[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

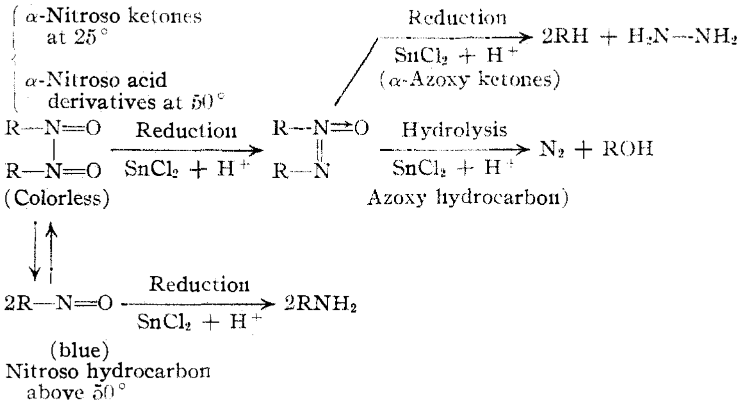
Aliphatic Azoxy Compounds. III. 2-Azoxy-2,5-dimethylhexane[1,2]

BY JOHN G. ASTON AND DAVID E. AILMAN

In order to study the reaction of the azoxy group in aliphatic organic compounds it was desirable to prepare an azoxy compound without any other functional groups. 2-Azoxy-2,5-dimethylhexane was chosen because of the availability of starting materials and lack of volatility with consequent ease of isolation of the product and intermediates.

It was soon found impossible to obtain this compound by reduction of the corresponding nitroso compound either at room temperature or at 57–60° with stannous chloride in acid solution. At room temperature the nitroso compound decomposed without reduction (see experimental section); at 57–60° a 58% yield of the corresponding amine was obtained. These results are important for above 55° the dissociation of the bis-nitroso compound is apparent. In the case of α-nitroso esters, where no such dissociation is evident at 55°,[1b,3] azoxy compounds may be obtained in good yields under similar conditions and no amine is produced. These facts indicate that the linkage in the bisnitroso compounds is through the nitrogens and that reduction to the amine proceeds through the monomolecular form since no amine has ever been found among the reduction products of aliphatic azoxy compounds.[1a]

The situation is made clear by the scheme



2-Azoxy-2,5-dimethylhexane eventually was prepared in 68–75% yield by condensing the corresponding nitroso compound with the corresponding hydroxylamine in the presence of solid potassium hydroxide at 50°. The use of concentrated sulfuric acid gave but 21% yield. Condensation of the corresponding nitro compound and amine in the presence of metallic sodium at reflux temperature gave a 10% yield. Both reactions are known in the aromatic series.[4]

Attempts to reduce this azoxy compound with stannous chloride and hydrochloric acid merely resulted in the hydrolysis of the compound to nitrogen, octenes, dimethylisoamylcarbinol and 2-chloro-2,5-dimethylhexane.

The accompanying mechanism seems plausible for this new type of decomposition as in the hypothetical intermediate II one sees a close analogy with the diazonium salts, the part enclosed by the dotted square being analogous to the $-N^{+}\equiv N$ of these salts.[5] While the hydrolysis occurs rapidly at reflux temperature in the presence of 6 *N* hydrochloric acid and stannous chloride, with 6 *N* hydrochloric acid alone (or with stannic chloride) the reaction is negligible.

The decomposition of the *bis*-nitroso compound by acid to yield nitrogen and nitrous oxide obviously can be formulated in a manner similar to the hydrolysis of the azoxy compound.

When treated with methylmagnesium iodide in diisoamyl ether at 100° for eighty minutes, less than 20% of addition was observed. This is hardly consistent with the open chain formula of the azoxy group since aromatic azoxy compounds seem to react as expected.[6] If the azoxy group in aliphatic compounds had the ring structure, the intermediate II postulated in the hydrolysis could be formed by ring cleavage.

It is hoped to report on the be-

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(1) The first two papers of this series are: (a) THIS JOURNAL, **54**, 1530 (1932); (b) *ibid.*, **56**, 1387 (1934).

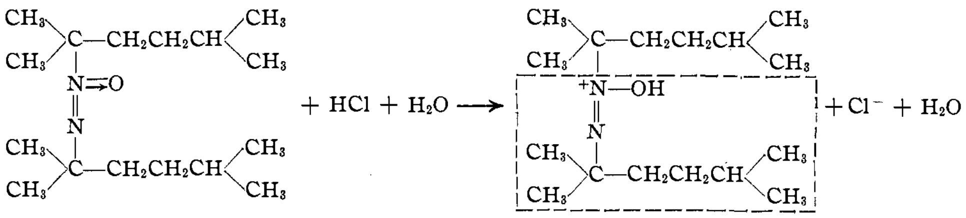
(2) Presented before the Organic Division of the American Chemical Society at Rochester, N. Y., September, 1937.

(3) Sidgwick, Taylor and Baker, "The Organic Chemistry of Nitrogen," Oxford University Press, 1937, p. 215.

(4) *Cf.* ref. 3, p. 427; Brand and Stohr, *Ber.*, **39**, 4065 (1906); Angeli and Marchetti, *Atti accad. Lincei*, [5] **15**, 480 (1906); *Brit. Chem. Abstracts*, i, 716 (1906).

(5) That the accompanying olefins are also a consequence of such a mechanism was kindly called to our attention by Dr. F. C. Whitmore (see Whitmore and Langlois, THIS JOURNAL, **54**, 3442 (1932).

(6) Cumming and Ferrier, *J. Roy. Tech. Coll. Glasgow*, **2**, 49 (1929); Bigelow, *Chem. Rev.*, **9**, 155 (1931).



I II

$\longrightarrow \mathrm{ROH} + \underset{\mathrm{III}}{\mathrm{R{-}N{=}N{-}OH}} + \mathrm{HCl}$ $\qquad \mathrm{R{-}N{=}N{-}OH} \longrightarrow \mathrm{ROH} + \mathrm{N_2}$

where R = $\mathrm{Me_2C}$-*i*-Am

havior of this compound with other reducing agents and the products of addition of organometallic compounds in the near future.

Experimental

Hydrolysis of 2-Nitroso-2,5-dimethylhexane.—Sixteen and four-tenths grams (0.115 mole, monomolecular basis) of nitroso compound was refluxed with 50 cc. of concentrated hydrochloric acid. The decomposition started explosively with the evolution of a large amount of nitrogen containing less than 2% of nitrous oxide. This gas sample, and all others in the work, was identified by distillation of the liquefied gas and vapor pressure measurements on the fractions. After refluxing for a half hour the oil was steam distilled. A tarry scum remained behind. The distillate gave, after drying with potassium carbonate, 0.85 g. (0.008 mole, 7% yield) of octenes, 6.0 g. (0.043 mole, 37% yield) of dimethylisoamylcarbinol and 2-chloro-2,5-dimethylhexane and 3.0 g. of high-boiling material, $n^{20}\mathrm{D}$ 1.430. The octene fraction boiled at 106–120° (730 mm.), $n^{20}\mathrm{D}$ 1.416, and gave positive reactions with bromine water and alkaline permanganate. From the carbinol–chloride fraction was obtained 4.6 g. of material boiling at 80–86° (100 mm.), $n^{20}\mathrm{D}$ 1.4232–1.4240, which was nearly pure chloride.

Anal. Calcd. for $C_8H_{17}Cl$: Cl, 23.8; mol. wt., 148.6. Found: Cl (Stepanoff), 23.3, 23.9; mol. wt. (cryoscopic in benzene), 146.5, 147.3.

The pure chloride was obtained by passing gaseous hydrogen chloride into dimethylisoamylcarbinol keeping the mixture cool with tap water until constant weight was obtained. It boiled at 86° (100 mm.), $n^{20}\mathrm{D}$ 1.4231.

The Action of Stannous Chloride and Concentrated Hydrochloric Acid on 2-Nitroso-2,5-dimethylhexane at 60°.—Six grams (0.042 mole) of 2-nitroso-2,5-dimethylhexane[7] was melted and added dropwise during twenty minutes to a rapidly stirred solution of 16 g. (0.071 mole) of crystalline stannous chloride dihydrate, in 50 cc. of concentrated hydrochloric acid held throughout the reaction at 57–60°. The blue color of the nitroso compound disappeared immediately with each addition; 90 cc. of 28% potassium hydroxide solution was added keeping the temperature below 45° to prevent loss of material by volatilization. Each addition of alkali precipitated basic tin salts which gradually redissolved. On neutralization and distillation of the solution 0.3 g. of octenes (0.0027 mole, 6.4% yield) and 0.54 g. (0.0039 mole, 9.2% yield) of a mixture of dimethylisoamylcarbinol and the corresponding chloride was obtained.

The solution was made strongly alkaline by the addition of 75 cc. more of 28% potassium hydroxide solution, and the amine was steam distilled. After drying with anhydrous potassium carbonate, distillation gave 3.17 g. (0.024 mole, 58% yield) of amine, b. p. 94° (150 mm.), 141.0° (733.6 mm.).[8]

Anal. Calcd. for $C_8H_{19}N$: C, 74.42; H, 14.73. Found: C, 73.63; H, 14.65.

The hydrochloride, after crystallization from alcohol, melted at 171°.

Anal. Calcd. for $C_8H_{20}NCl$: Cl, 21.5. Found: Cl (Volhard), 21.2.

A positive isonitrile test was obtained. The *p*-toluenesulfonamide[9] melted at 89.5–90°; mixed m. p. with an authentic sample showed no lowering.

The Action of Stannous Chloride and Concentrated Hydrochloric Acid on 2-Nitroso-2,5-dimethylhexane at Room Temperature.—A typical experiment is described; 8.5 g. (0.06 mole) of the solid *bis*-nitroso compound was added rapidly to a well-stirred solution of 8.3 g. (0.037 mole) of stannous chloride in 12.5 cc. of concentrated hydrochloric acid. The temperature, originally 27°, rose to 31° and fell slowly. The stirring was stopped as soon as the oily layer was colorless (not over ten minutes elapsed from the beginning of the addition). Nitrogen, containing a small amount of nitrous oxide, was evolved (the total gas was 5% of the nitrogen content of the sample).[10] Titration with permanganate showed that only 12% of the stannous ion had been oxidized. The mixture was diluted with 100 cc. of ice water and the oil was removed by solution in ether, washed with water, washed with sodium carbonate solution to remove acids, and dried with calcium chloride. Distillation gave 0.5 g. (0.0045 mole, 7.4% yield) of low-boiling material, $n^{20}\mathrm{D}$ 1.419, (probably octenes); 2.5 g. (0.018 mole, 30% yield) of liquid boiling at 100–105° (150 mm.), $n^{20}\mathrm{D}$ 1.422; and a residue amounting to 4.9 g. of a light yellow, very viscous oil, $n^{20}\mathrm{D}$ 1.472, which contained tin and chlorine and which could not be distilled at 80° under the pressures of a mercury vapor pump.

The liquid, b. p. 100–105° (150 mm.), was evidently a

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(7) Piloty and Ruff, *Ber.*, **31**, 457 (1898).

(8) Konowalow, *ibid.*, **28**, 1852 (1895); *Chem. Zentr.*, **77**, II, 312 (1906).

(9) Hinsberg and Kessler, *Ber.*, **38**, 906 (1906).

(10) If at this point the mixture is nearly neutralized with sodium hydroxide solution and steam distilled, the products are: 8% yield of low-boiling material (probably octenes), 53% yield of a mixture of dimethylisoamylcarbinol and chloride, and 3–9% yield of 2-amino-2,5-dimethylhexane.

mixture of dimethylisoamylcarbinol and the corresponding chloride. It was converted to the pure chloride, b. p. 98° (150 mm.), $n^{20}\mathrm{D}$ 1.4230, by gaseous hydrogen chloride.

Anal. Calcd. for $C_8H_{17}Cl$: Cl, 23.8; mol. wt., 148.6. Found: Cl (Stepanoff), 24.0; mol. wt. (cryoscopic in benzene), 150.

When the viscous oil was boiled with concentrated hydrochloric acid, a blue color was visible in the refluxing oil for a short time. Nitrogen was evolved, and the oily material had the odor of dimethylisoamylcarbinol.

Preparation and Properties of 2-Azoxy-2,5-dimethylhexane.—Four grams (0.0276 mole) of 2-β-hydroxylamino-2,5-dimethylhexane[11] and 3.6 g. (0.025 mole) of 2-nitroso-2,5-dimethylhexane and 1.0 g. of anhydrous potassium carbonate were heated together at 50° for nine hours without apparent reaction; 1.0 g. of solid potassium hydroxide was added to the mixture. After eighteen hours more at 50° the reaction mixture was yellow green in color, showing that a reaction of the blue nitroso compound had taken place. Water was added to dissolve the salts and the oil was taken up in ether and dried with sodium sulfate. Distillation gave 5.1 g. (0.019 mole, 75% yield) of the colorless azoxy compound, b. p. 111° (5 mm.), $n^{20}\mathrm{D}$ 1.4434, d^{20}_4 0.8564.

Anal. Calcd. for $C_{16}H_{34}ON_2$: C, 71.04; H, 12.68; N, 10.36; mol. wt., 270.3. Found: C, 70.67; H, 12.63; N (Dumas), 10.75; mol. wt. (cryoscopic in benzene), 273, 270.

2-Azoxy-2,5-dimethylhexane was also prepared by a procedure similar in every way to the above except that anhydrous magnesium sulfate followed by concentrated sulfuric acid were substituted for the potassium carbonate and potassium hydroxide, respectively. The yield of azoxy compound was 21%. The addition of the sulfuric acid caused some charring and not more than 0.5 cc. of acid was added. No other products were identified.

The Reaction of 2-Amino- with 2-Nitro-2,5-dimethylhexane in the Presence of Metallic Sodium.—Seven-tenths gram (0.03 gram atom) of sodium in the form of freshly cut chips was added gradually to a refluxing solution of 5.0 g. (0.039 mole) of the amine and 6.2 g. (0.039 mole) of the nitro compound. The products were worked up as above and gave 1.0 g. (0.0037 mole, 9.5% yield) of impure azoxy compound, b. p. 100–125° (4 mm.), $n^{20}\mathrm{D}$ 1.4415, which was not redistilled. Other products were not identified.

The reaction of 2-azoxy-2,5-dimethylhexane with methylmagnesium iodide in the apparatus of Kohler and Richtmyer[12] showed the absence of active hydrogen and gave less than 20% addition during 80 minutes at 100°.

The Action of Stannous Chloride and Dilute Hydrochloric Acid on 2-Azoxy-2,5-dimethylhexane.—Ten and three-tenths grams (0.038 mole) of azoxy compound was mixed with 25 g. (0.11 mole) of stannous chloride in 225 cc. of 6 *N* hydrochloric acid solution. The mixture was refluxed for four hours in an apparatus for collecting the evolved nitrogen (generally about 60% of the theoretical) over 50% potassium hydroxide solution, and then the oil layer was steam distilled. Titration showed that less than 5% of stannous ion had been oxidized. The oily product, neutralized with sodium carbonate, and dried with calcium chloride, gave on distillation: 3.3 g. (0.03 mole, 38% yield) of octenes b. p. 113–120° (730 mm.), $n^{20}\mathrm{D}$ 1.416; 3.6 g. (0.026 mole, 33% yield) of a mixture of dimethylisoamylcarbinol and 2-chloro-2,5-dimethylhexane, b. p. 98–103° (150 mm.), $n^{20}\mathrm{D}$ 1.4221; and 0.6 g. (0.0022 mole, 6% yield) of recovered azoxy compound.

Individual octenes were not identified. Positive reaction with bromine water and with alkaline permanganate demonstrated their olefinic character. The octenes were converted to dibromides by reaction with bromine vapor and expulsion of excess bromine with dry air. Calcd. for $C_8H_{16}Br_2$: mol. wt., 272. Found: (cryoscopic in benzene), 274. Attempts to distil this dibromide gave a colorless oil, b. p. 100–113° (30 mm.), $n^{20}\mathrm{D}$ 1.478, which rapidly turned red-brown and gave low analyses for bromine and mol. wt.

The carbinol–chloride mixture was analyzed. Calcd. for 65 mol. % $C_8H_{17}Cl$, 35 mol. % $C_8H_{18}O$: C, 67.5; H, 12.26; Cl, 16.20. Found: C, 66.7; H, 12.27; Cl, 16.21. The mixture was then converted with gaseous hydrogen chloride to pure chloride, b. p. 98° (150 mm.), $n^{20}\mathrm{D}$ 1.423. Calcd. for $C_8H_{17}Cl$: mol. wt., 148.6. Found: (cryoscopic in benzene), 150.

Attempts to hydrolyze 0.5-g. samples of the azoxy compound with 6 *N* hydrochloric acid alone, or with stannic chloride, resulted in only negligible amounts of gas being evolved on refluxing for several minutes. With stannous chloride, a sample gave up its nitrogen almost quantitatively on refluxing for a half hour without oxidation of the stannous ion. The nitrogen was pure as shown by vapor pressure measurements. Evidently stannous chloride is a specific catalyst for the hydrolysis.

In conclusion we wish to thank Dr. G. H. Messerly for help with the distillation of the small quantities of gases and their identification by vapor pressure measurements.

Summary

1. 2-Nitroso-2,5-dimethylhexane was reduced to 2-amino-2,5-dimethylhexane in 58% yield with stannous chloride and concentrated hydrochloric acid at 60°.

2. The action of stannous chloride and concentrated hydrochloric acid on 2-nitroso-2,5-dimethylhexane at room temperature did not give appreciable reduction but only decomposition. Nitrogen, nitrous oxide, octenes, dimethylisoamylcarbinol, 2-chloro-2,5-dimethylhexane, and very small amounts of 2-amino-2,5-dimethylhexane were among the decomposition products.

3. The hydrolysis of 2-nitroso-2,5-dimethylhexane by refluxing with concentrated hydrochloric acid produced nitrous oxide, nitrogen, octenes, dimethylisoamylcarbinol and 2-chloro-2,5-dimethylhexane.

4. 2-Azoxy-2,5-dimethylhexane was prepared in excellent yield by condensing the corresponding

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[11] Piloty and Steinbock, *Ber.*, **31**, 221 (1898).

[12] Kohler and Richtmyer, THIS JOURNAL, **52**, 3736 (1930).

β-hydroxylamine and nitroso compound in the presence of alkali.

5. 2-Azoxy-2,5-dimethylhexane was shown to be non-reactive with methylmagnesium iodide.

6. The hydrolysis of 2-azoxy-2,5-dimethylhexane with dilute hydrochloric acid catalyzed by stannous ion produced nitrogen, octenes and dimethylisoamylcarbinol.

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Aliphatic Azoxy Compounds. IV. The Preparation of Certain α-Azoxy Ketones. The Molecular Refractions and Parachors of Aliphatic Azoxy Compounds[1]

BY DAVID E. AILMAN

In order to study the molecular refractions and parachors of aliphatic azoxy compounds, additional liquid azoxy compounds are desirable. Ethyl 2-methyl-2-azoxy-propionate[2] and 2-azoxy-2,5-dimethylhexane[3] have been described elsewhere.

This paper describes the preparation and properties of ethyl α-azoxyisopropyl ketone and α-azoxyisopropyl isobutyl ketone of which only the former is a liquid whose molecular refraction and parachor have been compared with those of the compounds mentioned above.

Experimental

Ethyl α-Azoxyisopropyl Ketone.—Ten grams (0.039 mole, bimolecular basis) of bimolecular ethyl α-nitrosoisopropyl ketone[4] was reduced with 10.8 g. (0.048 mole) of crystalline stannous chloride $SnCl_2 \cdot 2H_2O$, in 15.8 cc. of concentrated hydrochloric acid,[5] keeping the temperature 30–36° for twenty minutes. A titration with permanganate showed that 0.040 mole of stannous ion had been oxidized. After nearly neutralizing the acid solution with sodium carbonate the liquid azoxy compound was removed by solution in ether, dried with potassium carbonate, and distilled, collecting 5.18 g. (0.021 mole; 55% yield), b. p. 126–126.5° (6 mm.), n^{20}_D 1.4587, d^{20}_4 1.0151.

Anal. Calcd. for $C_{12}H_{22}O_3N_2$: C, 59.45; H, 9.16; N, 11.57; mol. wt., 242.3. Found: C, 58.85; H, 9.09; N (Dumas), 11.72; mol. wt. (cryoscopic in benzene), 240, 241.

Reduction of Ethyl α-Azoxyisopropyl Ketone.—Eight grams (0.033 mole) of the azoxy compound on stirring with a solution of 31 g. (0.14 mole) of stannous chloride in 45 cc. of concentrated hydrochloric acid for seven hours at a maximum temperature of 65° (maintained for one hour), oxidized only 46% of the stannous ion (calculated for reduction to ketone and hydrazine[5]). (The excess stannous ion was determined by permanganate titration, which does not distinguish between stannous ion and hydrazine. This has been corrected for.) The isolation of 1.5 g. of a semicarbazone which melted a few degrees below the m. p. of ethyl isopropyl ketone semicarbazone (each recrystallization raised the m. p., but the amounts became too small to handle), together with the isolation of 0.5 g. of dibenzalazine (sharp m. p. and mixed m. p. with an authentic sample) showed that a reduction of the type observed with methyl α-azoxyisopropyl ketone[5] had occurred.

α-Azoxyisopropyl Isobutyl Ketone.—Eight grams (0.025 mole) of the *bis*-nitroso ketone[4] was reduced with 6.9 g. of stannous chloride in 13 cc. of concentrated hydrochloric acid. On chilling, after the reduction was complete, the oil crystallized. The product was recrystallized from lukewarm alcohol–water and then melted at 30–31°. The yield of purified product was 4.0 g. (0.013 mole, 52% yield).

Anal. Calcd. for $C_{16}H_{30}O_3N_2$: C, 64.39; H, 10.14; mol. wt., 298.2. Found: C, 63.97; H, 10.65; mol. wt. (cryoscopic in benzene), 310, 297, 300.

Molecular Refraction and Parachor

In Table I are given the properties of the liquid aliphatic azoxy compounds prepared to date. Densities were determined with a 2-cc. pycnometer. Surface tensions were measured with a DuNouy tensimeter which had been checked against water and alcohol.

TABLE I

No.	Compound	Mol. wt.	n^{20}_D	d^{20}_4	γ_{20}
1	2-Azoxy-2,5-dimethylhexane[3]	270.4	1.4434	0.8564	28.27
2	Ethyl α-azoxyisopropyl ketone	242.3	1.4587	1.0151	35.88
3	Ethyl 2-methyl-2-azoxypropionate[2]	274.3	1.4412	1.0562	33.56

In Table II are given in column 2 the observed molecular refractions; in column 3 the summation of Eisenlohr atomic refractivities,[6] exclusive of the azoxy grouping; and column 4 the refractivity

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(1) Presented in part before the Organic Division of the American Chemical Society at Rochester, N. Y., September, 1937. *Cf.* preceding paper.

(2) Aston and Parker, THIS JOURNAL, **56**, 1387 (1934).

(3) Aston and Ailman, *ibid.*, **60**, 1930 (1938).

(4) Aston and Mayberry, *ibid.*, **57**, 1888 (1935).

(5) *Cf.* Aston, Menard and Mayberry, *ibid.*, **54**, 1530 (1932).

(6) Eisenlohr, *Z. physik. Chem.*, **75**, 585 (1910); **79**, 129 (1912).