

PROPERTIES OF DINITROÖLEFINS: REACTIONS WITH BASES, CHLORINE, AND HYDROGEN

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Preparation of two dinitroölefins, 2,3-dinitro-2-butene and 3,4-dinitro-3-hexene, from available 1-chloro-1-nitroparaffins by the action of aqueous alkali has been reported in a patent (1a). In reactions with ammonia and some organic bases these dinitroölefins exhibit evidences of aromatic character. Their reactions with various bases, chlorine, and some catalytic reductions are here reported.

Ammonia displaced one nitro group from each of these dinitroölefins to yield a nitroimine, a reaction analogous to the preparation of *o*-nitroaniline by ammonolysis of *o*-dinitrobenzene, assuming a tautomeric shift in the aliphatic case. (The authors recognize the possibility of a tautomeric equilibrium between the nitroimine and an olefinic nitroamine but prefer the former structure.) The imino group was rapidly hydrolyzed by acid at room temperature and alkali liberated ammonia from the nitroimine in the cold, whereas *o*-nitroaniline must be heated with the base. Aniline formed *N*-substituted nitroimines with the dinitroölefins in an analogous manner (Table I).

The structure of the nitroimines was established by hydrogenating one of them, 2-nitro-3-iminobutane, to 2,3-diaminobutane, a known compound, with a platinum catalyst in 60% yield. Determination of the ammonia liberated at the same time accounted for the other 40% of the starting material. The dinitroölefins were also reduced to the corresponding diamines with platinum or nickel catalysts in low yields (25-33%). The catalytic reduction of 2-nitro-3-(*N*-phenyl)iminobutane resulted only in hydrogenolysis, from which aniline was recovered in essentially quantitative yield.

A molecular compound resembling in character the picrates of tertiary amines was formed from 2,3-dinitro-2-butene and quinoline. Similar molecular compounds are known in which the nitro moiety may be a polynitroparaffin such as tetranitromethane (1b) but the present case is the first example in which the polynitro component is a dinitroölefin. Nitroparaffins may also act as oxidizing agents for organic bases, yielding salts from which the base may be regenerated (1c). Whether such an oxidation-reduction took place in this instance cannot be said with certainty from the evidence. The analytical data, however, indicates that the molecular compound does not contain a simple ratio of components. Quinoline could still be regenerated from the adduct as was shown by precipitating it as the picrate from an alcohol solution of the molecular compound with a saturated solution of picric acid. The 2,3-dinitro-2-butene was not recovered as such but an alcohol solution of the molecular compound was converted to 2-nitro-3-iminobutane by treatment with aqueous ammonia.

Other tertiary amines such as pyridine, dimethylaniline, isoquinoline, quinal-

dine, and α -picoline gave deep colors with 2,3-dinitro-2-butene in carbon tetrachloride, 95% ethanol, and absolute ethanol, an evidence (2a) of molecular-compound formation but no solid products were isolated. In the case of the stronger bases, pyridine and α -picoline, the color deepening was followed by profound decomposition and evolution of heat.

Secondary amines (diethylamine, morpholine, piperidine, di-*n*-butylamine, methylaniline) likewise gave deep colors with both dinitroölefins but no crystalline substances were isolated.

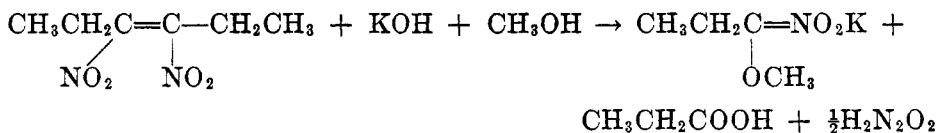
Whereas the base, ammonia, will displace one nitro group in a dinitroölefin, warm aqueous alkali has no apparent effect on these compounds. In fact, during their purification, the unreacted 1-chloro-1-nitroparaffin may be removed from

TABLE I
NITROIMINES OF FORMULA $RCHNO_2C(=NR')R$

R	R'	M.P. °C. ^a	CARBON, %		HYDROGEN, %		NITROGEN, %	
			Calc'd	Found	Calc'd	Found	Calc'd	Found
CH ₃	H	159-160					24.13	24.2
C ₂ H ₅	H	83-83.5					19.45	19.5 ^b
CH ₃	C ₆ H ₅	97-98	62.50	62.72	6.25	6.23	14.58	14.66
C ₂ H ₅	C ₆ H ₅	62.5-63	65.47	65.62	7.27	7.59	12.72	12.58
C ₂ H ₅	C ₆ H ₄ NH ₂ (<i>p</i>)	175.5-177	61.25	61.46	7.28	7.29		

^a All melting points reported in this paper are corrected. ^b Imino nitrogen: Calc'd, 9.72. Found, 10.4.

the desired product by washing with warm alkali. When alcoholic potassium hydroxide was added to a dinitroölefin, however, a vigorous reaction ensued, potassium nitrite precipitated, and a deep red solution of a polymer remained. When the order of addition was reversed, for example, by adding a methanol solution of 3,4-dinitro-3-hexene to a methanol solution of potassium hydroxide, a white salt formed, to which we have assigned the structure of the potassium salt of 1-nitro-1-methoxypropane. The yield is quantitative according to the following equation:



The formation of potassium hyponitrite was suggested by the following observations. Immediately after running the reaction, no nitrite was present in the alkaline filtrate but after standing overnight, nitrite was present. If the filtrate was acidified with acetic acid, it did not show the presence of nitrite upon standing. The filtrate gave the Rao test (2b) for hyponitrous acid.

Potassium acetate was identified in the filtrate from the preparation of the potassium salt of 1-nitro-1-ethoxyethane by an analogous reaction.

The dinitroolefins reduce alkaline permanganate solution rapidly giving nitric acid and the corresponding carboxylic acid. The compounds are slightly soluble in concentrated sulfuric acid but may be recovered unchanged upon pouring into water. Bromine and chlorine do not add to the olefinic bond under ordinary conditions but liquid chlorine in a closed tube added to the double bond and also substituted in the side chain of 2,3-dinitro-2-butene during the course of a week's exposure to sunlight.

EXPERIMENTAL

3-Nitro-4-imino-hexane. Five grams of 3,4-dinitro-3-hexene (1a) was shaken with 25 ml. of 28% ammonium hydroxide solution at room temperature for several minutes whereupon the imine separated, m.p. 81–84°, yield 3.4 g., 83%. The nitroimino-hexane was recrystallized from 95% ethanol (yellow rhombs) or water (white plates), to the pure compound, m.p. 83–83.5°. The reaction takes the same path in liquid ammonia at a slower rate.

For preparing the N-substituted iminonitro compounds, the dinitroolefin was dissolved in cold 95% ethanol and an alcohol solution of the amine was added slowly. Upon cooling in an acetone-Dry Ice bath, the nitroimines separated and were recrystallized from 95% ethanol. Yields, 50–70%.

When the alcohol filtrate from the preparation of 3-nitro-4-(N-phenyl)imino-hexane was poured into water, a yellow brown crystalline substance was obtained. After recrystallization from absolute ethanol, it gave m.p. 97–98° and was identified as diazoaminobenzene.

3,4-Diamino-hexane. A solution of 1.65 g. of pure 3-nitro-4-imino-hexane in 100 ml. of absolute ethanol was reduced in 9 minutes at room temperature in the presence of 0.6 g. of platinum oxide catalyst using a mechanical shaker at a pressure of 40–30 p.s.i. of hydrogen. After decanting the alcohol solution, distillation gave 1.2 g. of an oil, b.p. 165–180°. Conversion of this oil to the *bis*-benzamide indicated a yield of 63% of pure diamine in the reduction. From the alcohol distillate, ammonia was recovered as 0.038 g. of ammonium chloride, indicating hydrogenolysis had taken place to the extent of 6.2% during the reduction.

Reduction of 14.4 g. (0.1 mole) of the 3-nitro-4-imino-hexane gave 5.3 g. (46%) of 3,4-diamino-hexane (b.p. 168–175°) from which a pure fraction, b.p. 175–176°, was obtained, n_D^{25} 1.4499. The compound has the characteristic odor of the aliphatic diamines, is hygroscopic, colorless, and absorbs carbon dioxide rapidly. The following derivatives were prepared by methods described in the literature (3):

Bis-benzamide: m.p. (closed tube) 332–333°, from a large volume of 95% ethanol.

Anal. Calc'd for $C_{20}H_{24}N_2O_2$: N, 8.64. Found: N, 8.36, 8.59.

Bis-phenylthiourea: m.p. 193–194°, from absolute methanol.

Anal. Calc'd for $C_{20}H_{26}N_4S_2$: C, 62.13; H, 6.78.

Found: C, 62.30; H, 6.89.

Bis-acetamide: m.p. 297–298°, from 95% ethanol.

Anal. Calc'd for $C_{10}H_{20}N_2O_2$: N, 14.00; Found: N, 13.70.

Oxalate: m.p. 199–200°, after softening at 195°; recrystallized from water, followed by two sublimations at 0.2 mm. The oxalate was found to be unreliable as a means of estimating the diamine when ammonia was present. The two oxalates were difficult to separate by recrystallization and ammonium oxalate sublimed with the diamine oxalate. Melting points with two to three degree ranges between 195° and 224° were obtained from various preparations of the diamine where ammonia was not first removed.

Anal. Calc'd for $C_8H_{18}N_2O_4$: C, 46.59; H, 8.80.

Found: C, 46.15; H, 8.63.

With a W-6 Raney nickel catalyst (4) at an initial pressure of 3000 p.s.i. of hydrogen at 35°, yields of 62–70% of 3,4-diamino-hexane were obtained in reducing 0.03 mole of 3-nitro-4-imino-hexane. The loss of nitrogen as ammonia was 15%.

The catalytic reduction of 3,4-dinitro-3-hexene gave unsatisfactory results with both W-6 Raney nickel and platinum oxide catalysts. The reduction with W-6 catalyst was run as before, except that an initial temperature of 50° was required to start the reduction; yield of diamine, 25%; loss of nitrogen *via ammonia*, 15%. The reduction method of Kindler (5) with platinum oxide in glacial acetic acid to which concentrated sulfuric acid was added gave 23% yield of the diamine.

Reduction of 0.04 mole of 3-nitro-4-(N-phenyl)iminohexane with a platinum oxide catalyst at 45 p.s.i. of hydrogen resulted in complete hydrogenolysis as aniline was recovered in quantitative yield. Other products were not identified.

2,3-Diaminobutane. By reducing 0.05 mole of 2-nitro-3-iminobutane in the presence of 1 g. of platinum oxide in the same way as described for the higher homolog, 2,3-diaminobutane was obtained, b.p. 130–150° (6, 7). Yield, 60%; loss of nitrogen *via ammonia*, 40%.

The compound was identified as the oxalate, m.p. 237–238° (8), and as the dibenzamide, m.p. 296–297°. Morgan and Hickinbottom (6) report the dibenzamide, m.p. 236–238°.

Anal. Calc'd for $C_{18}H_{20}N_2O_2$: C, 72.95; H, 6.80; N, 9.45.

Found: C, 72.79; H, 6.59; N, 9.76.

The reduction of 2,3-dinitro-2-butene with W-6 Raney nickel catalyst under identical conditions described for the higher homolog gave a 33% yield of 2,3-diaminobutane.

Chlorination of 2,3-dinitro-2-butene. Two grams of 2,3-dinitro-2-butene, sealed with 5 ml. of carbon tetrachloride and 5 ml. of liquid chlorine in a Carius tube, was exposed to sunlight for one week. Fractionation of the reaction product gave 0.4 g. of colorless liquid, b.p. 170–176°, which did not reduce permanganate solution. A chlorine analysis indicated that substitution had taken place as well as addition to the double bond. The product was not further identified.

Anal. Calc'd for $C_4H_5Cl_3N_2O_4$: Cl, 42.30. Found: Cl, 42.74.

Attempts to chlorinate the dinitroolefin with chlorine gas and sulfuryl chloride were not successful.

Potassium salt of 1-nitro-1-methoxypropane. An ice-cold solution of 1.0 g. of 3,4-dinitro-3-hexene in 10 ml. of absolute methanol was added dropwise to a stirred solution of 5 g. of potassium hydroxide in 25 ml. of absolute methanol in an ice-bath. A slight yellow color appeared at the surface as the two solutions met but rapid stirring resulted in a white precipitate of the salt in a colorless solution. The potassium salt was filtered, after adding 15 ml. of dry acetone, and washed with methanol and dry ether. Yield, 0.85 g.; 96%. A sample was recrystallized twice from methanol to which a few drops of water were added. The compound remained white for a week over potassium hydroxide in a desiccator but slowly turned yellow.

Anal. Calc'd for $C_4H_9KNO_3$: K, 24.87; N, 8.92.

Found: K, 25.05; N, 9.39.

Using absolute ethanol as solvent, the potassium salts of 1-nitro-1-ethoxypropane and 1-nitro-1-ethoxyethane were prepared in an analogous manner. A quantitative yield of the first salt was obtained but the latter was more soluble and less stable. A sample of the potassium salt of 1-nitro-1-ethoxypropane was recrystallized from ethanol containing a few drops of water.

Anal. Calc'd for $C_5H_{10}KNO_3$: N, 8.18. Found: N, 8.2.

Molecular compound of 2,3-dinitro-2-butene and quinoline. Three grams of 2,3-dinitro-2-butene dissolved in 20 ml. of absolute ethanol was cooled to 10°. After adding 5 ml. of colorless quinoline¹ dropwise, the solution darkened and when it reached a red color it was cooled rapidly. A yellow-green solid separated which was recrystallized from 95% ethanol or chloroform and petroleum ether (b.p. 60–68°) to yield 3.0 g. of bright yellow crystals, m.p. 104–104.5°.

Anal. Calc'd for $C_{15}H_{18}N_2O_5$: C, 62.48; H, 6.29; N, 14.57.

Found: C, 62.67, 62.41; H, 6.22, 6.32; N, 14.36, 14.50.

¹ From the Skraup synthesis. Freshly distilled commercial quinoline failed to give a crystalline product.

The product was obtained only in absolute ethanol as solvent but showed a negligible amount of ethoxyl to be present by a quantitative determination. One gram of the complex was converted to 0.17 g. of 2-nitro-3-iminobutane by shaking an alcohol solution of the complex with aqueous ammonia. A few milligrams of quinoline picrate were precipitated from an alcohol solution of 0.1 g. of the complex by adding an excess of a saturated alcoholic solution of picric acid.

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SUMMARY

1. Nitroölefins exhibit aromatic character in reactions with ammonia and various amines, resembling *o*-dinitrobenzene in behavior.
2. The olefinic double bond in these compounds is inert to halogen addition.
3. With alcoholic solutions of strong alkalis, the nitroölefins give a new class of compounds, salts of nitro ethers.
4. Some catalytic reductions of nitroölefins and nitroketimines are described.

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