was filtered with suction, and dried at 60°; yield 0.33 g. (50%), m.p. 137–138° (dec.). Its infrared spectrum, characterized by strong bands at 6.70, 8.10, and 8.70μ,[7] was identical with that of an authentic specimen, prepared as follows:

1,1-Dinitroethane (12.0 g., 0.1 mole) was dissolved in 50 ml. of 95% ethanol. To this solution was added with shaking hydrazine hydrate (5.0 g., 0.1 mole). The mixture was cooled to 5° and filtered with suction. The yellow plates were washed with ethanol and dried at 60°; yield 14.0 g. (92%), m.p. 135.8° (dec.).

Anal. Calcd. for $C_2H_8N_4O_4$: C, 15.79; H, 5.26; N, 36.85. Found: C, 15.94; H, 5.22; N, 36.77.

1,1-Dinitropropane hydrazine salt. Ethyl α,α-dinitrobutyrate (1.2 g., 0.0058 mole), dissolved in 10 ml. of 95% ethanol, was refluxed with hydrazine hydrate (0.291 g., 0.00582 mole) for 2 hr. The oily product (0.97 g.) remaining after removing the solvent was crystallized from little 95% ethanol and furnished yellow needles; yield 0.29 g. (30%), m.p. 102° (dec.), which had the same infrared spectrum as the authentic salt described below.

Equimolar portions of 1,1-dinitropropane and hydrazine hydrate in ethanol gave an 81% yield of yellow hydrazine salt, m.p. 102–103° (dec.), with strong absorption bands at 6.76, 8.20 and 8.88μ.[7]

Anal. Calcd. for $C_3H_{10}N_4O_4$: C, 21.69; H, 6.06; N, 33.73. Found: C, 21.95; H, 6.18; N, 33.68.

Infrared absorption spectra were determined with a Perkin Elmer Model 21 spectrophotometer.

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[CONTRIBUTION FROM THE LOS ALAMOS SCIENTIFIC LABORATORY, UNIVERSITY OF CALIFORNIA]

Some Michael-Like Additions of Primary Nitramines*

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Several primary nitramines react with acrylonitrile, methyl acrylate, methyl vinyl ketone, acrylamide, and diethyl maleate under basic conditions to give secondary nitramines. Some chemical and physical properties of the adducts are given.

In the course of studies of the chemistry of nitramines we have observed Michael-like additions of several primary aliphatic nitramines to certain activated unsaturated systems giving secondary nitramines in good yields. The reaction offers an alternate route for the preparation of such substituted secondary nitramines which were reported previously by Frankel and Klager.[1] Primary aliphatic nitramines react with the unsaturated systems indicated below:

$$RNHNO_2 + XCH{=}CHY \xrightarrow{\text{Base}} RN(NO_2)CHX{-}CH_2Y$$

Y = acetyl, carbethoxy, amido, or cyano;
X = hydrogen except where X and Y are carbethoxy

The adducts are best obtained by warming the primary nitramine with an excess of the unsaturated compound in the presence of catalytic amounts of Triton B without solvent. The same compounds also arise when aqueous methanol solutions of the alkali metal salts of primary nitramines are treated with the unsaturated compounds. However, as is anticipated from the known retrogression of the Michael reaction,[2] the yields are much lower under these conditions. The simultaneous addition of methanol to the unsaturated systems to give the β-methoxy compounds also contributes to the low yields when the latter method is used. Thus, with acrylonitrile the secondary nitramines are accompanied by β-methoxypropionitrile.[3]

Reaction conditions, yields, physical properties, and analytical data for the individual adducts are given in Table I. 4-Nitro-4-aza-pentanenitrile (I) and methyl 4-nitro-4-azapentanoate (II) are reported by Frankel and Klager;[1] 4,7 dinitro-4,7-diazadecanedinitrile (X) was previously prepared by the nitration of the adduct obtained from ethylenediamine and acrylonitrile.[4]

The methyl vinyl ketone–methylnitramine adduct appears to form in a normal way and crude 5-nitro-5-aza-2-hexanone (III) can be washed free of methylnitramine with water to give a crude product which, however, is high in carbon. Attempts at purification by distillation give instead a mixture in which methylnitramine is a major constituent. The ketone III also resists purification by chromatographic treatment on an acid washed alumina packed column.

These compounds show ultraviolet[5] and infrared[6] absorption spectra typical of secondary nitramines, the most important features of which are also given in Table I.

The adducts are assigned the secondary nitramine structure primarily on the basis of their infrared and ultraviolet absorption spectra. Samples of

* This work was performed under the auspices of the U. S. Atomic Energy Commission.

(1) M. B. Frankel and K. Klager, *J. Am. Chem. Soc.*, **78**, 5428 (1956).

(2) C. K. Ingold, *Structure and Mechanism in Organic Chemistry*, Cornell Univ. Press, Ithaca, N. Y., 1953, p. 691.

(3) H. A. Bruson, U. S. Patent **2,280,791** [*Chem. Abstr.*, **36**, 5589 (1942)].

(4) M. H. Gold, Aerojet-General Corp., Azusa, Calif., personal communication.

(5) R. N. Jones and G. D. Thorn, *Can. J. Research*, **27B**, 828 (1949).

(6) L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, Wiley and Sons, New York, 1954, p. 252.

TABLE I

METHOD OF PREPARATION AND PROPERTIES OF SECONDARY NITRAMINES PREPARED

Reactants		Method and Conditions[a]			Product	Yield, %	B.P. °C.[b] mm.		$n_D^{25°}$
Nitramine	Conjugated compound		°C.	Hr.					
Methyl-	Acrylonitrile	A[a]	55	3	4-Nitro-4-azapentanenitrile (I)[1]	78	84–86	0.06	1.4858
	Methyl acrylate	A	55	6	Methyl 4-nitro-4-azapentanoate (II)	62	64	0.03	1.4694
	Methyl acrylate	B	40	36	Methyl 4-nitro-4-azapentanoate (II)	30	70–74	0.1	
	Methyl vinyl ketone	A	60	6	2-Nitro-2-aza-5-hexanone (III)	38	[Crude oil]		1.4795
Ethyl-	Acrylonitrile	A	75	5	4-Nitro-4-azahexanenitrile (IV)	72	110	0.1	1.4792
	Methyl acrylate	A	75	5	Methyl 4-nitro-4-azahexanoate (V)	51	62–65	0.1	1.4651
	Methyl acrylate	B	60	2	Methyl 4-nitro-4-azahexanoate (V)	15	62–65	0.1	
	Methyl vinyl ketone	A	60	6	3-Nitro-3-aza-6-heptanone (VI)	68	114	2	1.4715
	Acrylamide	A	60	24	4-Nitro-4-azahexanamide (VII)	75	[M.p. 95–96]		
	Diethyl maleate	A	80	96	Ethyl 3-carbethoxy-4-nitro-4-azahexanoate (VIII)	15	112–115	0.1	1.4544
n-Butyl-	Methyl acrylate	A	75	20	Methyl 4-nitro-4-azaoctanoate (IX)	45	110–113	0.1	1.4622
	Methyl acrylate	B	55	6	Methyl 4-nitro-4-azaoctanoate (IX)	22	110–113	0.1	1.4622
Ethylenedi-	Acrylonitrile	A	75	6	4,7-Dinitro-4,7-diazadecanedinitrile (X)	70	[M.p. 128–129]		
	Methyl acrylate	A	70	24	Dimethyl 4,7-dinitro-4,7-diazadecane dioate (XI)	72	[M.p. 122–124]		
	Methyl acrylate	B	50	2	Dimethyl 4,7-dinitro-4,7-diazadecanedioate (XI)	20	[M.p. 122–124]		
N-Methylethylenedi-	Acrylonitrile	A[c]	60	8	4,7-Dinitro-4,7-diazaoctanenitrile (XII)	70	[M.p. 91–92]		
	Ethyl acrylate	A[c]	55	8	Ethyl 4,7-dinitro-4,7-diazaoctanoate (XIII)	48	[M.p. 38–39]		
	Methyl acrylate	A[c]	60	8	Methyl 4,7-dinitro-4,7-diazaoctanoate (XIV)	74	[M.p. 61–62]		

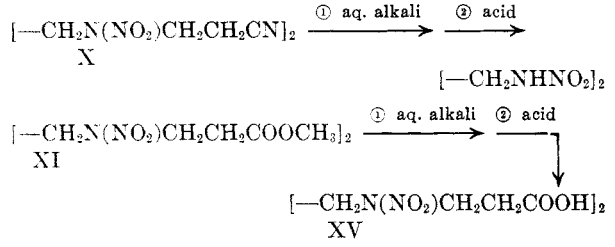
Compound	Analyses[d] Calcd. Formula	C	H	N	Found C	H	N	Infrared Absorption[e] λC = 0, μ	λ NO_2, μ	Ultraviolet Absorption[h] λ_{max}, mμ	Log ε
I	$C_4H_7N_3O_2$	37.21	5.46	32.54				[4.50][f]	6.53, 7.76	239	3.84
II	$C_5H_{10}N_2O_4$	37.03	6.22	17.28	37.29	6.49	16.82	5.72	6.63, 7.78		
II	$C_5H_{10}N_2O_4$	37.03	6.22	17.28	37.08	6.43	17.21				
III	$C_5H_{10}N_2O_3$	41.09	6.90	19.17	45.94	7.43		5.80	6.55, 7.75		
IV	$C_5H_9N_3O_2$	41.95	6.34	29.36	42.51	6.41	29.26	[4.49][f]	6.50, 7.82	240	3.84
V	$C_6H_{12}N_2O_4$	40.90	6.87	15.90	41.01	7.14	15.46	5.66	6.50, 7.77	241	3.86
V	$C_6H_{12}N_2O_4$	40.90	6.87	15.90	40.72	6.83	15.89				
VI	$C_6H_{12}N_2O_3$	44.99	7.55	17.49	45.01	7.50	17.52	5.80	6.60, 7.85		
VII	$C_5H_{11}N_3O_3$	37.26	6.88	26.08	37.49	6.92	26.16	5.92	6.61, 7.79	241	3.83
VIII	$C_{10}H_{18}N_2O_6$	45.79	6.92	10.68	45.95	7.19	10.19	5.78	6.57, 7.70		
IX	$C_8H_{16}N_2O_4$	47.05	7.90	13.72	47.09	7.40	14.24	5.74	6.61, 7.78	242[i]	3.89[i]
IX	$C_8H_{16}N_2O_4$	47.05	7.90	13.72			13.24				
X	$C_8H_{12}N_6O_4$	37.50	4.72	32.80	37.07	4.77	31.63		6.55,[g] 7.86[g]	239[i]	4.04[i]
XI	$C_{10}H_{18}N_4O_8$	37.27	5.63	17.39	36.79	5.02	16.95	5.77	6.57, 7.88		
XII	$C_6H_{11}N_5O_4$	33.18	5.11	32.25	32.91	5.22	31.90	[4.51][f]	6.55, 7.88		
XIII	$C_8H_{16}N_4O_6$	36.36	6.10	21.20	36.69	6.36	20.78	5.77	6.55, 7.87		
XIV	$C_7H_{14}N_4O_6$	33.60	5.64	22.39	33.75	6.09	22.12	5.75	6.55, 7.88		

[a] Refer to Experimental Section for details of methods A and B. [b] All temperatures are uncorrected. [c] At the end of the reaction period these products were isolated by stripping off the volatiles under reduced pressure and crystallizing the residues from methanol. [d] Microanalyses by M. J. Naranjo and C. A. Esquibel. [e] Infrared absorption spectra were determined with a Model 21 Perkin-Elmer recording instrument in matched 0.1-mm. sodium chloride cells in chloroform solution unless otherwise specified. [f] C≡N stretching absorption. [g] In acetonitrile solution. [h] Ultraviolet absorption spectra were determined by H. E. Ungnade with a Model DR Beckman instrument in 1-cm. fused silica cells in 95% ethanol unless otherwise specified. [i] In 92 parts of 95% ethanol and 8 parts acetonitrile.

compounds I and X kindly furnished by Gold[4] were indistinguishable from ours in other physical properties as well. Thus, we feel that the alternate structure, $R-N=\overset{\uparrow}{N}(\rightarrow O)-\overset{|}{C}H-CH_2Y$, arising by addition of the *aci*-form of the primary nitramine, is eliminated.

The secondary nitramines, with the exception of the ketones already noted, are chemically stable compounds undergoing reactions typical of the functional groups which they contain. Apparently only where there is sufficient activation on the carbon atom *beta* to the nitramine does strong alkali reverse the original condensation. Thus, 4,7-dinitro-4,7-diazadecanedinitrile (X) reacts rapidly with excess aqueous alkali to give ethylenedinitra-

mine and decomposition products of acrylonitrile while dimethyl 4,7-dinitro-4,7-diazadecanedioate (XI) under the same conditions is converted to the anion of 4,7-dinitro-4,7-diazadecanedioic acid (XV) which is stable in excess alkali.



EXPERIMENTAL

Methyl- and ethylnitramine, ethylenedinitramine, and *N*-methylethylenedinitramine were prepared as described by Franchimont and Klobbie;[7] *n*-butylnitramine was obtained by the method of van Erp.[8]

Michael additions: Method A. A mixture of the nitramine, 1.3–2.0 equivalents of the conjugated unsaturated compound, and a few drops of Triton B (commercial trimethylbenzyl ammonium hydroxide solution) was heated with stirring as specified in Table I. The progress of the reaction was followed by observing the relative intensities of the primary and secondary nitramine bands in the infrared. At the end of the reaction period the mixtures, except where noted, were poured into water and ether extracted. After decolorizing with charcoal and drying, solvent was removed from the ether extracts and liquid mixtures were separated by distillation through a small Vigreaux column; solid residues were purified by recrystallization from aqueous ethanol or methanol.

Method B. A solution of the sodium or potassium salt of the nitramine in 50% aqueous methanol was stirred while an equivalent weight of the conjugated unsaturated compound was added. After treating the mixture as specified in Table I, the product was isolated by diluting with an equal volume of cold water and extracting with ether. The dried ether extracts were then treated as described under Method A.

Action of alkali on 4,7-dinitro-4,7-diazadecanedinitrile (X). A suspension of 1 g. of 4,7-dinitro-4,7-diazadecanedinitrile (0.004 mole) in 6 ml. of water containing 1.3 g. (0.02 mole) of 85% potassium hydroxide was warmed on a steam bath for 1 hr. during which the suspension slowly cleared and ammonia was evolved. After chilling and acidification with 25% sulfuric acid, 0.49 g. (82%) of ethylenedinitramine, m.p. 174–178°, was obtained. The infrared spectrum of this sample in acetonitrile was indistinguishable from that of authentic ethylenedinitramine.

Action of alkali on dimethyl 4,7-dinitro-4,7-diazadecanedioate (XI); *preparation of 4,7-dinitro-4,7-diazadecanedioic acid* (XV). A suspension of 1 g. of dimethyl 4,7-dinitro-4,7-diazadecanedioate (0.003 mole) in 10 ml. of water containing 1.0 g. (0.018 mole) of 85% potassium hydroxide was warmed on a steam bath for 1 hr., cooled to room temperature, and acidified with concentrated hydrochloric acid. After chilling the mixture, 0.67 g. (76%) of 4,7-dinitro-4,7-diazadecanedioic acid (XV), m.p. 134.5–136.5°, was collected by filtration. Recrystallization from water gave plates melting at 142–143°, (Gold[4] gave the melting point of this compound as 141.5–142.5°.)

Anal. Calcd. for $C_8H_{14}N_4O_8$: C, 32.66; H, 4.80; N, 19.04; *neut. equiv.* 147. Found: C, 32.24; H, 4.58; N, 18.68; *neut. equiv.* 147.

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(7) A. P. N. Franchimont and E. A. Klobbie, *Rec. trav. chim.*, **7**, 343, 347, 354, and 356 (1888).

(8) M. H. van Erp, *Rec. trav. chim.*, **14**, 26 (1895).

[CONTRIBUTION NO. 830 FROM THE CHEMISTRY LABORATORIES OF INDIANA UNIVERSITY]

Reaction of Diethyl Oxalate with Some *ortho*-Substituted Anilines[1]

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Ethyl 2-benzothiazolecarboxylate (I) may be obtained in excellent yield by refluxing *o*-aminobenzenethiol with excess diethyl oxalate. However, *o*-aminophenol condenses with diethyl oxalate to yield a different type of product, the oxanilide III, while *o*-phenylenediamine formed still a third type of condensation product, the quinoxaline IV. The nature of the condensation products in these reactions was not altered by varying the conditions.

In connection with another problem, it was desirable to obtain large samples of esters of heterocyclic carboxylic acids, such as 2-benzothiazolecarboxylic acid. Ethyl 2-benzothiazolecarboxylate (I) has been previously prepared from the acid,[3] which, in turn, was prepared in several steps from other 2-substituted benzothiazoles.[4] A direct and more convenient method for preparing this ester from commercially available materials has now been found, which involves the condensation of 2-aminobenzenethiol with diethyl oxalate.

Hofmann,[5] in 1880, isolated 2,2′-bibenzothiazolyl (II) when these reactants were heated for "a long time and at a high temperature." It seemed reasonable that the reaction proceeded through the

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(2) Taken in part from the thesis of J. E. Van Verth, presented in partial fulfillment of the requirements for the degree of Doctor of Philosophy at Indiana University, 1957.

(3) (a) S. G. Fridman, *Zhur. Obshchet Khim.*, **20**, 1191 (1950); *Chem. Abstr.*, **45**, 1579 (1951); (b) A. Reissert, *Ber.*, **37**, 3708 (1904).

(4) (a) H. Gilman and J. A. Beel, *J. Am. Chem. Soc.*, **71**, 2328 (1949); (b) Y. Mizuno, *J. Pharm. Soc. Japan*, **72**, 1263 (1952); (c) H. Salkowski and W. Kunze, German Patent 613,067, May 11, 1935; *Chem. Abstr.*, **29**, 5461 (1935).

(5) A. W. Hofmann, *Ber.*, **13**, 1223 (1880).