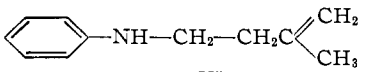
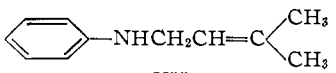


VI



VII

Anal. Calcd. for $C_{11}H_{15}N$: C, 81.93; H, 9.38. Found: C, 82.20, 82.10; H, 9.37, 9.50.

Reaction of Aniline with Butadiene at Higher Temperatures.—When aniline, butadiene and sodium are heated to a higher temperature, small quantities of N,N'-diphenylformamidine surprisingly are formed also. Thus, when a mixture of aniline (448 g., 4.7 moles), butadiene (358 g., 6.63 moles) and sodium (20 g., 0.87 moles) was heated at 170–190° for 18 hours, 4.2 g. of diphenylformamidine, m.p. 136–137° after crystallization from aqueous ethanol, was isolated by fractional distillation. The material (λ_{max}^{EtOH} 282 mμ, log *e* 4.34; λ_{min} 240.5 mμ, log *e* 371) was identified by analysis and mixed melting point with authentic diphenylformamidine.[12]

Under similar conditions, (a) 100 g. of N-crotylaniline and 5 g. of sodium, (b) 29 g. of N-crotylaniline, 19 g. of aniline and 3 g. of sodium, (c) 19 g. of aniline, 15 g. of butadiene and 8 g. of sodium hydroxide, (d) 29 g. of N-crotylaniline, 19 g. of aniline and 8 g. of sodium hydroxide, and (e) 28 g. of N-crotylaniline, 18 g. of aniline, 4 g. of sodium hydroxide and 2 g. of sodium yielded no detectable diphenylformamidine.

The reaction of equimolar quantities of N-crotylaniline and potassium hydroxide at 220° for six hours yielded largely aniline, characterized through its benzenesulfonamide, and an insoluble black solid.

2,3-Dimethylindole and *cis*-2,3-Dimethylindoline.—A mixture of N-crotylaniline (100 g. 0.67 mole) and polyphosphoric acid (50 g.) was refluxed with stirring under inert gas for seven hours. The two phase mixture was hydrolyzed with 20% aqueous potassium hydroxide, and the product was extracted with ether, washed and fractionally distilled *in vacuo* to yield three fractions: A, b.p. 50–70° at 2 mm., 8 g.; B, b.p. 72–76° at 2 mm., 32 g., and C, b.p. 150–165° at 12 mm., 32 g. Fraction A, $n^{25}D$ 1.5802 consisted largely of aniline characterized by its benzenesulfonamide, m.p. 111–112°. Fraction B, $n^{25}D$ 1.5513, boiled sharply at 74° at 2 mm. on redistillation.

Anal. Calcd. for $C_{10}H_{13}N$: C, 81.63; H, 8.84. Found: C, 81.62, 81.76; H, 8.94, 9.04. Kuhn-Roth C-methyl, calcd. for one C-methyl group: 10.2%. Found: 12.0%. λ_{max}^{EtOH} 242.5 mμ (log *e* 3.80); 294 mμ (log *e* 3.36); λ_{min} 272 mμ (log *e* 3.05).

Fraction B, *cis*-2,3-dimethylindoline, was characterized by its benzenesulfonamide which crystallized in needles from aqueous ethanol, m.p. 101–103°.

Anal. Calcd. for $C_{16}H_{17}NSO_2$: C, 66.87; H, 5.96. Found: C, 66.93, 67.00; H, 5.88, 5.72.

The infrared spectrum of *trans*-2,3-dimethylindoline,[8] b.p. 107–109° at 12 mm., differs from that of the *cis* isomer, and the *trans* isomer was characterized by a benzenesulfonamide melting at 70–71°.

Anal. Calcd. for $C_{16}H_{17}NSO_2$: N, 4.88. Found: N, 5.31, 5.28.

cis-2,3-Dimethylindoline was recovered unchanged after refluxing with polyphosphoric acid for 4 hours. Fraction C crystallized in the receiver, m.p. 103–104° after recrystallization from heptane.

Anal. Calcd. for $C_{10}H_{11}N$: C, 82.71; H, 7.64; N, 9.65. Found: C, 82.76; H, 7.59; N, 9.65. λ_{max}^{EtOH} 228.5 mμ (log *e* 4.50); 284 mμ (log *e* 3.84); 292 mμ (inflection, log *e* 3.79); λ_{min} 248 mμ (log *e* 3.27).

Its picrate[13] forms red needles from ethanol, m.p. 156–157°; its addition compound with picryl chloride[14] crystallizes in brown needles from ethanol, m.p. 135–136°.

Reaction of *cis*-2,3-Dimethylindoline with Chloranil.[9]—A mixture of *cis*-2,3-dimethylindoline (1 g.), xylene (50 cc.) and chloranil (2 g.) was refluxed for 4 hours, filtered, freed of solvent and the residue dissolved in ether. The ethereal solution was dried after extraction with dilute aqueous hydrochloric acid to remove the more strongly basic indoline, and distilled to yield 0.37 g. (38%) of 2,3-dimethylindole.

Acknowledgment.—We wish to thank Professors M. G. Ettlinger and C. D. Hurd for valuable advice.

(12) W. Weith, *Ber.*, **9**, 457 (1876).

(13) L. Wolff, *ibid.*, **21**, 125 (1888).

(14) M. Padoa and C. Chiaves, *Gazz. chim. ital.*, **38I**, 236 (1908).

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

The Alkaline Degradation of Some Polymethylenetrinitramines[1]

BY RUSSELL REED, JR.

RECEIVED JULY 22, 1957

The nature of the products formed when hydroxide ion, methoxide ion and benzylamine interact with certain esters of the 7-alkyl-2,4,6-trinitro-2,4,6-triazaheptanols-1 has been elucidated. Similar studies have been carried out with the bis-esters of the 2,4,6-trinitro-2,4,6-triazaheptandiol-1,7 and with the polymeric methylenenitramine $[CH_2N(NO_2)]_x$.

The alkaline decomposition of the simple nitramines has been studied extensively but little has been reported on compounds containing two or three nitramino groups. Compounds containing three nitramino groups which have been investigated are the trifluoroacetate esters of the 2,4,6-trinitro-2,4,6-triazaheptanol-1, $CH_3[N(NO_2)CH_2]_3OH$, and the 2,4,6-trinitro-2,4,6-triazaheptandiol-1,7, $HO[CH_2N(NO_2)]_3CH_2OH$.[2] The interesting and unusual behavior of these compounds prompted the present investigation of the alkaline degradation of compounds containing three methylenenitramine units.

Primary nitramines are acidic and readily form salts with alkalies and amines; the salts are not easily decomposed by bases except on prolonged boiling in concentrated aqueous alkali.[3] Van Erp[4] found that methylnitramine and potassium hydroxide yielded ammonia, hydrogen, formaldehyde and the salt of a nitrogen acid, perhaps hyponitrous. Lamberton and co-workers[5] found the mono- and diarylmethylnitramines to be cleaved easily by alkali with the formation of aldehydes or ketones,

(1) Presented in part before the Pacific Southwest Meeting of the American Chemical Society, San Diego, Calif., April 27, 1957.

(2) R. Reed, THIS JOURNAL, **78**, 801 (1956).

(3) H. J. Backer, *Sammlung Chem. und Chem. Tech. Vorträge*, **18**, 359 (1912).

(4) H. Van Erp, *Rec. trav. chim.*, **14**, 48 (1895); *Ber.*, **29**, 474 (1896).

(5) J. Barrott, M. I. Gillibrand and A. H. Lamberton, *J. Chem. Soc.*, 1282 (1951).

TABLE I

PROPERTIES OF TRINITRAMINE ESTERS I AND II

	R[N(NO2)CH2]3A R	A	M.p., °C. (cor.)	Yield, %	Formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Nitrogen, % Calcd.	Nitrogen, % Found
Ia	CH_3	$OCOCH_3$	154–155	86[a]							
Ib	CH_3	$OCOCF_3$	136–137	79[a]							
Ic	CH_3	ONO_2	145–146	87[a]							
Id	C_2H_5	$OCOCH_3$	133–134	78	$C_7H_{14}N_6O_8$	27.10	27.31	4.55	4.69	27.19	27.34
Ie	C_2H_5	$OCOCF_3$	94–95 d.	59	$C_7H_{11}F_3N_6O_8$	23.08	23.21	3.05	3.28	23.08	23.29
If	n-C_3H_7	$OCOCH_3$	115–116	75	$C_8H_{16}N_6O_8$	29.63	29.81	4.97	4.78	25.92	25.70
Ig	n-C_3H_7	$OCOCF_3$	114–115	60	$C_8H_{13}F_3N_6O_8$	25.40	25.82	3.46	3.56	22.22	22.48
Ih	n-C_3H_7	ONO_2	116–117	80	$C_6H_{13}N_7O_9$	22.02	22.29	4.00	4.28	29.97	29.70
Ii	n-C_8H_{17}	$OCOCH_3$	139–140	84	$C_{13}H_{26}N_6O_8$	39.59	39.78	6.65	6.88	21.31	21.14
Ij	n-C_8H_{17}	$OCOCF_3$	124.5–125.4	82	$C_{13}H_{23}F_3N_6O_8$	34.82	34.99	5.17	5.27	18.75	19.01
Ik	n-C_8H_{17}	ONO_2	136–137	83	$C_{11}H_{23}N_7O_9$	33.25	33.59	5.83	5.55	24.68	24.16
	$ACH_2[N(NO_2)CH_2]_3B$ B	A									
IIa	$OCOCH_3$	$OCOCH_3$	154–155	81[a]							
IIb	$OCOCH_3$	$OCOCF_3$	151–152	84[a]							
IIc	$OCOCF_3$	$OCOCF_3$	149.5–150.5	84[a]							

[a] Yield based on directions given in this report; these compounds were previously prepared.[2]

respectively; thus, where R = aryl and R′ = aryl or hydrogen

$$RR'CHNHNO_2 \xrightarrow{NaOH} RR'CO + N_2$$

Secondary nitramines $RN(NO_2)CH_2R'$ are more readily attacked by base, the products being nitrite ion, an amine RNH_2 and an aldehyde RCHO.[3,6,7] The larger alkyl group forms the amine, the other radical resulting in an aldehyde.[8,9] This rule was reversed with benzyl and substituted benzyl derivatives.[10] The degradation was believed to proceed *via* the imine RN=CHR′ which was formed by the loss of the elements of nitrous acid. (N-Butylmethyleneimine was shown to yield the same products.[11]) Jones[12] considered the reaction to be an E2 elimination of the elements of nitrous acid.

Compounds containing two nitramino groups separated by one or two carbon atoms are readily attacked by bases. Methylenedinitramine[13] and alkali produced nitrogen and nitrous oxide; ethylenedinitramine[14] has been reported to yield nitrogen. Cyclic methylenenitramines are also easily decomposed by alkali. Somlo[15] treated 1,3,5-trinitro-1,3,5-triazacyclohexane (RDX) with hot alkali and found that nitrate, nitrite, an organic acid, hexamine, formaldehyde, ammonia and nitrogen were produced. Jones studied the kinetics of the reactions of RDX[16] and 1,3-dinitro-1,3-diazacyclopentane[17] with sodium methoxide in methanol and found that the decompositions involved the loss of the elements of nitrous acid. High yields of ethylenedinitramine resulted from the action of dilute alkali on 1,5-dinitro-3-acetoxymethyl-1,3,5-triazacycloheptane and methylene-bis-3,6-dinitro-1,3,6-triazacycloheptane.[18]

Discussion of Results

The trinitramines studied in the present communication are the acetate and trifluoroacetate esters (I) of various 7-alkyl-2,4,6-trinitro-2,4,6-triazaheptanols-1 listed in Table I. The bis-acetate and bis-trifluoroacetate esters (II) of the diol 2,4,6-trinitro-2,4,6-triazaheptandiol-1,7 were again investigated. Also employed was the polymeric methylenenitramine, $[CH_2N(NO_2)]_x$ (III). The nitramines were degraded with aqueous potassium hydroxide, benzylamine and potassium or sodium methoxide. In general these acyclic trinitramines were found to be much more reactive with bases than the nitramines mentioned in the literature survey. Surprisingly, the linear trinitramines were found to yield no nitrite; the fate of the nitramino group was to produce nitrous oxide. The degradation began by an attack on the ester group rather than by the loss of a proton in an elimination of the elements of nitrous acid as in the case of the simpler nitramines containing no ester functional groups.

Dioxane solutions of the acetates or trifluoroacetates (I) were attacked by an aqueous solution of potassium hydroxide to yield the salt $K^+[RN(NO_2)]^-$ (IV) (see Table II), potassium acetate or trifluoroacetate, formaldehyde and nitrous oxide. The trifluoroacetates reacted rapidly with even 0.1 *N* alkali in the cold while the acetates were decomposed very slowly under these conditions but rapidly at 95°. A mechanism for the decomposition of the acetates is proposed, and is shown in Fig. 1. It is believed that the most likely course of events in the degradation would involve first an attack by hydroxyl ion upon the carbonyl atom of the ester to produce Iα and acetate ion as outlined by step 1; Iα would then lose formaldehyde to give

(6) H. Van Erp, *Rec. trav. chim.*, **14**, 327 (1895).
(7) J. Thiele and A. Lachmann, *Ann.*, **288**, 269 (1895).
(8) A. P. N. Franchimont and H. Van Erp, *Rec. trav. chim.*, **13**, 328 (1894); **14**, 247 (1895); **15**, 165 (1896).
(9) H. Umbgrove and A. P. N. Franchimont, *ibid.*, **15**, 195 (1896); **16**, 395, 397 (1897); **17**, 275 (1898).
(10) A. P. N. Franchimont and H. Van Erp, *ibid.*, **14**, 242 (1895).
(11) A. P. N. Franchimont and H. Van Erp, *ibid.*, **15**, 171 (1896).
(12) W. H. Jones, *Science*, **118**, 387 (1953).
(13) A. H. Lamberton, C. Lindley and J. C. Speakman, *J. Chem. Soc.*, 1650 (1949).
(14) A. P. N. Franchimont and E. A. Klobbie, *Rec. trav. chim.*, **7**, 246 (1888).
(15) H. F. Somlo, *Z. ges. Schiess- u. Sprengstoffw.*, **35**, 175 (1940); *C. A.*, **35**, 3191 (1941).
(16) W. H. Jones, THIS JOURNAL, **76**, 829 (1954).
(17) W. H. Jones, *ibid.*, **76**, 928 (1954).
(18) G. S. Myers and G. F Wright, *Can. J. Research*, **B27**, 501 (1949).

TABLE II

PROPERTIES OF THE POTASSIUM SALTS OF THE ALKYLNITRAMINES (IV)

$K^+[RN(NO_2)]^-$ R	M.p., °C. dec.	Yield, %		Formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Nitrogen, % Calcd.	Nitrogen, % Found
IVa CH_3	200	57[a]	50[b]	$CH_3N_2O_2K$	10.52	10.70	2.65	2.60	24.55	24.75
IVb C_2H_5	207	70[b]		$C_2H_5N_2O_2K$	18.74	18.67	3.93	4.19	21.86	22.01
IVc n-C_3H_7	240	80[b]	83[a]	$C_3H_7N_2O_2K$	25.34	25.10	4.96	5.09	19.70	19.91
IVd n-C_5H_{11}	260	81[b]	85[a]	$C_5H_{11}N_2O_2K$	45.25	44.99	8.07	8.24	13.20	13.56

[a] The yield as obtained from the trifluoroacetate ester. [b] The yield as obtained from the acetate ester.

Iβ. The intramolecular decomposition of Iβ as shown in step 3 might then yield Iγ.[19] The intermediates Iα and Iβ (R = CH_3) have been prepared and shown to yield, under these conditions, the same products.[2] Less likely but also possible would be the attack by hydroxyl ion on the number one methylene carbon atom of the ester to produce Iα and acetate ion *via* an alkyl–oxygen cleavage. This type of cleavage was exhibited by the bis-ester IIa when it was treated with benzylamine; *i.e.*, benzylammonium acetate and the cyclic trimer of benzylamine and formaldehyde, 1,3,5-tribenzyl-1,3,5-triazacyclohexane (V), were produced.

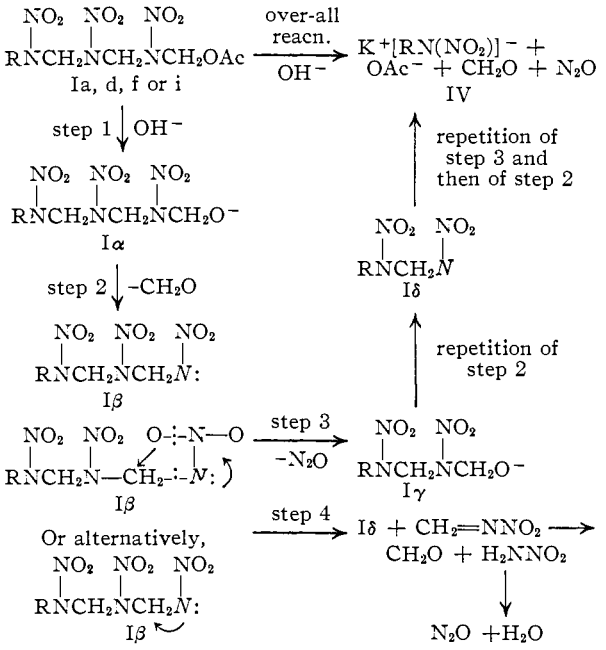


Fig. 1.

However in no other nitramine ester has this been observed. This fission is further rendered unlikely by the failure of any of the esters of I or II to yield methyl ethers of the type $R[N(NO_2)CH_2]_3OCH_3$ or $CH_3O[CH_2N(NO_2)]_3CH_2OCH_3$ when treated with potassium or sodium methoxide, respectively (see below). As an alternative to step 3 the elimination of Iδ (step 4) to form the N-nitro derivative of methylenimine must also be considered. This imine presumably would give formaldehyde and nitramide; the latter rapidly decomposes in base to yield nitrous oxide and water.[20] The degradation of the trifluoroacetate would be expected to proceed in a manner not significantly different from that of the acetates except that acyl–oxygen cleavage would be more favored than with the acetate esters.

Benzylamine reacted exothermically with the esters I or II so that dilute dioxane solutions of the reactants were used which contained 5 moles of benzylamine per mole of ester. The acetate esters of I thus gave V, N-benzylacetamide (VI), the benzylammonium salt of the alkylnitramine $[C_6H_5CH_2NH_3]^+$ $[RN(NO_2)]^-$ (VII) (see Table III) and nitrous oxide. The degradation caused by benzylamine is believed to occur *via* a mechanism similar to that operative in the case of the potassium hydroxide. The trifluoroacetate esters of the 7-alkyl-2,4,6-trinitro-2,4,6-triazaheptanol-1 reacted very rapidly with benzylamine to yield the same products as the acetate esters except that N-benzyltrifluoroacetamide (VIII) was produced instead of (VI). However, the methyl derivative of the trifluoroacetate Ib gave the same products, but in addition there was formed the di-(benzylammonium)-methylenedinitramine (IX). This salt was formed likewise, as previously noted,[2] when the bis-trifluoroacetate IIa and its monoacetoxy derivative 1-acetoxy-7-trifluoroacetoxy-2,4,6-trinitro-2,4,6-triazaheptane (IIb) were treated with benzylamine. However, the bis-acetate had been found to yield none of the salt IX, but instead gave only VI and benzylammonium acetate. No explanation is offered to explain the different behavior of these latter esters. The octyl-nitrate ester Ik reacted somewhat less rapidly than the corresponding trifluoroacetate to yield V, VIId and benzylammonium nitrate.

When any of the trifluoroacetate esters was treated with only one or two moles of benzylamine there was produced 1-nitro-3,5-dibenzyl-1,3,5-triazacyclohexane (X), an unstable crystalline solid which had been reported previously by Wright and co-workers[21] as a reaction product of nitramide, formalin and benzylamine.

The esters reacted immediately with potassium methoxide to produce the $K^+R[N(NO_2)CH_2]_2N(NO_2)^-$ (XI) from I and $Na_2^+[N(NO_2)CH_2]_2N(NO_2)^-$ (XII)[22] from the bis-esters II (see Table IV). The salts XI were gelatinous solids, difficult to purify and unstable so that their combustion analyses were only in rough agreement with that required. However, the salt XII was easily recrystallized and its elemental analysis was in good agreement with the theoretical. It slowly decomposed on standing and could be detonated easily. The latter salt was very soluble in water and moder-

(19) The intramolecular mechanism in step 3 was suggested by Dr. W. P. Norris of this laboratory.

(20) C. A. Marlies and V. K. La Mer, THIS JOURNAL, **57**, 1812 (1935).

(21) W. J. Chute, D. C. Downing, A. F. McKay, G. S. Myers and G. F Wright, *Can. J. Research*, **B27**, 233 (1949).

(22) Reference 13 mentions the potassium salt analog of XII as a compound prepared by Canadian workers; private communication.

TABLE III

PROPERTIES OF THE BENZYLAMMONIUM ALKYLNITRAMINES (VII), $C_6H_5CH_2NH_3^+[RN(NO_2)]^-$

	R	M.p., °C.	Yield, %	Formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Nitrogen, % Calcd.	Nitrogen, % Found
VIIa	CH_3	57–58	31,[a] 39[b]	$C_8H_{13}N_3O_2$	52.45	52.30	7.15	7.42	22.94	22.77
VIIb	C_2H_5	93–94	60,[a] 69[b]	$C_9H_{15}N_3O_2$	54.80	55.09	7.67	7.91	21.31	21.57
VIIc	n-C_3H_7	87–88	70,[a] 60[c]	$C_{10}H_{17}N_3O_2$	56.85	56.67	8.11	8.29	19.89	19.81
VIId	n-C_8H_{17}	65.5–66.5	86,[a] 80,[b] 61[c]	$C_{15}H_{27}N_3O_2$	64.09	63.91	9.67	9.50	14.93	14.77

[a] The yield as obtained from the acetate ester. [b] The yield as obtained from the trifluoroacetate ester. [c] The yield as obtained from the nitrate ester.

TABLE IV

PROPERTIES OF THE ALKALI SALTS OF THE POLYMETHYLENENITRAMINES (XI AND XII), $K^+[RN(NO_2)CH_2N(NO_2)CH_2N(NO_2)]^-$

	R	M.p., °C.	Yield, %	Formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Nitrogen, % Calcd.	Nitrogen, % Found
XIa	CH_3	60[a]	95	$C_3H_7N_6O_6K$	13.74	13.99	2.69	3.00	32.05	32.46
XIb	C_2H_5	60[a]	90	$C_4H_9N_6O_6K$	17.39	17.59	3.28	3.58	30.42	30.80
XIc	n-C_3H_7	70[a]	96	$C_5H_{11}N_6O_6K$	20.69	20.81	3.82	3.99	28.95	28.71
XId	n-C_8H_{17}	90[a]	94	$C_{10}H_{21}N_6O_6K$	33.32	33.60	5.87	5.69	23.32	23.59
XII	$Na_2^+[N(NO_2)CH_2N(NO_2)CH_2N(NO_2)]^-$	80[a]	91	$C_2H_4N_6O_6Na_2$	9.45	9.57	1.59	1.70	33.08	33.29

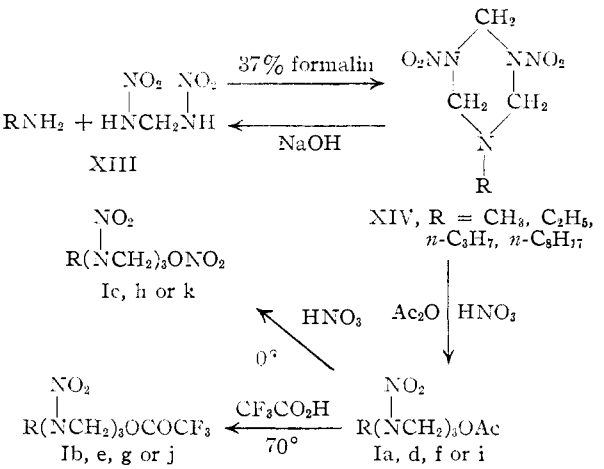
[a] Vigorous gas evolution but without melting.

ately soluble in methanol; solutions in methanol slowly precipitated the disodium salt of methylenedinitramine. Acidification of aqueous solutions of the salt with dilute mineral acid produced methylenedinitramine (XIII). Benzoyl chloride and alkali failed to react with XII as did a mixture of formalin and benzylamine; XII was also inert to 0.1 N sodium hydroxide at least for a period of several hours. The negative charge on the anion probably prevented attack by hydroxide ion.

The insoluble polymer $[CH_2N(NO_2)]_x$ (III) could be titrated with aqueous 0.1 N sodium hydroxide in 50% acetone solution; a neutral equivalent of 74 was obtained.[23] As the titration proceeded the insoluble III gradually dissolved, solution being complete near the end-point. Unfortunately, the insolubility of III prevented a determination of its molecular weight. The infrared spectrum indicates NH, OH and nitramino (see Experimental). Benzylamine dissolved III with the formation of di-(benzylammonium)-methylenedinitramine (IX).

Synthesis of Compounds

The esters I were prepared easily by the nitrolysis of the 1-alkyl-3,5-dinitro-1,3,5-triazacyclohexanes (XIV) (see Table V) with a mixture of nitric acid–acetic anhydride. Good yields of the linear trinitramine acetate esters I were obtained; the esters were then heated with a solution of sodium acetate in acetic acid which converted any nitrate ester that may have been present to the acetate. The pure nitrate esters of I were obtained by dissolving the acetates in 99.8% nitric acid at 0°. The trifluoroacetate esters were prepared by refluxing the acetates in a large excess of trifluoroacetic acid. Preparation of the cyclic derivatives XIV was accomplished readily by the condensation of XIII, formalin and the appropriate primary alkylamine.[24]



Hot 1.0 N sodium hydroxide rapidly converted any of the derivatives of XIV to the corresponding amine and the disodium salt of XIII.

The methylenenitramine polymer was prepared according to Wright and co-workers[25] and possessed a satisfactory elemental analysis. Its insolubility in all organic solvents did not permit a determination of molecular weight.

Experimental[26]

Part I. Degradation. Decomposition of the Esters of the 7-Alkyl-2,4,6-trinitro-2,4,6-triazaheptanols-1 (I). A. Decomposition with Aqueous Potassium Hydroxide.—The decompositions of the 7-octyl acetate ester derivative 1-acetoxy-2,4,6-trinitro-2,4,6-triazatetradecane (Ii) is typical and is described. A suspension of 1.97 g. (0.00500 mole) of Ii in 15 ml. of 2.0 N potassium hydroxide was allowed to stand 2 days (1 hour in the case of the trifluoroacetates) at room temperature. During this time all of I had dissolved and plates of the potassium salt of octylnitramine (IVd) had formed. The solution was cooled to 0° and filtered to yield 0.86 g. (81%) of IVd which was then recrystallized from

(23) The value of 74 for the neutral equivalent was considered reasonable since if it be assumed that on the average the polymer molecules contain equal numbers of the end groups $HN(NO_2)$- and $-CH_2OH$, *e.g.*, $H[N(NO_2)CH_2N(NO_2)]_nCH_2OH$, then for $n = 2$ a neutral equivalent of 78.5 should result if the cleavage occurred so as to produce formaldehyde and the maximum yield of the disodium salt of XIII; as n approaches infinity the neutral equivalent would then be expected to approach the value for the nitramine XIII itself, namely 68.0.

(24) This reaction has been used to synthesize the methyl and benzyl derivatives of XIV; F. Chapman, P. G. Owston and D. Woodcock, *J. Chem. Soc.*, 1638 (1949).

(25) E. Aristoff, J. A. Graham, R. H. Meen, G. S. Myers and G. F. Wright, *Can. J. Research*, **B27**, 531 (1949).

(26) All melting points are corrected.

TABLE V

PROPERTIES OF THE 1-ALKYL-3,5-DINITRO-1,3,5-TRIAZACYCLOHEXANES (XIV) RN(CH_2—$N(NO_2)$—CH_2—$N(NO_2)$—CH_2)

	R	M.p., °C. (cor.), dec.	Yield, %	Formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Nitrogen, % Calcd.	Nitrogen, % Found
XIVa	CH_3	104–105	47[a]							
XIVb	C_2H_5	96–97	20	$C_5H_{11}N_5O_4$	29.27	29.07	5.41	5.26	34.14	33.91
XIVc	n-C_3H_7	84–85	75	$C_6H_{13}N_5O_4$	32.87	32.59	5.98	5.73	31.95	32.17
XIVd	n-C_8H_{17}	80.5–81.5	57	$C_{11}H_{23}N_5O_4$	45.66	46.15	8.01	7.66	24.21	24.50

[a] The yield obtained in this work. This compound had been prepared previously, ref. 24.

methanol; IVd exhibited prominent absorption maxima in the infrared at 7.65 (N-NO_2) and 13.03 μ (characteristic of acyclic nitramines[27]). When the above experiment was conducted under a vacuum and the solution carefully degassed beforehand, the evolved gases were found to consist of nitrous oxide, 99%, and nitrogen, 1% by analysis with a mass spectrograph. The mother liquor from IVd which gave a negative test for nitrite ion was evaporated to dryness and the residue treated cautiously with concentrated sulfuric acid. The mixture was placed in a distilling apparatus and heated to 70° under reduced pressure. Titration of the distillate with potassium hydroxide indicated that 93% of the calcd. amount of acetic acid had been isolated. Evaporation of the solution gave potassium acetate, identified by a comparison of its X-ray powder pattern with that of an authentic sample. In the case of Ia the potassium salt of methylnitramine (IV) did not precipitate and was "salted-out" by the addition of 10 g. of potassium bromide.

B. Decomposition with Benzylamine.—A solution of 1.97 g. (0.00500 mole) of Ii in 40 ml. of dioxane (freshly distilled from sodium) was treated with 2.68 g. (0.0250 mole) of benzylamine. In the case of the trifluoroacetate the solution was cooled to 10° and the amine added dropwise so that the temperature of the reaction mixture did not exceed 20°. The solution was allowed to stand 20 hours (1 hour for the trifluoroacetate) at room temperature; it gave a negative test for nitrite ion. The solution was then distilled at reduced pressure leaving a colorless pasty solid A which became crystalline upon trituration with three 50-ml. portions of pentane. Filtration gave 1.21 g. (86%) of crude benzylammonium octylnitramine (VIId), m.p. 62–65°, soluble in hexane (boiling), ether or methanol; two recrystallizations from ether raised the melting point to 65.5–66.5°. The salt VIId was identified by a comparison of its infrared spectrum with that of an authentic sample; a mixed melting point of VIId with the authentic material was not lowered. The infrared spectra of the salts VII all exhibited absorption maxima at 3.5–3.7 shoulder (NH_2^+), 6.2, 6.5, 7.8 and 13.1 μ (N-NO_2).

The pentane filtrate from A (above) was evaporated to yield an oil B which could not be crystallized after repeated efforts. A slight excess of 6 N hydrochloric acid was added to the oil and the mixture extracted with methylene chloride; the methylene chloride was evaporated to a volume of 10 ml. and then cooled to 0°. After standing several hours, there was obtained 1.38 g. (70% assuming that 1 mole of I yielded 1 mole of the salt) of the **hydrochloride of 1,3,5-tribenzyl-1,3,5-triazacyclohexane (XV)** as plates, m.p. 121–123°, m.p. 122.4–123.0° after recrystallization. Titration of XV with silver nitrate (dichlorofluorescein indicator) gave an equivalent weight of 390 (calcd. 394). The infrared spectrum of **XV** was identical with that of the authentic material (prepared from the free base V[28] and an equivalent quantity of 1 N hydrochloric acid).

Anal. Calcd. for $C_{24}H_{28}ClN_3$: C, 73.17; H, 7.16; N, 10.67. Found: C, 72.99; H, 7.26; N, 10.81.

When an excess of 6 N hydrochloric acid was used to acidify the oil B there was obtained the **trihydrochloride XVI of the base V** (again by extraction with methylene chloride), m.p. >250°; equivalent weight by silver nitrate titration, 150 (calcd. 156); XVI exhibited an infrared spectrum identical with that of the authentic material (prepared from V and excess hydrochloric acid).

Anal. Calcd. for $C_{24}H_{30}Cl_3N_3$: C, 61.74; H, 6.48; N, 9.00. Found: C, 61.88; H, 6.41; N, 9.29.

The mother liquor from the crystallization of the hydrochloride XV was evaporated to a volume of 0.5 ml. and repeatedly frozen and thawed while being scratched with a glass rod. In this manner there was finally obtained 0.60 g. (80%) of crystalline N-benzylacetamide, m.p. 60–61° (lit. reports[29] 60–61°) after one recrystallization from 2:1 methanol–water. The mixture melting point with an authentic sample of N-benzylacetamide was not depressed; the infrared spectrum was identical with that of the authentic material.

When the trifluoroacetate ester Ib, the bis-trifluoroacetate ester IIc or the mixed ester IIb was treated with benzylamine under the above conditions there was immediately precipitated di-(benzylammonium)-methylenedinitramine (IX) in yields of 63, 68 and 60%, respectively; IX melted at 99–100°, and at 100–101° after recrystallization from 1:1 methanol–dioxane. The salt was soluble in water, methanol, isopropyl alcohol or acetone but insoluble in dioxane; IX exhibited prominent absorption maxima in the infrared at 3.5–3.8 shoulder (NH_2^+), 6.0, 6.2, 7.7, 8.0 and 12.9 μ (N-NO_2). When an acetone solution of IX was treated with sodium iodide and allowed to stand 1 day at 0° there was precipitated the disodium salt of XIII in 60% yield.

Dioxane solutions of any of the trifluoroacetate esters (including the mixed ester IIb) were treated with only 2 moles of benzylamine and the resulting clear solution allowed to stand 2 days at room temperature. The dioxane was removed under reduced pressure to yield an oil which upon trituration with a 1:1 mixture of hexane and ether yielded plates of 1-nitro-3,5-dibenzyl-1,3,5-triazacyclohexane (X), m.p. 108.5–109.4° after recrystallization (lit. reports[21] 109°). After standing several days a strong odor of benzylamine accompanied by the formation of traces of oil was noted in bottles of X; the yields were 45, 50 and 40% (based on one mole of the ester giving one mole of X), respectively, from Ia, IIb and IIc. The infrared spectrum was observed to have absorption maxima at 6.4, 6.6 and 7.8 μ (N-NO_2).

C. Decomposition with Alkaline Methoxide.—To a stirred solution of 1.97 g. (0.00500 mole) of Ia in 50 ml. of dioxane at 10° was added (dropwise) 3 ml. of methanol in which 0.20 g. (0.0051 mole) of potassium had been dissolved. The first drop of potassium methoxide caused an immediate precipitation of a white gelatinous solid. After all of the base had been added, the mixture was filtered and the precipitate washed with acetone and then with ether to give 1.69 g. (94%) of the unstable and explosive salt K^+-$[CH_3N(NO_2)CH_2N(NO_2)CH_2N(NO_2)]^-$ (XIa), soluble in water (in which it slowly decomposed) but only slightly soluble in common organic solvents. The infrared spectra of all of the salts exhibited absorption maxima at 6.2–6.5, 7.8 and 13.1 μ (N-NO_2).

When the bis-esters IIa or IIc or the mixed ester IIb were treated with sodium methoxide as above there was obtained a gelatinous precipitate, which after washing with acetone and ether, amounted to a yield of about 91% (the yield was the same from each ester) of the disodium-1,3,5-trinitro-1,3,5-triazapentane (XII). The explosive salt was recrystallized by dissolving it in the minimum volume of cold water followed by the addition of methanol to yield needles of XII, which were immediately analyzed. The infrared spectrum of XII exhibited absorption maxima at 5.96, 6.05,

(27) The infrared spectra of many acyclic nitramines have been observed in these laboratories and in all cases to date a prominent band at 12.90 to 13.15 μ has been noted.

(28) The free base VI has been prepared; H. Hock, German Patent 139,394; A. Henry, *Bull. Acad. Roy. Belg.*, **29**, 23 (1895).

(29) H. Amsel and A. W. Hofmann, *Ber.*, **19**, 1286 (1886).

7.72 and 12.96 μ (N-NO_2). The salt was very soluble in water, moderately soluble in methanol, but insoluble in a large number of organic solvents. When methanol solutions of XII were heated to 50° the disodium salt of methylenedinitramine was precipitated slowly. Acidification of XII with cold dilute mineral acid yielded XIII, the only isolable product. An attempt to condense XII, formalin and benzylamine yielded only an oil which contained no nitramine. Benzoyl chloride, alkali and XII did not interact. An attempt to titrate XII with 0.1 *N* sodium hydroxide showed that the salt was completely inert to dilute base, at least for a period of several hours.

Decomposition of the Nitrate Ester Ik by Benzylamine.—A solution of 1.84 g. (0.00500 mole) of Ik in 40 ml. of dioxane was treated with 2.68 g. (0.025 mole) of benzylamine. After standing 2 hours at 25°, the solution became yellow but did not undergo further color change; large plates slowly were deposited. The solution was filtered after standing 17 hours to yield 0.26 g. (61%) of benzylammonium nitrate, m.p. 133–134° (lit. reports[30] 136°). The salt was identified by a comparison of its infrared spectrum with that of authentic material; a mixture melting point was not depressed. The mother liquor from the salt was an intractable oil from which no solids were obtained.

Decomposition of the Polymeric Methylenenitramine. $[CH_2N(NO_2)]_x$ (III).—A suspension of 0.100 g. of III in 20 ml. of acetone was titrated with 0.1005 *N* sodium hydroxide (carbonate free) using a Beckman *p*H meter (model H-2). Plotting the volume of base against the *p*H gave an equivalent weight of 74.[23] The titrated solution was acidified with hydrochloric acid and then evaporated at reduced pressure to a volume of 5 ml. which was then extracted with four 20-ml. portions of ether. The ether extracts were combined, dried over magnesium sulfate and the ether removed by evaporation to yield 0.057 g. of methylenedinitramine (XIII). It was found that only 85% of XIII could be recovered under these conditions so that the corrected yield would be 0.67-g. of XIII; this corresponds to a yield of 79% if it be assumed that all of the nitrogen in the polymer (35.1% found, 35.2% calcd. for $[CH_2N(NO_2)]$) was used to form XIII.

Benzylamine dissolved III to give a clear yellow solution. Evaporation of the benzylamine at reduced pressure left an oil which crystallized upon stirring with ether to yield the di-(benzylammonium)-methylenedinitramine (IX) in 65% yield.

Part II. Synthesis.—The preparations of the *n*-octyl derivatives are typical and are described.

Formation of the 1-*n*-Octyl-3,5-dinitro-1,3,5-triazacyclohexane (XIVd).—To a stirred solution of 13.6 g. (0.100 mole) of XIII in 200 ml. of 36% formalin (maintained at 0°) was added (dropwise and over the course of 20 minutes) 12.9 g. (0.100 mole) of *n*-octylamine. The addition of the first drop of amine caused the immediate precipitation of some XIVd. When the addition was completed, the mixture was allowed to stand for 30 minutes at 0°; it was then filtered and the precipitate washed with water to yield (after drying) 16.4 g. (57%) of the crude white powder XIVd. After two recrystallizations from hexane there was obtained 12.5 g. of XIVd as thin plates, m.p. 80.5–81.5°. The infrared spectrum of XIVd exhibited absorption bands at 6.45, 6.57, 7.70–7.85 and 13.0 μ (N-NO_2). Hot 1 *N* sodium hydroxide rapidly cleaved XIVd to yield octylamine (81%), formaldehyde and the disodium salt of XIII (68%); basic cleavage of the other alkyl derivatives of XIV gave approximately the same yields of the salt of XIII and the corresponding amine.

1-Acetoxy-2,4,6-trinitro-2,4,6-triazatetradecane (Ii).—A stirred solution of 5.78 g. (0.0200 mole) of XIVd (R = *n*-C_8H_{17}) in 20 ml. of acetic anhydride was treated with 4.20 ml. (0.100 mole) of colorless 99.7% nitric acid. The temperature rose to 35° and the mixture was then cooled to room temperature in a water-bath. After standing 10 minutes the solution was poured onto ice and the solid removed by filtration to yield 6.70 g. (84%) of the crude Ii, m.p. 122–125°. A solution containing 6.7 g. of Ii and 5.0 g. of sodium acetate in 50 ml. of acetic acid was refluxed for 20 minutes, cooled and then poured onto ice. The precipitated Ii was collected on a funnel and recrystallized twice from ethanol to yield 5.21 g. of colorless plates, m.p. 138–139°. The prominent infrared absorption maxima were 5.70 (CO), 6.25, 6.50, 7.8–7.9 and 13.0 μ (N-NO_2).

1-Trifluoroacetoxy-2,4,6-trinitro-2,4,6-triazatetradecane (Ij).—A solution of 5.00 g. (0.0127 mole) of the acetate Ij (R = *n*-C_8H_{17}) in a mixture containing 20 ml. of trifluoroacetic acid and 5 ml. of trifluoroacetic anhydride was boiled 30 minutes in a distillation apparatus, during which time the volume of liquid was reduced to 10 ml. The residue was cooled to 5° and let stand for 30 minutes while plates of the trifluoroacetate were deposited; the yield was 4.65 g. (82%), m.p. 122–125°. Three recrystallizations from cyclohexane raised the m.p. to 124.5–125.4°. The infrared spectrum showed absorption maxima at 5.56 (CO), 6.25, 6.52, 7.85 and 13.0 μ (N-NO_2).

1-Nitroxy-2,4,6-trinitro-2,4,6-triazatetradecane (Ik).—To 20 ml. of colorless 99.7% nitric acid at 0° was added 5.00 g. (0.0127 mole) of the acetate Ik. The clear colorless solution was immediately poured onto ice and the precipitated nitrate ester was removed by filtration and washed with water to yield (after drying *in vacuo*) 4.17 g. (83%). The ester was recrystallized from 1:1 methylene chloride–hexane giving plates, m.p. 127–128°. The infrared spectrum of the nitrate exhibited prominent absorption maxima at 5.99 (ONO_2), 6.30, 6.55, 7.8 and 13.0 μ (N-NO_2).

A boiling solution of sodium acetate in acetic acid converted the nitrate to the acetate Ii. Hot ethanol and the nitrate produced the crystalline **1-ethoxy-2,4,6-trinitro-2,4,6-triazatetradecane**, m.p. 109–110°.

Anal. Calcd. for $C_{13}H_{28}N_6O_7$: C, 41.05; H, 7.42; N, 22.10. Found: C, 41.22; H, 7.60; N, 21.99.

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(30) R. Dhommée, *Compt. rend.*, **134**, 1314 (1902).