated. When hydrogen chloride was used to decompose IV a



66% yield of the bromopyrazole V was obtained together with a small quantity of VI (10.6%). When sodium bicarbonate was used a 73.5% yield of the nitropyrazole was obtained together with a small amount of V (10.4%). It is possible that the small amount of VI obtained from the acid decomposition of V resulted from decomposition of the pyrazoline before the acid catalyst was added for it was observed that under the conditions used for its preparation the bromonitropyrazoline slowly decomposes to give a mixture of V and VI.

3-Bromo-4-phenylpyrazole (m.p. 146–147°) and 3-nitro-4-phenylpyrazole (m.p. 209–210°) have not been previously reported, although the isomeric pyrazoles 3-phenyl-4-bromopyrazole[7] (m.p. 116°[8]) and 3-phenyl-4-nitropyrazole (m.p. 192°) are known. Pyrazoles such as V and VI cannot be prepared by direct nuclear substitution since attack on the pyrazole ring occurs preferentially at C_4. If a phenyl group is at C_4, nitration will occur in the benzene ring.[5]

In order to establish the structure of 3-nitro-4-phenylpyrazole with certainty VI was reduced catalytically to 3-amino-4-phenylpyrazole (99% yield) and the latter was synthesized from 4-phenyl-3-carbethoxypyrazole by means of a Curtius degradation. The identity of the two amines was established by a mixed melting point determination of the amines and also of their corresponding picrates.

It was observed that 3-bromo-4-phenylpyrazole could be recovered essentially unchanged after prolonged treatment with boiling aqueous alkali. In the presence of strong base the pyrazole anion is formed, as evidenced by its solubility, which is less susceptible to further attack by nucleophilic reagents.

The availability of halonitroölefins[9] suggests that the reaction described may prove a useful method to obtain the otherwise difficultly accessible 3-nitro- and 3-halopyrazoles.

Experimental

1-Bromo-1-nitro-2-phenylethylene.—The following procedure was found to be more effective than that reported by Priebs.[10]

In a one-liter three-necked flask fitted with a condenser, dropping funnel and stirrer was placed 100 g. (0.323 mole) of ω-nitrostyrene dibromide and 400 ml. of cyclohexane. The mixture was heated to the reflux temperature and a solution of 30 ml. of pyridine and 100 ml. of cyclohexane was slowly added. After the addition was complete, heating was continued for 15 minutes. The mixture was transferred to a separatory funnel by washing with ether (500 ml.) and water (150 ml.) and the resulting solution was washed with dilute hydrochloric acid and water and then dried over sodium sulfate. The drying agent was removed and the resulting solution was concentrated to 200 ml. by distillation. The residue was cooled and the product was separated by filtration. There was obtained 68.3 g. (92.7%) of yellow needles, m.p. 64–67°. The product was recrystallized from glacial acetic acid and then cyclohexane, m.p. 67–68° (reported[10] m.p. 67–68°).

Reaction of 1-Bromo-1-nitro-2-phenylethylene with Diazomethane.—In a 250-ml. erlenmeyer flask was placed 11.2 g. (0.050 mole) of 1-bromo-1-nitro-2-phenylethylene dissolved in 50 ml. of ether and 150 ml. of ether containing about 2.8 g. (0.065 mole) of diazomethane.[11] The flask was loosely stoppered and allowed to stand at room temperature for 24 hours. The yellow needles which had formed were collected by filtration and dried by vacuum. The product, 3-nitro-4-phenylpyrazole, weighed 4.0 g. (42.3%), m.p. 205–206°. Recrystallization of the product from methanol gave yellow plates, m.p. 209–210°.

Anal. Calcd. for $C_9H_7N_3O_2$: C, 57.14; H, 3.73; N, 22.22. Found: C, 57.48; H, 3.87; N, 22.62.

The mother liquor was evaporated to dryness and the residue was recrystallized from methanol to give 4.4 g. of yellow crystals, m.p. 150–190°. This mixture gave additional amounts of the nitropyrazole only after many recrystallizations.

Acid Decomposition of 3-Bromo-3-nitro-4-phenylpyrazoline.—In a 250-ml. erlenmeye :flask was placed 11.2 g. (0.050 mole) of 1-bromo-1-nitro-2-phenylethylene dissolved in 50 ml. of absolute ether and 150 ml. of absolute ether containing about 2.8 g. (0.065 mole) of diazomethane. The mixture was allowed to stand for three hours at the temperature of an ice-bath. At the end of this time dry hydrogen chloride and dry nitrogen were passed through the mixture for 30 minutes. The mixture was swept for an additional 30 minutes with nitrogen. The resulting mixture was evaporatively distilled to dryness and the residue was dissolved in absolute ether and washed with sodium bicarbonate and water. The ether solution was dried with anhydrous sodium sulfate and magnesium sulfate. The desiccant was removed by filtration and the filtrate was diluted to 1000 ml. with absolute ether.

A 300-ml. aliquot of the above solution was subjected to chromatography through a column of alumina (22 × 340 mm.). A yellow band 5 cm. long was formed. This band was developed with anhydrous ether. The eluents were evaporatively distilled in 100-ml. portions. In this manner

(6) *Cf.* Ingold, *et al.*, *J. Chem. Soc.*, 2041 (1948); Hughes and Shapiro, *ibid.*, 1177 (1937), for the rate of elimination of halide from alkyl halides in E-1 and E-2 elimination reactions.

(7) Wenglein, Jena Dissertation (1895).

(8) E. Buchner and C. Hachumian, *Ber.*, **35**, 37 (1902).

(9) E. Schmidt and G. Rutz, *Ber.*, **61**, 2145 (1928).

(10) B. Priebs, *Ann.*, **225**, 342 (1884).

(11) "Organic Syntheses," Coll. Vol. II, 1943, p. 165. The diazomethane was not purified and its solution contained some alkali.

there was obtained 2.20 g. (66%) of almost white crystals, m.p. 144–147°. Recrystallization of this solid from 50% methanol gave white needles, m.p. 146–147°. The product, 3-bromo-4-phenylpyrazole (V), was soluble in sodium hydroxide but insoluble in sodium bicarbonate.

Anal. Calcd. for $C_9H_7N_2Br$: C, 48.45; H, 3.16; N, 12.56. Found: C, 48.49; H, 3.29; N, 12.73.

The column was extruded and eluted with 15% glacial acetic acid–ethyl acetate solution. There was obtained 0.03 g. (10.6%) of light yellow needles, m.p. 205–206°, which were identified as 3-nitro-4-phenylpyrazole (VI).

Decomposition of 3-Bromo-3-nitro-4-phenylpyrazoline with Sodium Bicarbonate.—An ether solution of the pyrazoline was prepared as described above from 9.85 g. (0.04 mole) of 1-bromo-1-nitro-2-phenylethylene and 2.8 g. (0.065 mole) of diazomethane dissolved in 150 ml. of absolute ether. The mixture was allowed to stand at room temperature for four hours and then 50 ml. of 5% sodium bicarbonate was added. This mixture was allowed to stand at room temperature for 24 hours. The solutions were separated and the ether solution was washed with water and dried with anhydrous sodium sulfate and magnesium sulfate. The desiccants were removed by filtration and the filtrate was diluted to 1000 ml. with absolute ether.

A 300-ml. aliquot of the above solution was subjected to chromatography through a column of alumina (22 × 340 mm.) in the usual manner. There was no material eluted through the column. The column was extruded and divided into six sections. Each section was eluted with 15% glacial acetic acid–ethyl acetate and the eluents evaporated to dryness.

No.	Band width, cm.	Band color	Yield, g.	M.p., °C.
1	1	Orange	0.05	Oil
2	9	Yellow	1.15	203–207
3	4	Yellow	0.65	203–207
4	4	Light yellow	.10	145–190
5	8	Light yellow	.30	132–142
6	8	Colorless	.00	...

Fractions 2 and 3 (1.80 g., 73.5%) were almost pure 3-nitro-4-phenylpyrazole (VI). After crystallization from methanol the melting point was 209–210°.

Fraction 5 (0.30 g., 10.4%) was shown to be principally 3-bromo-4-phenylpyrazole (V). The product was crystallized from 50% methanol, m.p. 146–147°.

The reduction of 3-nitro-4-phenylpyrazole to 3-amino-4-phenylpyrazole was effected by low pressure hydrogenation in 95% ethanol using platinum oxide catalyst. The amine, m.p. 170–172°, was obtained as almost white crystals in 99% yield. The product was crystallized three times from chloroform to give white needles, m.p. 173–173.5°.

Anal. Calcd. for $C_9H_9N_3$: C, 67.91; H, 5.70; N, 26.40. Found: C, 67.61; H, 5.60; N, 26.25.

The picrate of 3-amino-4-phenylpyrazole was prepared in the usual manner and recrystallized from ethanol, m.p. 202–203°.

Anal. Calcd. for $C_{15}H_{12}N_6O_7$: C, 46.39; H, 3.11; N, 21.64. Found: C, 46.32; H, 2.79; N, 21.25.

4-Phenylpyrazole-3-carbohydrazide.—In a 125-ml. flask was placed 15.3 g. (0.071 mole) of 4-phenyl-3-carbethoxypyrazole,[12] 15 ml. (15.8 g., 0.25 mole) of 80% hydrazine hydrate, and 20 ml. of 50% ethanol–water. The mixture was heated at reflux temperature for eight hours. The mixture was cooled and the crystalline material which formed was collected, washed with cold water and dried. There was obtained 13.50 g. (94.5%) of white crystals, m.p. 183–186°. Recrystallization of the product from water gave white needles, m.p. 186–186.5°.

Anal. Calcd. for $C_{10}H_{10}N_4O$: C, 59.39; H, 4.98; N, 27.71. Found: C, 59.18; H, 4.78; N, 27.48.

Ethyl 4-Phenylpyrazole-3-carbamate.—A solution containing 10.4 g. (0.051 mole) of the hydrazide, 8.5 ml. of 6 *N* hydrochloric acid and 100 ml. of water was cooled to 5° and a solution of 3.1 g. (0.052 mole) of sodium nitrite in 50 ml. of water was added slowly. The mixture was kept below 10° during the addition. The white solid which formed during the reaction was collected by filtration and washed with water. The dry product, 10.78 g. (98% calculated as azide), was placed in a 200-ml. round-bottomed flask fitted with a reflux condenser and 100 ml. of absolute ethanol was added. The mixture was heated under reflux for seven hours, and then filtered while hot. The filtrate was concentrated to 50 ml. and then diluted to 500 ml. with water. The resulting oil solidified (8.75 g., 75% yield) and melted at 159–160°. The crude carbamate was purified by recrystallization from dilute ethanol; m.p. 170–171°.

Anal. Calcd. for $C_{12}H_{13}N_3O_2$: C, 62.32; H, 5.66. Found: C, 62.31; H, 5.66.

Conversion of Ethyl 4-Phenylpyrazole-3-carbamate into 3-Amino-4-phenylpyrazole.—In a 200-ml. round-bottomed flask fitted with a reflux condenser was placed 0.75 g. (0.0032 mole) of ethyl 4-phenylpyrazole-3-carbamate, 60 ml. of water, 5 ml. of alcohol and 1.0 g. (0.025 mole) of sodium hydroxide. The mixture was heated on a steam-bath for three hours. The mixture was cooled and extracted with three 50-ml. portions of ether and the combined ether solutions were extracted with 50 ml. of dilute hydrochloric acid. The acid solution was then neutralized with 10% sodium hydroxide solution and the white solid amine which formed was collected and washed with water. The dry product weighed 0.46 g. (89%). A melting point and mixed melting point with a sample of amine prepared by the reduction of 3-nitro-4-phenylpyrazole was 172–173°. The picrate of the amine melted at 202–203° and did not depress the melting point of the picrate of the amine obtained by reduction of 3-nitro-4-phenylpyrazole.

Attempted Hydrolysis of 3-Bromo-4-phenylpyrazole.—In a large test-tube fitted with a cold finger was placed 0.65 g. (0.0029 mole) of 3-bromo-4-phenylpyrazole, 10 ml. of water and 0.2 g. (0.005 mole) of sodium hydroxide. The solution was heated at reflux temperature for six hours after which time it was cooled and acidified with nitric acid. The mixture was extracted with ether using a small continuous extractor. The ether extract was evaporated to dryness and 0.50 g. (0.0022 mole) of white crystals, m.p. 120–130°, was obtained. Recrystallization of the product from 25% methanol gave 0.45 g. (70%) of unchanged starting material, m.p. 146–147°.

MINNEAPOLIS 14, MINN. RECEIVED FEBRUARY 8, 1951

(12) E. P. Kohler and L. L. Steele, THIS JOURNAL, **41**, 1104 (1919).