

The authentic salts of the two 1,1-dinitroparaffins have been prepared by action of hydrazine hydrate on the dinitroparaffins in ethanol.

TABLE I
 α, α -Dinitro Esters, $\text{RC}(\text{NO}_2)_2\text{COOEt}$

R	B.P., °C. (0.1 Mm.)	n_D^{25}	Yield, %	λ (μ) ^a		
				$\lambda(\text{C}=\text{O})^a$	$\lambda(\text{NO}_2)^a$	$\lambda(\text{NO}_2)^a$
H	—	1.4321	11	5.65	6.31	7.51
Me	45	1.4327	17	5.66	6.31	7.52
Et	50	1.4340	17	5.66	6.31	7.54
Bu	60	1.4393	8	5.67	6.32	7.58

R	Calcd.			Found		
	C	H	N	C	H	N
H	—	—	—	—	—	—
Me	31.26	4.19	14.58	31.24	3.83	14.60
Et	34.95	4.89	13.59	35.11	4.62	13.20
Bu	41.03	6.02	11.96	41.58	5.93	11.93

^a Determined in capillary cells as liquid films.

EXPERIMENTAL⁴

Preparation of monoethyl alkylmalonates. Monoethyl malonate was obtained according to Freund,⁵ whereas the homologs were prepared by a modified procedure³ which is given in detail for monoethyl *n*-butylmalonate. Ethyl *n*-butylmalonate (100 g., 0.462 mole), dissolved in 250 ml. of absolute ethanol, was added to a cold solution of potassium hydroxide (26.0 g., 0.462 mole) in 250 ml. of absolute ethanol. The mixture was stirred and allowed to stand at room temperature for 16 hr. It was refluxed for 0.5 hr., filtered, and evaporated under reduced pressure. The semisolid opaque residue was dissolved in 100 ml. of water and extracted twice with 50 ml. of petroleum ether. The extract was dried and evaporated giving 10 g. (10% of starting ester, n_D^{25} 1.4213). The aqueous layer was acidified with concentrated hydrochloric acid (with cooling) and extracted with benzene. The extracts were washed with water, dried by distilling the benzene-water azeotrope, and evaporated from a steam bath at 50 mm. The colorless oil was used without further purification. The yields and properties of the half esters are listed in Table II.

TABLE II

PREPARATION OF MONOETHYL ALKYL MALONATES, $\text{RCH}(\text{COOH})\text{COOEt}$

R	Recovered Diester, %	n_D^{25}	Half Ester Yield, %	λ (μ) ^a		
				n_D^{25}	$\lambda_{\text{C}=\text{O}}$	μ^a
H	0	1.4121	51	1.4233	5.75	5.80
Me	7-11	1.4126	51-63	1.4253	5.75	5.80
Et	16	1.4153	72	1.4281	5.74	5.80
<i>n</i> -Bu	10	1.4213	82	1.4352	5.75	5.80

^a Determined as liquid films.

(4) All temperatures are uncorrected. Analyses by M. Naranjo.

(5) M. Freund, *Ber.*, **17**, 780 (1884)

The nitration of monoethyl methylmalonate with 100% nitric acid.

Monoethyl methylmalonate (7.3 g., 0.05 mole) was added dropwise with stirring and cooling to 30 ml. of 100% nitric acid. The exothermic reaction was controlled by ice cooling. The reaction mixture was allowed to stand at room temperature for 22 hr. Then it was poured on ice and extracted with chloroform. The extract was washed with water, dried over sodium sulfate, and distilled to remove the solvent. The residue (4.0 g.) was distilled from a Hickman still, giving 3 g. of a colorless oil, b.p. 80° (0.1 mm.), n_D^{25} 1.4432. Besides carbonyl absorption at 5.67 μ and the nitro band at 6.29 μ , this oil had bands at 6.07 and 7.88 μ and increased absorption at 11-12 μ .

Anal. Calcd. for $\text{C}_5\text{H}_8\text{N}_2\text{O}_7$ (nitronitrate ester): C, 28.86; H, 3.87; N, 13.46. Found: C, 29.96; H, 3.98; N, 12.92.

Ethyl α -nitratopropionate,⁶ b.p. 64° (7 mm.), n_D^{25} 1.4129, had the following absorption bands: $\lambda(\text{C}=\text{O})$ 5.70 μ , $\lambda(\text{NO}_2)$ 6.06, 7.84, 11.74 μ .

The nitration of monoethyl alkylmalonates with 70% nitric acid. The monoethyl alkylmalonate (10 g.) was added in small portions with stirring to 70 ml. of 70% nitric acid maintained at 45-50°. The reaction had an induction period of 15-20 min. and was exothermic. The mixture turned green and evolved carbon dioxide and nitrogen dioxide which were removed by suction. After the addition had been completed, the mixture was stirred for 1 hr. at 45-50° and poured on ice. The aqueous solution was extracted with chloroform and the extract was washed with water and dried over sodium sulfate. The dry chloroform solution was evaporated at 50 mm. and below 25°. The residual pale yellow oil was distilled from a Hickman still under reduced pressure. The yields and properties of the dinitro esters appear in Table I.

Ethyl dinitroacetate hydrazine salt. A yellow solution was formed when ethyl dinitroacetate (3.56 g., 0.02 mole) was dissolved in 10 ml. of 95% ethanol. The solution became orange and warmed exothermically on addition of hydrazine hydrate (1.0 g., 0.02 mole). On cooling, yellow plates separated which were filtered with suction, washed with ice-cold methanol, and dried at 60°; yield 3.17 g. (75%), m.p. 119-121°. A small second crop was combined with this material and the mixture was recrystallized from hot 95% ethanol. The salt separated in pale yellow needles weighing 2.44 g. It was not sensitive to heat or impact, melted at 119.5-120°, and had strong absorption bands at 6.69, 7.88, and 8.83 μ .⁷

Anal. Calcd. for $\text{C}_4\text{H}_8\text{N}_4\text{O}_6$: C, 22.86; H, 4.79; N, 26.67. Found: C, 23.14, 23.16; H, 4.62, 5.31; N, 26.48.

Dinitroacetylhydrazide hydrazine salt. The hydrazine salt of ethyl dinitroacetate (1.05 g., 0.005 mole) was dissolved in 10 ml. of water. To this solution was added hydrazine hydrate (0.25 g., 0.005 mole) and the mixture was allowed to stand at room temperature for 18 hr. The yellow aqueous solution was evaporated under reduced pressure (1 mm.). The residue was a yellow sirup which solidified on standing, yield 1.01 g. (theory 0.98 g.). It was crystallized twice from 95% ethanol and dried at 60° to yield 0.15 g. of yellow plates, m.p. 106° (dec.), $\lambda(\text{NH})$ 3.14 μ , $\lambda(\text{C}=\text{O})$ 5.94 μ , $\lambda(\text{NH def.})$ 6.22 μ , $\lambda[-\text{C}(\text{NO}_2)_2]$ 6.75, 7.94, 8.90 μ .⁷

Anal. Calcd. for $\text{C}_2\text{H}_5\text{N}_4\text{O}_5$: C, 12.24; H, 4.11; N, 42.88. Found: C, 12.29; H, 3.94; N, 42.76.

1,1-Dinitroethane hydrazine salt. Pure ethyl dinitropropionate (0.84 g., 0.0043 mole) was dissolved in 10 ml. of 95% ethanol and treated with 0.225 g. (0.0045 mole) of hydrazine hydrate. The solution was allowed to stand. A yellow product crystallized in plates after 0.5 hr. at room temperature,

(6) A. F. Ferris, K. W. McLean, I. G. Marks, and W. D. Emmons, *J. Am. Chem. Soc.*, **75**, 4078 (1953).

(7) According to J. F. Brown [*J. Am. Chem. Soc.*, **77**, 6346 (1955)], potassium salts of 1,1-dinitroparaffins absorb at 8.05 and 8.69 μ . The salts investigated in this laboratory always showed a third strong band at 6.72 \pm 0.03 μ (in KBr disks).

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 8.70 μ ,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 C₂H₈N₄O₄: 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 8.88 μ .⁷

Anal. Calcd. for C₃H₁₀N₄O₄: 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]

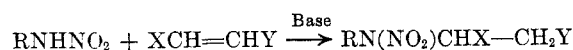
Some Michael-Like Additions of Primary Nitramines*

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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:



Y = acetyl, carboethoxy, amido, or cyano;

X = hydrogen except where X and Y are carboethoxy

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 ultraviolet⁵ and infrared⁶ 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

(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.

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(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.