Its 2,4-dinitrophenylhydrazone could be prepared by the usual method, yielding red needles, m.p. 271–272°.

Anal. Calcd. for $C_{15}H_{11}O_5N_5$: C, 52.78; H, 3.22. Found: C, 52.87; H, 3.54.

Diazomethane Reaction of (a) 3-Hydroxymethyleneoxindole and (b) 1-Methyl-3-hydroxymethyleneoxindole.—(a) 4.0 g. of 3-hydroxymethyleneoxindole was added in small portions to 100 ml. of an ether solution of excess diazomethene with shaking. Evolution of nitrogen started immediately, and the mixture was left standing for four hours. The separated solid (m.p. 179–180°) was filtered and shaken with warm chloroform for a few minutes. The residue (m.p. 220–245°) obtained from the suspension after filtration was crystallized several times from 95% ethanol, yielding 0.5 g. of 2-methoxy-3-formylindole, m.p. 252–253°; 0.3 g. more of product could be obtained from the mother liquors, resulting in a total 18% yield.

Anal. Calcd. for $C_{10}H_9O_2N$: C, 68.6; H, 5.14; N, 8.00. Found: C, 68.7; H, 5.34; N, 7.95.

Its 2,4-dinitrophenylhydrazone was prepared readily and on recrystallization from a large volume of ethyl acetate, glistening black needles, m.p. 305–306°, were obtained.

Anal. Calcd. for $C_{16}H_{13}O_5N_5$: C, 54.1; H, 3.7. Found: C, 54.07; H, 3.74.

The filtrate from the above chloroform solution was concentrated under vacuum and the remaining residue crystallized from 95% ethanol; 0.4 g. (10%) of pure 3-methoxymethylene oxindole, m.p. 191–192° (literature[24] m.p. 189°), was obtained. The 2,4-dinitrophenylhydrazone formation of this compound produced the derivative of its 3-hydroxymethylene precursor, m.p. 271–272° (*vide supra*).

Modification of the diazomethane reaction by varying concentration or solvent never greatly improved the process. The products 2-methoxy-3-formylindole and 3-methoxymethyleneoxindole could be obtained in yields of 10–20% and 10–40%, respectively.

(b) A similar procedure to the above was used for the conversion of 1-methyl-3-hydroxymethyleneoxindole to its two methyl derivatives. As high as 23% of 1-methyl-2-methoxy-3-formylindole, colorless crystals, m.p. 138°, could be isolated.

Anal. Calcd. for $C_{11}H_{11}O_2N$: C, 69.82; H, 5.86; N, 7.40. Found: C, 69.83, 69.74; H, 6.14, 6.11; N, 7.44, 7.48.

This could be converted to its 2,4-dinitrophenylhydrazone which on recrystallization from a large volume of ethyl acetate gave black needles, m.p. 283–284°.

Anal. Calcd. for $C_{17}H_{15}O_5N_5$: C, 55.28; H, 4.07; N, 18.95. Found: C, 55.18; H, 3.89; N, 19.00.

The yield of 1-methyl-3-methoxymethyleneoxindole, m.p. 134–135°, proved never to be much higher than 10%. The compound was shown to be identical by m.p., mixed m.p. and infrared spectrum with the O-alkylation product of 1-methyl-3-hydroxymethyleneoxindole by methyl iodide.[3,10]

Hydrolysis of 1-Methyl-2-methoxy-3-formylindole.—The indole (75 mg.) was dissolved in 10 ml. of 95% slightly warm ethanol and 200 mg. of sodium hydroxide was added thereto with shaking, and water was poured into it until a homogeneous solution was achieved. After standing at room temperature for 50 hours, the solution was added to water and extracted with ether. The aqueous fraction gave a precipitate on acidification with hydrochloric acid, which on filtering, washing with small amounts of ether and alcohol, and drying yielded 50 mg. of a white solid, m.p. 189–190°. This compound gave no depression of melting point on admixture with authentic 1-methyl-3-hydroxymethyleneoxindole, m.p. 190–191°, and also showed an identical infrared spectrum therewith. The ether fraction yielded 15 mg. of a compound, m.p. 120–121°, after washing with water, drying and evaporation of solvent. The latter proved to be crude starting material by inspection of its infrared spectrum and formation of its 2,4-dinitrophenylhydrazone.

AMES, IOWA

[CONTRIBUTION FROM THE CHEMISTRY DIVISION, RESEARCH DEPARTMENT, U. S. NAVAL ORDNANCE TEST STATION]

Tetramethylenetrinitramine Trifluoroacetates

BY RUSSELL REED, JR.

RECEIVED JULY 8, 1955

1-Trifluoroacetoxy-2,4,6-trinitro-2,4,6-triazaheptane (III), 1-acetoxy-7-trifluoroacetoxy-2,4,6-trinitro-2,4,6-triazaheptane (IV) and 1,7-bis-trifluoroacetoxy-2,4,6-trinitro-2,4,6-triazaheptane (V) were obtained from the corresponding acetates by treatment with trifluoroacetic acid. V was also prepared from hexamine, nitric acid and trifluoroacetic anhydride. These trifluoroacetate esters reacted readily with alcohols, amines, water, nitric acid, acetic acid and hydrogen chloride as follows: methanol and III, IV or V gave the corresponding methylol derivatives; excess benzylamine degraded III, IV or V to di-(benzylammonium)-methylenedinitramine; aqueous acetone and III, IV or V yielded the theoretical amount of trifluoroacetic acid; nitric acid produced the corresponding nitrate esters; acetic acid gave the corresponding acetates; hydrogen chloride cleaved these trifluoroacetates with the formation of chlorides.

While the acetates 1-acetoxy-2,4,6-trinitro-2,4,6-triazaheptane, $CH_3[N(NO_2)CH_2]_3OCOCH_3$ (I),[1,2] and 1,7-diacetoxy-2,4,6-trinitro-2,4,6-triazaheptane, $CH_3COO[CH_2N(NO_2)]_3CH_2OCOCH_3$ (II),[3-5] are known, the corresponding trifluoroacetates have not been investigated. The acetates are reactive toward both acids and bases, and it was believed that the trifluoroacetates would be even more reactive and thus of value in the synthesis of linear nitramines. These trifluoroacetates were readily prepared by dissolving the acetates in anhydrous trifluoroacetic acid (Table I). Although a solution of the monoacetate I in trifluoroacetic acid at 25° deposited crystals of the ester $CH_3[N(NO_2)CH_2]_3OCOCF_3$ (III), the diacetate II gave the mixed ester $CF_3COO[CH_2N(NO_2)]_3CH_2OCO\cdot CH_3$ (IV). However, at 70° both IV and II gave the bis-trifluoroacetate, $CF_3COO[CH_2N(NO_2)]_3CH_2OCOCF_3$ (V).

The bis-trifluoroacetate V was also obtained in good yield by the nitrolysis of hexamine in a mixture of trifluoroacetic acid, trifluoroacetic anhydride and nitric acid at 0°. This reaction was very rapid while the corresponding reaction employing acetic acid–acetic anhydride was much slower and gave at 0° mainly 1,5-endomethylene-3,7-dinitro-1,3,5,7-tetraazacycloöctane (DPT).[6] Higher tem-

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[1] F. Chapman, P. G. Owston and D. Woodcock, *J. Chem. Soc.*, 1647 (1949).

[2] R. N. Jones and G. D. Thorn, *Can. J. Res.*, **B27**, 828 (1949).

[3] W. E. Bachmann and J. C. Sheehan, THIS JOURNAL, **71**, 1842 (1949).

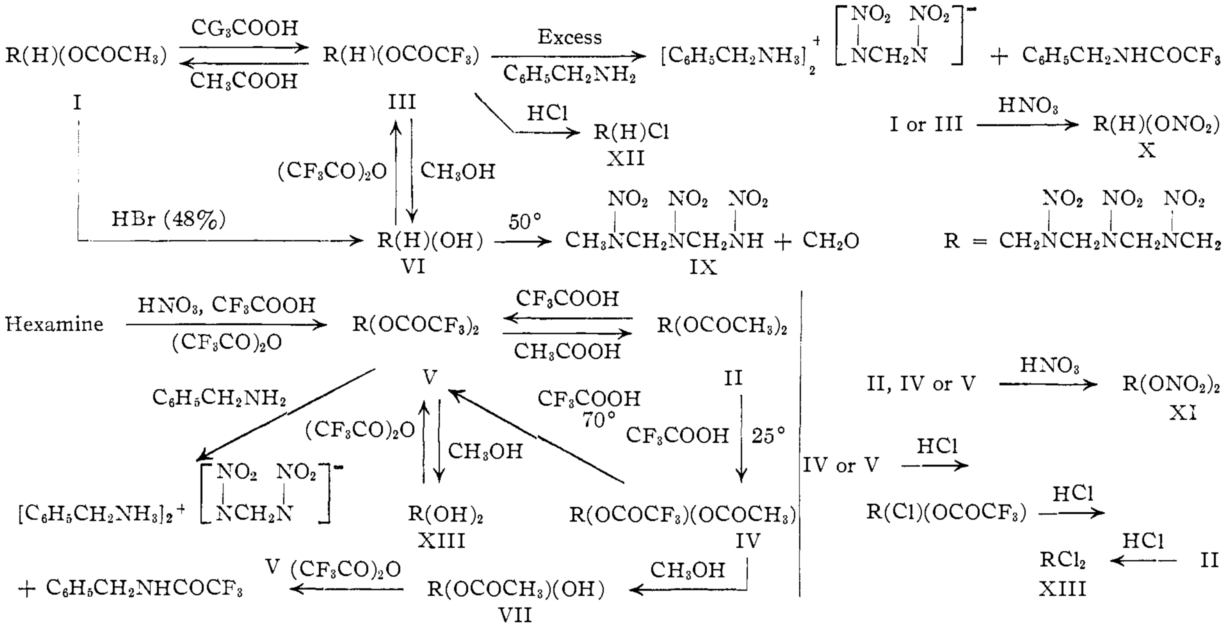
[4] W. J. Chute, A. F. MacKay, R. H. Meen, G. S. Meyers and G. F Wright, *Can. J. Res.*, **B27**, 503 (1949).

[5] W. E. Bachmann, W. J. Horton, E. L. Jenner, N. W. MacNaughton and L. B. Scott, THIS JOURNAL, **73**, 2772 (1951).

[6] W. S. Chute, D. C. Downing, A. F. McKay, G. S. Myers and G. F Wright, *Can. J. Res.*, **B27**, 218 (1949).

TABLE I

THE REACTIONS OF THE TETRAMETHYLENETRINITRAMINE TRIFLUOROACETATES

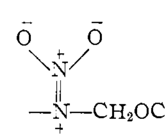


peratures and longer reaction times were necessary to produce II. Thus, the trifluoroacetic anhydride–nitric acid mixture is a very powerful nitrolyzing medium,[7] much more so than acetic anhydride–nitric acid.

The trifluoroacetates III, IV and V reacted rapidly with water, alcohols, amines and nitric acid, and more slowly with acetic acid and hydrogen chloride. Their acetone solutions could be easily titrated with 0.1 *N* sodium hydroxide. Potentiometric titration gave two inflection points; the first inflection point at *p*H 4.5 corresponded to the titration of trifluoroacetic acid and the second at *p*H 11.5 to the titration of a weak acid. With each ester three equivalents of hydroxyl ion were consumed between the first and second inflection points. This may be related to the titration of the three nitramino groups present in each ester. No nitramines were isolable from the titrated solutions nor was nitrite ion found to be present.

Treatment of III, IV and V with methanol or ethanol produced the methylol nitramines $R(H)(OH)$ (VI), $R(OH)OCOCH_3)$ (VII) and $R(OH)_2$ (VIII), respectively, as well as methyl or ethyl trifluoroacetate. The dimethylol compound VIII was unstable and lost formaldehyde in solvents at 25°; the monomethylol compound VI, somewhat more stable, was demethylolated on warming to 50° giving 1,3,5-trinitro-1,3,5-triazahexane (IX). These methylol compounds gave reasonable combustion analyses, and each showed a hydroxyl band at 2.8 μ. Trifluoroacetic anhydride converted them to the parent trifluoroacetates, except that $R(OCOCH_3)(OH)$ (VII) gave V. $R(H)(OH)$ (VI) was also formed by the reaction of I with warm hydrobromic acid (48%).

Excess benzylamine rapidly converted III, IV or V to di-(benzylammonium)-methylenedinitramine and N-benzyltrifluoroacetamide; in the case of the mixed ester IV, N-benzylacetamide was also found among the products. In contrast the diacetate II was slowly decomposed by excess benzylamine; only benzylammonium acetate and the cyclic trimer of benzylamine and formaldehyde, 1,3,5-tribenzyl-1,3,5-triazacyclohexane,[8,9] were isolated, indicating that the reaction occurred *via* alkyl–oxygen cleavage, with the subsequent degradation of the methylene nitramine chain. The greater reactivity of the trifluoroacetates as compared to the acetates, as well as their acyl–oxygen cleavage, may be explained by the strongly electron-attracting nature of the trifluoromethyl group which facilitates the attack by nucleophilic reagents upon the carbonyl carbon of the ester. However, in the case of the acetate II, benzylamine attacked the α-carbon rather than the acyl carbon indicating that the combined inductive effects of the acetoxy and nitramino groups play an important role. The inductive effect of the latter results from the contribution of the form



Structures of this type have been criticized by Llewellyn and Whitmore[10] because they violate Pauling's adjacent charge rule. But since dimethylnitramine has been shown to be planar in both the crystalline[11a] and the vapor state[11b] and to possess an N–N bond distance of only 1.26 Å. in the crystal lattice (compared to 1.40 Å. in substituted hydrazines) it is strongly indicated that the form makes an important contribution to the resonance

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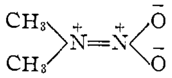
[7] J. H. Robson, THIS JOURNAL, **77**, 107 (1955).

[8] H. Hock, German Patent 139,394.

[9] A. Henry, *Bull. acad. roy. Belg.*, **29**, 23 (1895).

[10] F. J. Llewellyn and F. E. Whitmore, *J. Chem. Soc.*, 1316 (1948).

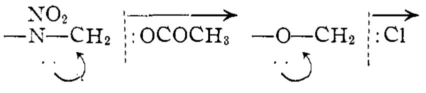
[11] (a) W. Costain and E. G. Cox, *Nature*, **160**, 826 (1947); (b) P. W. Allen and L. E. Sutton, *Acta Cryst.*, **3**, 53 (1950).



hybrid. Although a weak base such as aniline did not react with the diacetate II, it readily degraded the bis-trifluoroacetate V; the only products isolated were mixtures containing nitroanilines condensed with formaldehyde.

Nitric acid rapidly nitrolyzed II, IV and V to the corresponding nitrate esters, $R(H)(ONO_2)$, (NSX[1], X) and $R(ONO_2)_2$ (ATX[4], XI). Refluxing acetic acid converted the trifluoroacetates to the corresponding acetates. Hydrogen chloride and I or III gave the corresponding chloro compound OFX[2] (XII); the bis-ester V produced a mixture of the dichloro compound GSX[2] (XIII) and the chloro-trifluoroacetate XIV. The mixed ester and hydrogen chloride gave a mixture containing only XIII and the XIV, thus demonstrating that hydrogen chloride cleaved the acetoxy group more readily, possibly because the acetate ester is the more easily protonated. It is likely that the attack of chloride ion as well as the loss of the acetoxy moiety would be facilitated by protonation of the ester.

The ease with which these nitramine esters undergo alkyl–oxygen fission under acid conditions presumably is due to the +M[12] effect of the amino nitrogen in the nitramino group which aids in the separation of the leaving group and stabilizes the resulting carbonium ion intermediate. The acetoxy group in an N-(acetoxymethyl) amide of a sterically hindered acid might be expected to react similarly to the acetoxy group in the nitramine esters I and II. The acyl and nitro group both possess —I and —T effects; however, the amido nitrogen may still exert a +M effect to assist in the departure of the acetoxy group. Unfortunately the cleavage of these amides has not been investigated sufficiently to test this comparison. The α-chloroethers,[13] which have been studied in considerable detail, are also analogous since the oxygen atom exercises a +M effect thus



Experimental

All melting points are corrected.

1. **Preparation of the Trifluoroacetates. 1-Trifluoroacetoxy-2,4,6-trinitro-2,4,6-triazaheptane (III).**—To 100 ml. (1.34 moles) of trifluoroacetic acid was added 15.0 g. (0.0506 mole) of 1-acetoxy-2,4,6-trinitro-2,4,6-triazaheptane (I) (m.p. 154–155°). After standing 4 hr., there was obtained 12.8 g. (72%) of III as colorless crystals which partly melted at 123–124°, resolidified at 128–130°, and remelted at 136–137°. Recrystallization from ethylene chloride gave 10.1 g. of III, m.p. 136–137°. Similar yields of III were obtained when a solution of I in trifluoroacetic acid refluxed for 15 min.

Anal. Calcd. for $C_6H_9O_8N_6F_3$: C, 20.58; H, 2.59; N, 24.00. Found: C, 20.51, 20.67; H, 2.83, 2.35; N, 23.72.

III and 99% nitric acid readily gave XII,[14] m.p. 145–146° after two recrystallizations from 2-nitropropane.

A solution of 0.20 g. (5.7×10^{-4} mole) of III in 1 ml. of glacial acetic acid was refluxed 15 min. On cooling, 0.15 g. of I, m.p. 153.5–155°, crystallized. A mixed melting point with an authentic sample of I showed no depression; the infrared spectra were identical.

1-Acetoxy-7-trifluoroacetoxy-2,4,6-trinitro-2,4,6-triazaheptane. (IV).—To 150 ml. (2.02 moles) of trifluoroacetic acid was added 26.0 g. (0.0734 mole) of 1,7-diacetoxy-2,4,6-trinitro-2,4,6-triazaheptane (II), m.p. 154–155°. After standing 3 hr. the solution had deposited 25.2 g. (84%) of crystalline IV, m.p. 145.5–147.0°. Four recrystallizations from ethylene chloride raised the melting point to 151–152°. A mixed melting point with V (1:1) melted at 120–130°. The infrared spectrum possessed an acetate carbonyl peak at 5.67 μ and a trifluoroacetate carbonyl peak at 5.57 μ.

Anal. Calcd. for $C_8H_{11}O_{10}N_6F_3$: C, 23.54; H, 2.72; N, 20.59. Found: C, 23.42; H, 2.54; N, 20.53, 20.18.

IV and 99% nitric acid produced the dinitroxy compound XIII, m.p. 154–155° (lit. reports[4] 153–154°).

1,7-Bis-trifluoroacetoxy-2,4,6-trinitro-2,4,6-triazaheptane (V) from the Diacetate II.—To 250 ml. (3.35 moles) of boiling trifluoroacetic acid (b.p. 70°, 710 mm.) was added 40.1 g. (0.113 mole) of II. The clear solution was refluxed for 10 min. and then let stand 1 hr. at room temperature and 1 hr. at −5°. Filtration of the crystalline mass gave 44.0 g. (84%), m.p. 147.5–149°, of V. Three crystallizations from ethylene chloride produced 32.7 g. of V, m.p. 149.5–150.5°.

Anal. Calcd. for $C_8H_8O_{10}N_6F_6$: C, 20.79; H, 1.74; N, 18.19. Found: C, 20.61; H, 1.53; N, 18.01.

V from Hexamine.—To a stirred solution of 13.3 g. (0.095 mole) of hexamine in 50 ml. (0.67 mole) of trifluoroacetic acid maintained at 10–15°, was added over the course of 30 min., a solution of 18.0 ml. (0.43 mole) of 99.6% nitric acid in 80 ml. (0.58 mole) of trifluoroacetic anhydride. The addition of the first drop of the nitric acid solution caused a permanent crystalline precipitate. After standing at room temperature for 3 hr., the mixture was filtered and washed with three 100-ml. portions of ether to give 20.4 g. of colorless crystalline V, m.p. 125–132°. Dilution of the filtrate with the wash-ether yielded an additional 4.5 g. of V, m.p. 125–132°. The total yield (based on hexamine) was 57%. Four recrystallizations from ethylene chloride raised the melting point to 148–149°, and resulted in 9.7 g. of V. A mixed melting point with V derived from II showed no depression; infrared spectra were also identical.

II. **Reactions of the Trifluoroacetates. The Titration of III, IV and V with 0.1 *N* Sodium Hydroxide.**—Solutions of 1.000 millimole of III, IV and V in 50 ml. of acetone were titrated with aqueous 0.1038 *N* sodium hydroxide (carbonate free) using a Beckman *p*H meter (Model H-2). Plotting the volume of base against the *p*H gave two inflection points with each ester, corresponding to the following neutral equivalents: III, 362 found (350 calcd. for 1 equiv. per mole), 94 found (88 calcd. for 4 equiv. per mole); IV, 249 found (231 calcd. for 2 equiv. per mole), 96 found (92 calcd. for 5 equiv. per mole); and II, 384 found (408 calcd. for 1 equiv. per mole), 95 found (102 calcd. for 4 equiv. per mole). The titrated solutions gave a negative test for nitrite; evaporation of the solutions, followed by acidification and ether extraction, gave no nitramines.

Methanolyses of the Trifluoroacetate Esters. A. 2,4,6-Trinitro-2,4,6-triazaheptanol-1 (VI).—A solution of 3.85 g. (0.0110 mole) of III in 90 ml. of methanol, after standing 3 to 4 min., deposited 2.04 g. (73%) of VI as crystals, m.p. 138–140°. Recrystallization from 50% aqueous acetone produced 0.45 g. of VI, m.p. 141–142°. The infrared spectrum contained a peak at 2.80 μ (OH) but none in the carbonyl region. VI gassed vigorously and dissolved on treatment with dilute base. Acetone solutions of VI were acidic to litmus; the titration of VI with 0.1 *N* standard base gave an equivalent weight of 96.4, corresponding to 2.64 equiv. of base per mole of VI.

Anal. Calcd. for $C_4H_{10}N_6O_7$: C, 18.90; H, 3.97; N, 33.07. Found: C, 18.75; H, 3.60; N, 33.49.

Treatment of VI with trifluoroacetic anhydride gave a 60% yield of III, m.p. 136–137° (after two recrystallizations from ethylene chloride). III was identified by mixed melting point and by comparison of its X-ray powder pattern with that of an authentic sample.

B. **1-Acetoxy-2,4,6-trinitro-2,4,6-triazaheptanol-7 (VII).**—The treatment of IV with methanol (as described above

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(12) A. E. Remick, "Electronic Interpretations of Organic Chemistry," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1947, p. 58.

(13) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p. 333.

(14) The authors of ref. 1 did not purify XII.

in A) gave a 51% yield of VII, m.p. 130° dec. The infrared spectrum contained a peak at 2.80 (hydroxyl) and 5.67 μ (acetate carbonyl).

Anal. Calcd. for $C_6H_{12}N_6O_9$: C, 23.08; H, 3.88; N, 26.92. Found: C, 23.42; H, 3.60; N, 26.57.

VII and cold trifluoroacetic anhydride produced a 67% yield of IV, m.p. 150–152°.

C. 2,4,6-Trinitro-2,4,6-triazaheptanediol-1,7 (VIII).—V and methanol gave a 67% yield of VIII, m.p. 145–147° (after one recrystallization from acetone). The infrared spectrum of VIII possessed a peak at 2.81 μ (hydroxy) but none in the carbonyl region.

Anal. Calcd. for $C_4H_{10}N_6O_8$: C, 17.78; H, 3.73; N, 31.11. Found: C, 17.53; H, 3.57; N, 30.84.

VIII and trifluoroacetic anhydride gave a 70% yield of V, m.p. 149–150°.

Formation of VI from I and Hydrobromic Acid.—To 60 ml. of 48% hydrobromic acid was added 20.0 g. (0.068 mole) of I. After stirring at 55° for 10 min., a yellow-orange solution was produced which was filtered to remove a small amount of insoluble material, and then poured onto ice giving 14.1 g. (81%) of VI, which was dissolved in acetone and the solution diluted with two volumes of ether to yield 7.5 g. (40%) of VIII, m.p. 143.7–145°. A mixed melting point with VI obtained from III showed no depression; infrared spectra were also identical.

Anal. Calcd. for $C_4H_{10}N_6O_7$: C, 18.90; H, 3.97; N, 33.07. Found: C, 18.98; H, 3.67; N, 32.79.

Demethylolation of VI to 1,3,5-Trinitro-1,3,5-triazahexane (IX).—The crystallization of VI from boiling ethylene chloride produced impure IX, m.p. 125–126°, soluble, with gas evolution in base. Infrared spectrum showed a band at 3.0–3.2 μ (NH) but none at 2.80 μ.

Anal. Calcd. for $C_3H_8N_6O_6$: C, 16.07; H, 3.60; N, 37.50. Found: C, 16.18, 15.83; H, 3.29, 3.20; N, 37.31.

The Reaction of III, IV and V with Benzylamine.—To each of separate solutions of 0.0100 mole of III, IV and V in 75 ml. of dioxane was added 6.42 g. (0.060 mole) of benzylamine. Evaporation of the dioxane at 25° (reduced pressure) gave a crystalline solid in each case. The solids were extracted with three 25-ml. portions of ether and the insoluble residues dissolved in 3 ml. of water; the addition of 10 ml. of methanol to each of the aqueous solutions caused the crystallization of di-(benzylammonium)-methylenedinitramine; 1.40 g. (40%) from III, 1.05 g. (30%) from IV, and 1.29 g. (37%) from V. The ethereal solutions from III and V yielded 1.28 g. (63%) and 2.84 g. (70%), respectively, of N-benzyltrifluoroacetamide, m.p. 73.4–75.0° (m.p. 74.5–75.5° after one recrystallization from hexane). The ethereal solution from IV was shaken with 3 ml. of cold 3 *N* potassium hydroxide solution; acidification of the basic solution produced 1.11 g. (54%) of N-benzyltrifluoroacetamide, m.p. 74–75° after crystallization; the infrared spectrum was identical with that from an authentic sample. The ether solution was evaporated and the residue crystallized from hexane giving 0.51 g. (34%) of N-benzylacetamide, m.p. 60–61° (reported[15] 60–61°); the infrared spectrum was identical with that from an authentic sample.

Reaction of II with Benzylamine.—To a solution of 5.00 g. (0.0141 mole) of II in 120 ml. of dioxane was added 25.0 g. (0.234 mole) of benzylamine. After standing 2 days at 5°, the frozen mass was warmed to 15° and 1.30 g. of benzylamine acetate, m.p. 95.5–98.0°, was removed by filtration. Evaporation of the mother liquor gave a colorless, viscous oil (liquid A). Addition of ether to one-half of liquid A yielded 1.50 g. of moist, crystalline benzylamine acetate; the total yield was 2.80 g. (91%). Recrystallization of the combined salt from a mixture of ether and methanol produced 2.0 g. of benzylamine acetate, m.p. 97–99° (mixed melting point with an authentic sample showed no depression). The remainder of liquid A was shaken with 50 ml. of water (no nitrite ion was found to be present in this extract) to remove benzylamine acetate, the heavier organic phase was separated, cooled to 0°, and treated with 10 ml. of methanol. The slow addition of 15 ml. of cold water precipitated 3.0 g. of 1,3,5-tribenzyl-1,3,5-triazacyclohexane, m.p. 50.2–51.0° (mixed melting point with an authentic sample showed no depression; infrared spectra were identical).

Anal. Calcd. for $C_{24}H_{27}N_3$: C, 80.63; H, 7.61; N, 11.76. Found: C, 80.43; H, 7.41; N, 11.58.

Aniline and V.—To a solution of 4.62 g. (0.010 mole of V in 50 ml. of dioxane was added 18.6 g. (0.20 mole) of aniline. After standing 6 days the mixture had become dark red. Removal of the dioxane under reduced pressure at room temperature left a dark red, viscous oil. Extraction of an ethereal solution of the oil with base yielded on acidification 2.65 g. (70%) of N-phenyltrifluoroacetamide, m.p. 89.5–90.5°, identified by comparison of its infrared spectrum and the X-ray powder pattern with that of an authentic sample.

The ethereal solution gave a mixture of low melting orange solids, soluble in dilute hydrochloric acid, which could not be crystallized either as the free bases or the hydrochlorides. The infrared spectrum showed bands at 2.95 μ (NH), 6.17 μ (phenyl), 6.56 μ (NO_2) and 7.60 μ (NO_2).

1-Chloro-2,4,6-trinitro-2,4,6-triazaheptane (XII).—A solution of 3.00 g. (8.6×10^{-3} mole) of III in 60 ml. of anhydrous dioxane (refluxed over sodium and distilled) containing 8.0 equiv. of anhydrous hydrogen chloride per liter, was allowed to stand at room temperature for 5 days. Evaporation of the dioxane under reduced pressure at 25° left a colorless solid which upon crystallization from ethylene chloride yielded 1.90 g. (81%) of XII, m.p. 140.6–141.6°; two further crystallizations gave 1.10 g., m.p. 140.7–141.7°. XII rapidly precipitated silver chloride when treated with alcoholic silver nitrate.

Anal. Calcd. for $C_4H_9O_6N_6Cl$: C, 17.62; H, 3.33; N, 30.83; Cl, 13.01. Found: C, 17.60; H, 3.23; N, 30.40; Cl, 13.29.

XII was also prepared (in similar yield) from I using dioxane or tetrahydrofuran[16] as the solvent.

1,7-Dichloro-2,4,6-trinitro-2,4,6-triazaheptane (XIII) and 1-Trifluoroacetoxy-2,4,6-trinitro-7-chloro-2,4,6-triazaheptane (XIV).—A solution of 3.00 g. (0.0074 mole) of IV in 50 ml. of anhydrous dioxane was saturated with anhydrous hydrogen chloride at 10°. After standing overnight, the solution was evaporated at room temperature (reduced pressure), giving 2.50 g. of colorless solid. The solid was dissolved in 6 ml. of boiling acetone and the solution cooled to yield 1.70 g. of XIII as fine crystals, m.p. 130–140°. Addition of 10 ml. of ether to the acetone filtrate precipitated 0.67 g. (24%) of crude XIV, m.p. 112–115°; two recrystallizations from 1:1 benzene–cyclohexane raised the melting point to 114–115°.

Anal. Calcd. for $C_6H_{11}O_8N_6Cl$: C, 18.73; H, 2.10; N, 21.85; Cl, 9.22. Found: C, 18.60; H, 2.37; N, 21.62; Cl, 8.99.

Two recrystallizations of XIII (above) from benzene gave 1.24 g. (55%), m.p. 144.5–145.5°.

Anal. Calcd. for $C_4H_8N_6O_6Cl_2$: C, 15.65; H, 2.63; N, 27.37; Cl, 23.09. Found: C, 15.83; H, 2.91; N, 27.05; Cl, 23.17.

The infrared spectra of both IV and XIV contained a strong trifluoroacetoxy carbonyl band at 5.6 μ; XIV had no acetoxy carbonyl band. Either XIII or XIV and alcoholic silver nitrate rapidly precipitated silver chloride.

XIII and boiling methanol produced 1,7-dimethoxy-2,4,6-trinitro-2,4,6-triazaheptane, m.p. 104–105° (reported[4] 104–105°). XIII was similarly prepared with hydrogen chloride in 75% yield from the diacetate II; V and hydrogen chloride gave a mixture from which XIII and XIV were isolated in yields of 20 and 16%, respectively.

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CHINA LAKE, CALIF.

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(15) H. Amsel and A. W. Hoffman, *Ber.*, **19**, 1286 (1886).

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