Preparation of 2,4,6-Trinitrazaheptane

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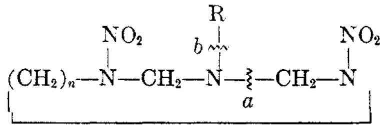
Chapman, Owston, and Woodcock[1] found that in the nitrolysis of aminomethylnitramines, I,

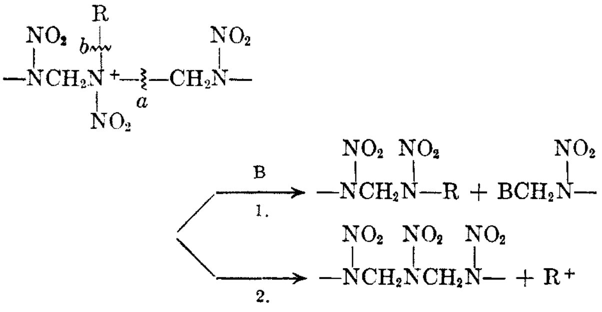


I

$R = CH_3, C_2H_5, (CH_3)_2CH, CH_3(CH_2)_3, \overline{CH_2(CH_2)_4CH}$
$n = 1, 2$

cleavage always occurred at *a* when the nitrolyzing medium was acetic anhydride and nitric acid. When ammonium nitrate was added to the acetic anhydride-nitric acid medium cleavage occurred at *b* when R = isopropyl or cyclohexyl and at *a* when R = methyl and butyl. With R = ethyl a little cleavage was detected at *b* but most of it occurred at *a*. The authors did not offer any explanation for the change in cleavage site, in the case of R = isopropyl and cyclohexyl when ammonium nitrate was added to the system.

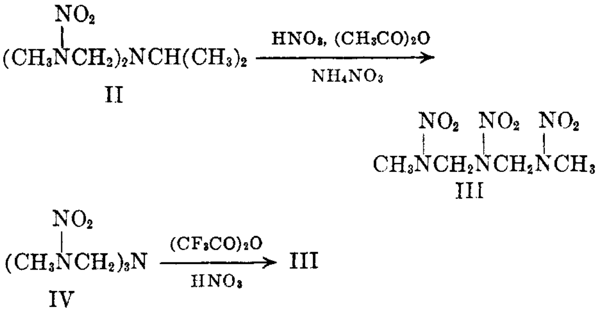
By analogy with the mechanism expressed for the von Braun reaction,[2] the initial step in the nitrolysis reaction would be the formation of a complex between the amine and a nitronium ion. The next step, (Path 1), when using only acetic anhydride and nitric acid, would be the attack of a nucleophile, B, on one of the adjacent methylenes to break the carbon-nitrogen bond. The methylenes, because of the adjacent electron withdrawing nitramine groups,[3] would be attacked in preference to the alkyl R groups. The addition of ammonium nitrate to the reaction medium increases the ionizing power of the system sufficiently so that the carbon-nitrogen bond of the secondary alkyl group in the nitronium ion-amine complex is ionized partially or completely resulting in preferential cleavage at *b* (Path 2).



$B = NO_3^-, CH_3CO_2^-, CH_3CO_2H$

Lamberton[4] suggests that nitrolysis reactions in general may proceed by Path 2. However, it appears that this mechanism is operative only where R may readily form a carbonium ion.

When nitrolysis reactions were conducted with acyclic systems the same effects were noted as with the cyclic systems. The nitrolysis of uncharacterized bis-(*N*-nitro-*N*-methylaminomethyl)-2-propylamine (II) with nitric acid, acetic anhydride, and ammonium nitrate gave 2,4,6-trinitrazaheptane (III). Here the reaction proceeds according to Path 2.



$$\underset{\text{II}}{(CH_3\overset{NO_2}{N}CH_2)_2NCH(CH_3)_2} \xrightarrow[NH_4NO_3]{HNO_3,\ (CH_3CO)_2O} \underset{\text{III}}{CH_3\overset{NO_2}{N}CH_2\overset{NO_2}{N}CH_2\overset{NO_2}{N}CH_3}$$

$$\underset{\text{IV}}{(CH_3\overset{NO_2}{N}CH_2)_3N} \xrightarrow[HNO_3]{(CF_3CO)_2O} \text{III}$$

The nitrolysis of tris(*N*-nitro-*N*-methylaminomethyl)amine (IV) with nitric acid and trifluoroacetic anhydride also gave III. As all three groups on the central amino nitrogen are the same, the nitrolysis product would be the same regardless of whether the reaction went by Path 1 or 2. However, in consideration of the reactions of I with acetic anhydride and nitric acid, compound IV probably reacts by Path 1 under the conditions used. Acetic anhydride and nitric acid did not yield III from IV. The success of the trifluoroacetic anhydride-nitric acid medium may have been due to the high concentration of dinitrogen pentoxide that can be achieved from these two reagents.[5]

2,4,6-Trinitrazaheptane is a white crystalline compound which melts to a clear liquid, without visible decomposition, at 168–169°. The cyclic analog, 1,3,5-trinitrazacycloheptane is reported by Myers and Wright to melt with decomposition at 165–165.5°.[6] No immediate explanation accounts for this difference in thermal stability between the two compounds.

It was not possible to nitrolyze a group from the central amino nitrogen of tris[*N*-nitro-*N*-(β-cyanoethyl)aminomethyl]amine (V). The failure of V to nitrolyze may be due to the lesser basicity of V compared with IV, thereby preventing formation of sufficient nitronium ion-amine complex to allow the reaction to proceed in the desired manner.

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EXPERIMENTAL

Preparation of 2,4,6-trinitrazaheptane (III) *from* IV. Six and three-tenths grams (0.10 mole) of 99% nitric acid and 31.5 g. (0.15 mole) of trifluoroacetic anhydride were mixed at −10°, then allowed to warm to 10°. Two and eight-tenths grams (0.010 mole) of tris(*N*-nitro-*N*-methylaminomethyl)amine[7] (IV), m.p. 116–117°, was added portionwise with stirring and cooling. The temperature was maintained at 10°. After addition was complete the temperature was raised to 20° for 5 min. The volatile materials were then removed under reduced pressure and the viscous residue treated with ether. One gram of solid, m.p. 150–160°, was filtered. This was recrystallized from butanone to give 0.5 g. (21% yield) of 2,4,6-trinitrazaheptane, m.p. 166–168°. Another recrystallization from butanone raised the melting point to 168–169°. The compound melts to a clear liquid with no apparent decomposition.

Anal. Calcd. for $C_4H_{10}N_6O_6$: C, 20.17; H, 4.23; N, 35.29; mol. wt. 238. Found: C, 20.26; H, 4.21; N, 35.56; mol. wt. 246 (Rast).

The infrared spectrum showed nitramino absorption at 6.40 μ (broad), 6.55 μ, and 7.80 μ, and a strong band at 13.07 μ.[8]

Preparation of 2,4,6-trinitrazaheptane (III) *from* II. Two and one-half grams (0.008 mole) of crude bis(*N*-nitro-*N*-methylaminomethyl)(2-propyl)amine (II) was dissolved in 20 ml. of acetic anhydride and heated to 55°. To this was added a solution of 3.4 g. (0.042 mole) of ammonium nitrate in 4.6 g. (0.073 mole) of 99% nitric acid. After 15 min. at 55° the solution was poured into 500 ml. of ice and water. One-half gram of solid, m.p. 110–120°, separated. This was recrystallized from chloroform to give 0.3 g. of material, m.p. 155–160°. Recrystallization from butanone gave 0.1 g. of material, m.p. 166–168°. The infrared spectrum of this material was identical with the spectrum of III prepared in the previous experiment.

Anal. Calcd. for $C_4H_{10}N_6O_6$: C, 20.17; H, 4.23; N, 35.29. Found: C, 20.43; H, 4.67; N, 36.02.

Treatment of IV with acetic anhydride and nitric acid. Three and six-tenths grams (0.013 mole) of IV was added to a solution of 8.8 ml. (0.21 mole) of 99% nitric acid and 24 ml. (0.26 mole) of acetic anhydride at 0°. After addition was complete, the solution was warmed to 30° and maintained there 25 min. The slightly yellow solution was poured into 250 ml. of ice and water. No insoluble material separated.

Treatment of tris-[N-nitro-N-(β-cyanoethyl)aminomethyl]-amine (V) with trifluoroacetic anhydride and nitric acid. Six and three-tenths grams (0.10 mole) of 99% nitric acid was added to 31.5 g. (0.15 mole) of trifluoroacetic anhydride at 0°. The solution was warmed to 10°. Four grams (0.010 mole) of V was added, with stirring, to the solution. There was no noticeable temperature rise. The temperature was raised to 15° where the solid dissolved. The solution was then poured into 250 ml. of ice and water. About 2 g. of oil separated. The oil was dissolved in 25 ml. of methylene chloride and 0.025 g. of solid separated, m.p. 135–138°. A mixed melting point with a sample of V gave no depression; hence, the solid was starting material. The oily material, soluble in methylene chloride, was not investigated but probably was not the desired 1,9-dicyano-3,5,7-trinitrazanonane, as this compound should be a relatively high melting, insoluble material as judged by the character of other 2,4,6-trinitrazaheptane derivatives.

Preparation of bis(N-nitro-N-Methylaminomethyl)(2-propyl)amine (II). Two grams (0.026 mole) of methylnitramine was added to 2.1 g. (0.026 mole) of 37% formaldehyde solution. This solution was cooled to 0° and 0.77 g. (0.013 mole) of isopropylamine was added. After a few minutes an oil separated and settled to the bottom. The reaction mixture was warmed to 25°. After 30 min. the water was evaporated under reduced pressure to leave 2.5 g. of material, m.p. 27–30°. The material was not characterized but was assumed to be II on the basis of the analogous preparation of bis(*N*-nitro-*N*-methylaminomethyl)methylamine.[9]

Preparation of tris[N-nitro-N-(β-cyanoethyl)aminomethyl]-amine (V). Eleven and one-half grams (0.10 mole) of β-cyanoethylnitramine was dissolved in 8.33 g. of 37% aqueous formaldehyde solution and chilled to 0°. Then 2.02 g. (0.33 mole) of 28% aqueous ammonia was added to the solution. The solution was poured into a shallow dish and left uncovered at room temperature until the water had evaporated. There was 12.9 g. (97% yield) of white solid remaining, m.p. 100–120°. Two recrystallizations from acetonitrile gave 7 g. of V, m.p. 136–138°.

Anal. Calcd. for $C_{12}H_{18}N_{10}O_6$: C, 36.18; H, 4.55; N, 35.17; mol. wt. 398. Found: C, 36.03; H, 4.51; N, 35.11, 35.30; mol. wt. 354 (cryoscopic method using ethylene carbonate).

The low value for the experimentally determined molecular weight may be due to partial dissociation of the compound. After V was kept in a closed bottle for any length of time, the odor of formaldehyde was evident when the bottle was opened. Also the melting point always dropped when the material was stored for several months.

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Orientation in the Nitration of 2′,5′-Dimethoxyacetophenone[1]

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The nitration of 2′,5′-dimethoxyacetophenone has been studied under a variety of conditions and found to lead to the formation of a mixture of the 4′- and 6′-nitro isomers, with the 6′-nitro isomer accounting for approximately 50 to 80% of the product, depending on the conditions. Extensive substitution in the 6′ position has previously been reported for several compounds of similar structure;[4] this behavior has been considered to be anomalous.[4a,b] The high proportion of substitution in the 6′ position is consistent with the predicted relative stabilities of the transition states. Only in the case of substitution in this position is the tran-

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(2) This paper is based partly on a thesis submitted by C. R. Hamel in partial fulfillment of the requirements for the degree of Master of Science at Clarkson College of Technology, January 1959.

(3) Participant, National Science Foundation Research Participation Program for High School Science Teachers, Clarkson College of Technology, June–August, 1959.

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