STUDY OF NITRATION OF N,N'-DISUBSTITUTED HYDRAZINES[1]

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Abstract

The nitration of N, N'-disubstituted hydrazines (RNH–NHR) by means of nitric acid – acetic anhydride mixtures has been found to yield, in most cases, the azo derivatives (RN = NR). For example, when R = CH_3, $(CH_3)_2(CN)C$, CH_3CO, or C_2H_5OCO, azo derivatives were formed. When R = HCO, nitrogen, carbon dioxide, and nitrogen oxides were evolved. An exception was observed with N, N'-dibenzoylhydrazine which, under the same conditions, yielded the N, N'-dinitro-N, N'-dibenzoylhydrazine.

Introduction

A recent survey of the literature has revealed the existence of four dinitroso derivatives of substituted hydrazines (3, 4, 12, 13), but the N, N'-dinitro derivatives of disubstituted hydrazines are still unknown. In the light of these facts it was of interest to investigate the formation of nitrate salts and nitro derivatives of some N, N'-disubstituted hydrazines. The substituted hydrazines prepared for the present study are listed in Table I.

TABLE I

Nitration products of disubstituted hydrazines

R-NH-NH-R (I)			R-N = N-R (III)		% HNO_3 in nitrates of I		% N in III	
R	M.p., °C.	Ref.	M.p., °C.	B.p. °C.	Calc.	Found	Calc.	Found
CH_3	168d[a]	5		102	67.7	67.0		
$(CH_3)_2(CN)C$	92–93	12	100–101		43.1	43.9	33.7	34.0
CH_3CO	140	9, 10, 11	104				24.5	24.1
C_6H_5	124	2	68					
HCO	160	8						
C_2H_5OCO	130–131	1	180d[b]	108–110 (15 mm.)				
C_6H_5CO	237–240	5, 7	118–119					

[a] *Isolated as the dihydrochloride.*
[b] *Azodicarbonamide, R = $CONH_2$.*

The N, N'-disubstituted hydrazines (I) were added to nitric acid – acetic anhydride mixture in the ratio of four moles of nitric acid per mole of hydrazo compound. By carrying out the reaction at low temperature, it was found that two of the disubstituted hydrazines used in this study (R = CH_3 and $(CH_3)_2$ C(CN), (Table I) yielded the dinitrate salt (II). As the reaction proceeded, the material went into solution, and simultaneous oxidation took place as seen from the formation of nitrous acid. When the reaction mixture was allowed to warm

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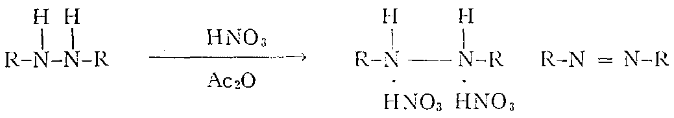
to room temperature, gases were evolved. In most cases the only materials isolated were nitrogen oxides and the azo derivatives (III) of the starting materials.

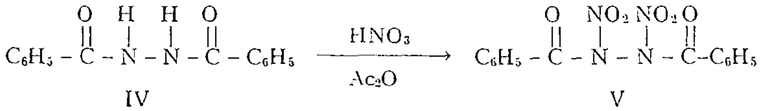


$$R{-}\overset{H}{N}{-}\overset{H}{N}{-}R \xrightarrow[\text{Ac}_2\text{O}]{\text{HNO}_3} R{-}\underset{\cdot\,HNO_3}{\overset{H}{N}}{-}\underset{\cdot\,HNO_3}{\overset{H}{N}}{-}R \qquad R{-}N=N{-}R$$

I II III

For example, N,N'-disubstituted hydrazines, where R = CH_3, C_6H_5, $(CH_3)_2C(CN)$, CH_3CO, or C_2H_5OCO, yielded the azo derivatives only, whereas N,N'-diformylhydrazine (I, R = HCO) was decomposed completely, giving gaseous products.

An exception was observed in the case of N, N'-dibenzoylhydrazine (IV) which, under the same conditions, yielded the N, N'-dinitro-N, N'-dibenzoylhydrazine (V), in admixture with its azo derivative (III, R = C_6H_5CO). This nitrated hydrazine was hydrolyzed by dilute alkalies to benzoic acid and nitrogen oxides. The ultraviolet absorption spectrum of V (Fig. 1), exhibits an absorption band at 2390Å which is characteristic of a secondary nitroamine, as was pointed out by Jones and Thorn (6).



$$C_6H_5-\overset{O}{\overset{\|}{C}}-\overset{H}{N}-\overset{H}{N}-\overset{O}{\overset{\|}{C}}-C_6H_5 \xrightarrow[\text{Ac}_2\text{O}]{\text{HNO}_3} C_6H_5-\overset{O}{\overset{\|}{C}}-\overset{NO_2}{N}-\overset{NO_2}{N}-\overset{O}{\overset{\|}{C}}-C_6H_5$$

IV V

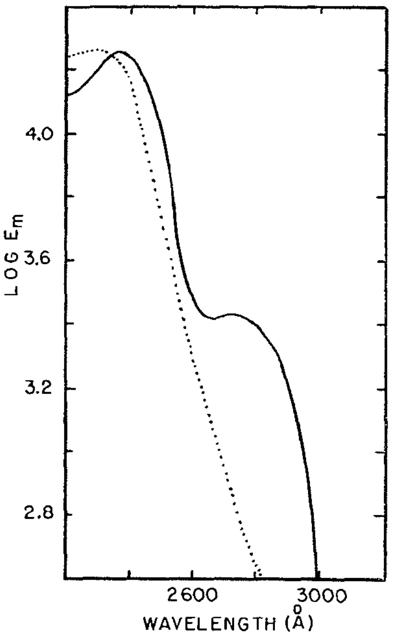


FIG. 1. *Ultraviolet absorption spectra.*
———— *N, N'-Dinitro-N, N'-dibenzoylhydrazine (ethanol).*
.... *1, 9-Diacetoxy-2, 4, 6, 8-tetranitro-2, 4, 6, 8-tetrazanonane (ethanol)* (7).

This behavior of N,N′-disubstituted hydrazines toward nitric acid – acetic anhydride mixture seems to be dominated by the basic character and reducing power of the hydrazine molecule itself, and appears to be dependent on the substituents employed.

The replacement of two hydrogens of hydrazine by benzoyl groups results in the formation of a weaker base. This effect is not surprising; it is analogous to the effect produced by the replacement of hydrogen in methyl amine by the benzoyl group, whereby a more easily nitrated secondary amine is formed.

Experimental[1]

The action of nitric acid – acetic anhydride mixture on N, N′-disubstituted hydrazines was studied at five different temperatures: -30°C., -20°C., -10°C., 0.5°C., and room temperature. Typical experimental procedures are given below.

Nitrations of N, N′-dimethylhydrazine (I, $R = CH_3$) and of N, N′-diformylhydrazine (I, $R = HCO$)

In a flask equipped to catch the gases formed in the reaction mixture were placed nitric acid (100%; 6.3 gm.; 0.1 mole) and acetic anhydride (30 ml.) previously mixed at -30°C. To this solution at -30°C. was added the dihydrochloride of I (3.3. gm.; 0.025 mole) and the mixture was allowed to warm to room temperature over a period of half an hour, during which time gases were evolved and condensed into a dry ice – acetone trap after they had been washed in alkaline solution. The reaction mixture was evaporated at 40°C. (1 mm.) and a trace of unidentified material remained in the flask. In the trap was present a low boiling liquid, b.p. 1–2°C., which was azomethane. When the reaction was held at -30°C., one could isolate from the mixture, by filtration through a sintered glass funnel, a white solid. This crystalline material was very hygroscopic, and after several washings with dry ether was identified as the dinitrate salt of N, N′-dimethylhydrazine. Calc. for $C_2H_{10}N_4O_6$: HNO_3, 67.7%. Found: HNO_3, 67.0%, after making a correction for the water content of the sample.

When N,N′-diformylhydrazine was treated in the same way as above, no nitrate salt could be obtained, and the gaseous product insoluble in alkaline solution was found to be nitrogen. After evaporation of the reaction mixture under reduced pressure, nothing remained in the flask.

Nitrations of Hydrazoisobutyronitrile (I, $R = (CH_3)_2(CN)C$) and Hydrazobenzene (I, $R = C_6H_5$)

To a solution of nitric acid (100%; 6.5 gm.; 0.1 mole), previously mixed at -30°C. with acetic anhydride (30 ml.), was added I ($R = (CH_3)_2(CN)C$) (4.15 gm.; 0.025 mole) in the solid form. During the addition the temperature was kept at -30°C., then the temperature was allowed to rise slowly. When

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[1] *All melting points were corrected against reliable standards.*

the reaction mixture was held at –25°C. a white solid separated: this was filtered out by suction through a sintered glass funnel. This material, although quite hygroscopic, after several washings with dry ether was identified as a dinitrate salt. Calc. for $C_8H_{16}N_6O_6$: HNO_3, 43.1%. Found: HNO_3, 43.9%, after making a correction for the water content of the sample.

At –20°C. the crystalline compound began to dissolve and a green color appeared. At 5°C., solution was complete. After stirring at 25°C. for half an hour, the solution was poured into 100 gm. of cracked ice and water. The solid that separated out was filtered and washed free from acid with water, m.p. 95–100°C. Recrystallization from ethanol (50%) and from ether raised the melting point to 105°C. Yield 2.5 gm. (60%). Calc. for $C_8H_{14}N_4$: N, 33.7%. Found: N, 34.0%. This compound was identified as the azo derivative by a mixed melting point determination with an authentic sample.

When attempting the nitration of hydrazobenzene in the same manner, the only material isolated was azobenzene, which formed at temperatures as low as –30°C.

Nitration of N, N′-diacetylhydrazine (I, R = CH_3CO)

To the same proportions of acids as used in the former nitration was added an equivalent quantity of N, N′-diacetylhydrazine. When the reaction temperature was kept at –30°C. for 15 min. a white powder could be isolated by drowning the reaction mixture in ice-water. If the reaction mixture was allowed to warm up, nitrogen and nitrogen oxides were evolved. This white solid material was soluble in ether, and melted at 104°C. with decomposition. A mixed melting point determination with a material prepared by the oxidation of N, N′-diacetylhydrazine with hypochlorous acid at low temperature showed no depression. Calc. for $C_4H_6N_2O_2$: N, 24.5%. Found: N, 24.1%.

Nitration of N, N′-dicarbethoxyhydrazine (I, R = C_2H_5OCO)

To a solution of nitric acid (100%; 7.0 gm.; 0.11 mole) in acetic anhydride 100 ml.) was added N, N′-dicarbethoxyhydrazine (8.8 gm.; 0.05 mole) at –30°C. The temperature of the colorless mixture was allowed to rise slowly to room temperature while the mixture was stirred. At 0°C. the solid dissolved with production of nitrous acid, and as the temperature rose the color deepened to red. After stirring at 25–30°C. for one hour, the red solution was poured into ice-water (300 gm.). A red oil separated out, ethyl azodicarboxylate, b.p. 108–110°C. (15 mm.). By treatment of this ester with ammonia, azodicarbonamide, a solid, was obtained, m.p. 180°C. with decomposition. Yield, 4.0 gm. (69%).

Nitration of N, N′-dibenzoylhydrazine (I, R = C_6H_5CO)

The same proportions as in the above described nitrations were used; the precipitated solid in ice-water was extracted with ether. The ethereal solution was washed thoroughly with dilute sodium hydroxide to get rid of the unchanged starting material, dried over anhydrous sodium sulphate, and evaporated *in vacuo*. A white crystalline solid remained, m.p. 90–95°C. Recrystallizations from ethanol raised the melting point to 101.5°C. Yield, 2.5 gm. (31%). This compound gave a positive Franchimont test for nitramino groups and reacted with concentrated sulphuric acid, giving off nitrogen oxides. Calc. for $C_{14}H_{10}O_6N_4$: C, 50.9; H, 3.03; N, 16.9%. Found: C, 51.3; H, 3.15; N, 16.0%. From the mother liquor, another compound was obtained as a white powder which, after recrystallization from hot water, has a melting point of 118–119°C. This compound was shown by a mixed melting point determination with an authentic sample to be azodibenzoyl.

Hydrolysis of N, N'-dinitro-N, N'-dibenzoylhydrazine (V)

This compound (0.478 gm.), melting at 101.5°C., was boiled overnight in a solution of 1 gm. of sodium hydroxide in 50 ml. of ethanol (50%). The solution was evaporated to dryness under reduced pressure and the residue dissolved in water (20 ml.). The addition of an excess of concentrated hydrochloric acid to the solution precipitated a solid while nitrogen oxides (mainly NO_2) were evolved. The mixture was extracted with ether. The ethereal extract was washed with water, dried over anhydrous sodium sulphate and evaporated in a weighed platinum dish, leaving 0.375 gm. of solid melting at 120–121°C. After recrystallization from water this compound melted at 122°C. and was identified as benzoic acid. The yield of pure substance was 0.330 gm. or 94% if it is assumed that two moles of benzoic acid were produced from one mole of the material melting at 101.5°C.

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