g. of red crystalline product, m.p. 90–91°, which could be recrystallized from ligroin without change in melting point.

Anal. Calcd. for $C_{17}H_{22}N_2O_2S$: C, 64.11; H, 6.96; N, 8.80. Found: C, 64.36; H, 7.06; N, 8.64.

Chromatography of mother liquors material in benzene on florisil gave 0.20 g. of methylene-di-*o*-nitrobenzenesulfide (XIIc), m.p. 175–177° (lit.[14] m.p. 170°).

Anal. Calcd. for $C_{13}H_{10}N_2O_4S_2$: C, 48.45; H, 3.13; N, 8.69; S, 19.90. Found: C, 48.52; H, 3.07; N, 8.63; S, 19.87.

Reaction of 1-Pyrrolidinocyclohexene (I) with *m*- and *p*-Nitrobenzene Disulfides (Xa,b).—To a solution of 7.5 g. (0.05 mole) of enamine and 5.0 g. (0.05 mole) of triethylamine in 50 ml. of methylene chloride was added 7.7 g. (0.025 mole) of (a) *p*-nitrobenzene disulfide or (b) *m*-nitrobenzene disulfide with 180 ml. of methylene chloride, slowly with stirring and cooling in ice. After standing at room temperature for 20 hr., the solvent was removed under vacuum and the residue triturated with cyclohexane to give the following compounds.

(a) 1.4 g. of methylene-di-*p*-nitrobenzene sulfide (XIIa), m.p. 181–182° (lit.[15] m.p. 179°), recrystallized from benzene.

Anal. Calcd. for $C_{13}H_{10}N_2O_4S_2$: C, 48.45; H, 3.13; N, 8.69; S, 19.90. Found: C, 48.75; H, 3.11; N, 8.70; S, 19.82.

(b) 7.7 g. of solid which could be separated by methanol into soluble amine hydrosulfide and 4.3 g. of insoluble methylene-di-*m*-nitrobenzene sulfide (XIIb), m.p. 140–141°, recrystallized from ethanol.

Anal. Calcd. for $C_{13}H_{10}N_2O_4S_2$: C, 48.45; H, 3.13; N, 8.69; S, 19.90. Found: C, 48.62; H, 3.11; N, 9.43; S, 19.79.

Concentration of cyclohexane filtrates, solution in methylene chloride, washing with dilute hydrochloric acid, concentration, and crystallization from cyclohexane gave (a) 2.1 g. (33% yield), m.p. 97–98°, of Va and (b) 5.0 g. (79% yield), m.p. 56–57°, of Vc. In another experiment 7.7 g. (0.025 m.) of *p*-nitrophenyl disulfide and 180 ml. of methylene chloride were added slowly to 3.8 g. (0.025 mole) of enamine and 5.0 g. (0.050 mole) of triethylamine in 50 ml. of methylene chloride with cooling in ice. After 20 hr. at room temperature the concentrated reaction mixture yielded 2.9 g. of methylene-di-*p*-nitrobenzene sulfide (XIIa), 1.7 g. of water-soluble amine hydrosulfide material and 1.3 g. of 2,6-di(4-nitrobenzenesulfenyl)-2-pyrrolidinocyclohexene (IVa), crystallized from 100 ml. of methanol and 20 ml. of ether. Concentration of the mother liquors, and hydrolysis of the residue with excess 1% hydrochloric acid at room temperature for 2 hr. gave 4.0 g. of 2-(4-nitrobenzenesulfenyl)cyclohexanone (Va), 63% yield, after recrystallization from hexane.

1,5-Dithiaspiro[5.5]undecan-1-one (XVI).—A solution of 9.0 g. (0.021 mole) of propane-1,3-dithiol-di-*p*-toluenesulfonate, 4.0 g. (0.068 mole) of triethylamine, and 3.2 g. (0.021 mole) of enamine in 50 ml. of dry dioxane was stirred under nitrogen for 3 hr. and then refluxed 20 hr. After concentration under vacuum, solution in ether, washing with dilute hydrochloric acid, and reconcentration, the crude product was passed over Florisil in 1:1 benzene–petroleum ether. Distillation at 120–180° (0.001 mm.) gave 1.85 g. of oily product which could be purified further by preparative thin layer chromatography on Merck Alumina G with 3:1 cyclohexane–benzene as solvent and redistillation at 140° (0.001 mm.) to give 1.20 g. (28% yield) of product, m.p. 53–54°, from petroleum ether; infrared, ν_{max} 1690 cm.$^{-1}$ (C=O) in potassium bromide.

Anal. Calcd. for $C_9H_{14}S_2O$: C, 53.43; H, 6.98. Found: C, 53.45; H, 7.01.

A dinitrophenylhydrazone, m.p. 154–155°, crystallized from ethanol.

Anal. Calcd. for $C_{15}H_{18}N_4O_4S_2$: C, 47.10; H, 4.74; N, 14.65. Found: C, 47.36; H, 4.96; N, 14.41.

A semicarbazone crystallized from ethanol, m.p. 235–236°.

Anal. Calcd. for $C_{10}H_{15}N_3OS_2$: C, 46.10 H, 6.97; N, 16.13. Found: C, 45.88; H, 6.55; N, 16.26.

Acknowledgment.—The author is greatly indebted to Mr. L. Dorfman and associates of CIBA, Summit, New Jersey, for n.m.r. spectra. Mr. G. Warner provided the *m*-nitrobenzenesulfenyl chloride and gave assistance in some initial experiments and Mr. J. Nelson provided the propane-1,3-dithiol-di-*p*-toluenesulfonate. Professor E. Eliel helpfully discussed some of the n.m.r. spectra. Microanalyses were given by Mr. G. I. Robertson. The work was supported by National Science Foundation grant G.P. 225.

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[14] D. G. Foster and E. E. Reid, *J. Am. Chem. Soc.*, **46**, 1936 (1924).

[15] W. R. Waldron and E. E. Reid, *ibid.*, **45**, 2399 (1923).

Michael Additions of Nitroform. II. The Nitrite Elimination Reaction[1]

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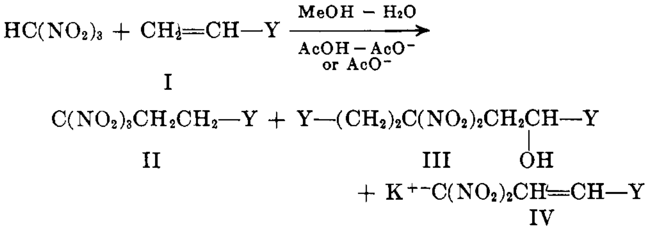
In absolute methanol, potassium trinitromethide adds to methyl acrylate, acrylonitrile, and acrylamide to yield the potassium salts of methyl 4,4-dinitro-2-butenoate, 4,4-dinitro-2-butenenitrile, and 4,4-dinitro-2-butenamide. With acrylamide as the augend, a second product, potassium 4,4-dinitro-2-hydroxybutyramide, was formed. Proofs of structure of these new dinitromethyl derivatives are described.

In the first paper in this series,[2] it was reported that the reaction of nitroform with methyl acrylate (I, Y = $COOCH_3$) or methyl vinyl ketone (I, Y = $COCH_3$) yielded, in addition to the Michael adducts II methyl 4,4-dinitro-2-hydroxypimelate (III, Y = $COOCH_3$) and 5,5-dinitro-2-hydroxy-2,8-nonanedione (III, Y = $COCH_3$). In the case of the augend methyl acrylate, a second nitrite elimination product, the potassium salt of methyl 4,4-dinitro-2-butenoate (IV, Y = $COOCH_3$) was isolated in 34% yield from an aqueous methanol system at pH 4.5.



$$\underset{\text{I}}{HC(NO_2)_3 + CH_2{=}CH{-}Y} \xrightarrow[\substack{AcOH-AcO^- \\ \text{or } AcO^-}]{MeOH - H_2O} \underset{\text{II}}{C(NO_2)_3CH_2CH_2{-}Y} + \underset{\text{III}}{Y{-}(CH_2)_2C(NO_2)_2CH_2\underset{\displaystyle OH}{\underset{|}{CH}}{-}Y} + \underset{\text{IV}}{K^{+-}C(NO_2)_2CH{=}CH{-}Y}$$

We now wish to report that derivatives analogous to IV can be obtained from the heterogeneous reaction of the potassium salt of nitroform with the appropriate acrylic augend in methanol. Thus stirring a slurry of potassium trinitromethide in absolute methanol with methyl acrylate or acrylonitrile until a constant ultraviolet spectrum was obtained for the insoluble potassium salts, afforded a 48 and 50% yield, respectively, of the potassium salts of methyl 4,4-dinitro-2-butenoate (IV, Y = $COOCH_3$) and 4,4-dinitro-2-butenenitrile (IV, Y = CN). With acrylamide, in addition to the expected potassium salt of 4,4-dinitro-2-butenamide, there also was obtained a yellow potassium salt (V).

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[1] Presented in part at the 137th National Meeting of the American Chemical Society, Cleveland, Ohio, April, 1960, Abstracts of Papers, p. 560.

[2] L. A. Kaplan and M. J. Kamlet, *J. Org. Chem.*, **27**, 780 (1962).

$$K^{+-}C(NO_2)_3 + CH_2{=}CHCONH_2 \xrightarrow{\text{MeOH}} \text{IV, } Y = CONH_2 + \text{V}$$

Derivatives of 4,4-Dinitro-2-butenoic Acid.—The potassium salts (IV, Y = $COOCH_3$, CN, and $CONH_2$) were obtained as orange crystalline materials which were soluble in water, slightly soluble in methanol, and generally insoluble in organic solvents. Elemental analyses agreed well with those values calculated for the respective empirical formulas, and their ultraviolet spectra (Table I) showed them to be structurally similar. A comparison of the ultraviolet spectra of the potassium salts IV with that of the dipotassium salt of 4,4-dinitro-2-butenoic acid[3] (Table I) indicated that the salts IV also had the 3,3-dinitro-1-propene chromophore with the residual functionality: *viz.*, $-COOCH_3$, $-CN$, or $-CONH_2$, attached to C-1.

TABLE I

ULTRAVIOLET ABSORPTION SPECTRA OF $K^{+-}C(NO_2)_2CH{=}CH{-}Y$

Y	$\lambda_{max}^{H_2O}$	log ε
$-COOCH_3$	326	4.24
	396–402	3.98
$-CONH_2$	322	4.23
	401–406	3.96
$-CN$	320	4.29
	396–402	4.00
$-COO^-$	313	4.20
	406–413	3.92

Evidence for the four-carbon chain structure containing the C_2–C_3 double bond came from the results of the hydrolysis of the salts IV with hydrochloric acid. Under these conditions,[4] the dinitromethyl anion is converted to a carboxyl group. The product isolated from the hydrolysis of the salts IV was the expected fumaric acid.[5]

Confirmation of the structural assignments given to the potassium salts IV was based upon their convertibility to the previously prepared[3] dipotassium salt of 4,4-dinitro-2-butenoic acid with alkali. This conversion was found to be essentially quantitative.

The Yellow Salt V.—This salt was formed in roughly equimolar amounts together with the potassium salt of 4,4-dinitro-2-butenamide in the reaction of acrylamide with potassium trinitromethide in absolute methanol. Following a tedious fractional crystallization procedure, an analytical sample of the salt V was obtained which agreed with the empirical formula $C_4H_6N_3O_6K$. This formula is consistent with that of the monohydrate of potassium 4,4-dinitro-2-butenamide.[6] However, extended drying at 70° and 20 μ produced no change in the analytical results and, therefore, the previously mentioned empirical formula was presumed not to be a hydrate.

The infrared spectrum of the salt V afforded considerable information as to the functionality present in the molecule (Table II). The spectrum exhibited three –NH absorption bands, the frequencies of which were essentially identical with those of the potassium salt of 4,4-dinitrobutyramide (VI). In addition the band at 3400 cm.$^{-1}$, absent in the salt VI, was assigned to the hydroxyl group

TABLE II

PRINCIPAL INFRARED ABSORPTION BANDS OF THE POTASSIUM SALTS[a]

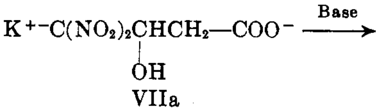
Compound	–NH	–OH	$>C{=}O$	Amide II	$-C(NO_2)_2^-$
Salt V	3160, 3350, 3450	3400[b]	1680	1580	1170, 1270
Amide VI	3180, 3350, 3450	...	1665	1595	1160, 1260
Salt VII	...	3380[c]	1600	...	1168, 1270
Acid VIII	...	...[d]	1570	...	1170, 1270

[a] ν_{max} in cm.$^{-1}$, samples run as Nujol mulls. [b] A strong band at 1080 cm.$^{-1}$ may be assigned to the –OH group. [c] A strong band at 1090 cm.$^{-1}$ may be assigned to the –OH group. [d] Two weak bands present at 3200 and 3500 cm.$^{-1}$ are probably due to water of hydration.

The carbonyl stretching frequencies for both V and VI agreed with the range given for the amide I band[7] and both the salts exhibited the amide II band. The presence of the dinitromethyl anion was evidenced by two strong absorption bands at about 1170 and 1270 cm.$^{-1}$.[8] On the basis of the previous spectral interpretation, it was evident that the salt V was a primary amide containing both the dinitromethyl anion and a hydroxyl group.

On treating V with aqueous alkali, ammonia was evolved and a new salt was produced. Elemental analyses after normal drying procedures agreed fairly well with the empirical formula $C_4H_4N_2O_7K_2 \cdot H_2O$. After drying at 70° and 20 μ for seven days, the resulting product analyzed well for the anhydrous salt VII. A comparison of the infrared spectrum of the salt VII with that of the dipotassium salt of 4,4-dinitrobutyric acid (VIII)[6] (Table II) indicated that the net effect of alkaline hydrolysis was the conversion of the amide function to the carboxylate anion. Thus the –NH and amide II absorption bands were no longer present in the salt VII and the amide I (>C=O) band had shifted to 1600 cm.$^{-1}$ which is characteristic of the carboxylate anion.[9]

The fact that the salt V or the hydrolysis product VII was not degraded completely to small fragments in alkaline media suggested that the hydroxyl group was not attached to the carbon atom α to the dinitromethyl group. Such a structure (VIIa) would be expected to be degraded by alkali as shown.



$$K^{+-}C(NO_2)_2\underset{OH}{\underset{|}{C}}HCH_2{-}COO^- \xrightarrow{\text{Base}}$$

VIIa

$$H\bar{C}(NO_2)_2 + O{=}CHCH_2COO^-$$

This path for hydrolytic cleavage of the structural fragment, $^-C(NO_2)_2CH(OH)-$, has been observed previously in the case of α-dinitromethylcarbinols,[10]

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[3] D. J. Glover, *Tetrahedron*, in press.

[4] M. J. Kamlet, L. A. Kaplan, and J. C. Dacons, *J. Org. Chem.*, **26**, 4371 (1961).

[5] Extensive decomposition occurred when potassium 4,4-dinitro-2-butenenitrile was hydrolyzed under these conditions. No fumaric acid was isolated.

[6] The dipotassium salt of 4,4-dinitrobutyric acid was found to form a stable hydrate. Private communication, D. J. Glover, these laboratories.

[7] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1958, p. 203.

[8] J. F. Brown, *J. Am. Chem. Soc.*, **77**, 6341 (1955).

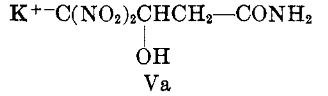
[9] R. N. Jones in "Chemical Applications of Spectroscopy," in "Techniques of Organic Chemistry," A. Weissberger, Ed., Interscience Publishers, New York, N. Y., 1956.

[10] P. Duden and G. Ponndorf, *Ber.*, **38**, 2031 (1905).

a 4,4-dinitro-5-hydroxyvalerate,[11] and 2,2-dinitro-1,3-propanediol.[12]

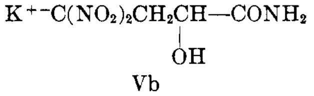
Confirmation of the four-carbon chain was obtained by refluxing the salt V with concentrated hydrochloric acid. Under these conditions, the dinitromethyl anion is converted to the carboxyl group.[13] However, instead of the expected product, malic acid, fumaric acid was isolated in about 25% yield.[14]

The isolation of fumaric acid taken together with the infrared spectral evidence suggested two possible structures for the salt V: 4,4-dinitro-3(or 2)-hydroxybutyramide, Va or Vb.



$K^{+-}C(NO_2)_2CH(OH)CH_2—CONH_2$

Va

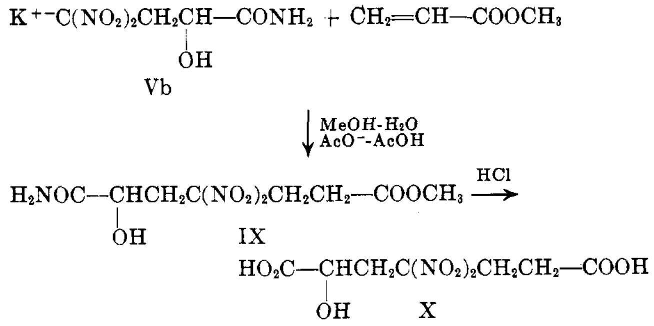


$K^{+-}C(NO_2)_2CH_2CH(OH)—CONH_2$

Vb

Preliminary evidence for the preference of the α-hydroxyamide structure Vb was based upon absorption maximum for the salt V in the ultraviolet; $\lambda_{\max}^{H_2O}$ mμ (log ε), 380 (4.21). Not only was this spectrum quite different from those of the unsaturated potassium salts IV, but the presence of a single maximum at 380 mμ (log ε >4.0) was shown to be characteristic of the chromophore $^-C(NO_2)_2CH_2$-Y, where Y is hydrogen, alkyl, or substituted alkyl.[15] By contrast, when Y is hydroxyl, $\lambda_{\max}$ is shifted to shorter wave lengths. Thus for potassium 2,2-dinitroethanol, $\lambda_{\max}^{\text{dil KOH}}$ mμ (log ε), is 365 (4.29).[15]

Final proof of the structural assignment given to the salt V was based upon its conversion to the previously characterized[2] 4,4-dinitro-2-hydroxypimelic acid (X). When the salt V was used as an addend in a Michael addition to methyl acrylate, the α-hydroxyamide ester IX was isolated as a crystalline solid. The conversion of IX to the dibasic acid X was readily accomplished by refluxing with constant boiling hydrochloric acid. Since the acid X is the α-hydroxy acid, the salt V must be the α-hydroxy amide, Vb.



$$K^{+-}C(NO_2)_2CH_2CH(OH)—CONH_2 \ (\text{Vb}) + CH_2{=}CH—COOCH_3 \xrightarrow{\text{MeOH-H}_2\text{O},\ \text{AcO}^-\text{-AcOH}} H_2NOC—CH(OH)CH_2C(NO_2)_2CH_2CH_2—COOCH_3 \ (\text{IX}) \xrightarrow{HCl} HO_2C—CH(OH)CH_2C(NO_2)_2CH_2CH_2—COOH \ (\text{X})$$

Experimental[16, 17]

Potassium 4,4-dinitro-2-butenoate (IV, Y = $COOCH_3$) was prepared by adding 0.32 mole (60 g.) of potassium trinitromethide (99% assay) to a solution of 0.48 mole (39.4 g.) of methyl acrylate in 750 ml. of absolute methanol. The resulting slurry was stirred at room temperature for 20 hr. During this time the insoluble potassium salts had changed from a fine yellow to a coarser orange solid, and the solvent phase became cherry-red in color. The insoluble material was filtered off, washed with ether, and dried *in vacuo*. Twenty-four grams of orange crystals (32.9%) *were obtained,* $\epsilon_{326}/\epsilon_{399}$ 1.81. *Concentration of the filtrates to* about one-half their original volume caused the precipitation of an additional 12.2 g. of similar material. Combined yield, 48%.

Recrystallization of a portion of the above combined product from methanol gave an analytical sample as thick hexagonal yellow-orange plates, $\epsilon_{326}/\epsilon_{399}$ 1.82.

Anal. Calcd. for $C_5H_5N_2O_6K$: C, 26.3; H, 2.2; N, 12.3; K, 17.1. Found: C, 26.4, 26.2; H, 2.5, 2.7; N, 12.8, 12.5; K, 17.1.

Further concentration of the mother liquors afforded a light yellow solid which proved to be mainly potassium nitrite. Three crops of this material totaling 6.5 g. were collected. This amounted to 50% of the theoretical amount based on the yield of IV (Y = $COOCH_3$) obtained. The remainder of the nitrite was probably lost as nitrous acid or methyl nitrite.

The red oil remaining after the removal of potassium nitrite was extracted with low boiling petroleum ether. Evaporation of the solvent from the combined extracts left a solid product (17.7 g.), m.p. 24–29°, which proved to be methyl 4,4,4-trinitrobutyrate (II). Authentic II had m.p. 27–28°.

The residue from the petroleum ether extraction was then taken up in ether, treated with charcoal, and concentrated. A white solid precipitated (4.1 g.), melting at 72.4–74.5°. This material did not depress the melting point of an authentic sample of dimethyl 4,4-dinitro-2-hydroxypimelate, m.p. 75.6–76.4°.[2]

Potassium 4,4-dinitro-2-butenenitrile (IV, Y = CN), was prepared by adding 1.0 mole (189 g.) of potassium trinitromethide to a solution of 1.5 moles (80 g.) of freshly distilled acrylonitrile in 1500 ml. of absolute methanol. The mixture was stirred continuously at room temperature. After 48 hr., the spectrum of the suspended solids exhibited two maxima: 322 and 380 mμ. The maximum at 380 mμ decreased in intensity and shifted to longer wave lengths with time, until after 235 hr. the insoluble material exhibited a constant ultraviolet spectrum with maxima at 320 and 396 mμ.

At this point the solids were filtered from the mixture, washed with 300 ml. of methanol, then 300 ml. of ether, and air dried. One hundred and four grams of a finely divided yellow solid were obtained. This crude product was recrystallized once from methanol–water to yield 97 g. (50%) of IV (Y = CN) as dichromatic orange crystals.

Anal. Calcd. for $C_4H_2N_3O_4K$: C, 24.6; H, 1.0; N, 21.6. Found: C, 24.2, 24.0; H, 1.2, 1.0; N, 23.0, 22.8.

Potassium 4,4-Dinitro-2-butenamide (IV, Y = $CONH_2$) and Potassium 4,4-Dinitro-2-hydroxybutyramide (Vb).—To a solution of 1.5 moles (107 g.) of acrylamide in 1500 ml. of absolute methanol was added 1.0 mole (189 g.) of potassium trinitromethide. The resulting slurry was stirred at room temperature and from time to time samples of the suspended solids were withdrawn for ultraviolet spectrophotometric analysis. After 14 days the intensity of the trinitromethide ion maximum (350 mμ) had decreased, while absorption on both sides of this peak had increased. At the end of 19 days, the trinitromethide ion maximum had been replaced by two new maxima at 328 and 380 mμ. After 26 days the ultraviolet spectrum of the suspended solids was essentially constant and it was presumed that the reaction had gone to completion. The suspended solids were separated from the mixture by filtration, washed with methanol, and dried. The yield of crude yellow salts was 125 g.

The crude salts were dissolved in a minimum amount of warm water, the solution heated to boiling, and an equal volume of methanol added. On slow cooling, the following crops of crystals were obtained: (a) 75.2 g. of mixed orange and yellow crystals; (b) 22.5 g. of mixed orange and yellow crystals containing about

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(11) L. Herzog, M. H. Gold, and R. D. Geckler, *J. Am. Chem. Soc.*, **73**, 749 (1951).

(12) H. Feuer, G. B. Bachman, and W. May, *ibid.*, **76**, 5124 (1954).

(13) The acid hydrolysis of potassium 4,4-dinitrobutyramide yields succinic acid,[4] while potassium 4,4-dinitro-2-butenamide yields fumaric acid under these conditions (*vide supra*).

(14) An equilibrium between fumaric and malic acids undoubtedly exists under the conditions of acid hydrolysis [J. M. Weiss and C. R. Downs, *J. Am. Chem. Soc.*, **44**, 1118 (1922)]. Because of the difference in solubility between the two acids in water, the malic acid present probably was lost during the work-up procedure.

(15) M. J. Kamlet and D. J. Glover, *J. Org. Chem.*, **27**, 537 (1962).

(16) Microanalyses were performed by Mary Aldridge, Department of Chemistry, American University, Washington, D. C. Ultraviolet spectra were determined in 1-cm. quartz cells with either a Cary Model 14 or Beckman Model DU spectrophotometer. Infrared spectra were determined with a Beckman Model IR-4 spectrophotometer with the samples prepared as Nujol mulls. All melting points are uncorrected.

(17) Many of the compounds described are explosive in nature and quite sensitive to impact or grinding. Appropriate precautions should be taken in their handling.

50% of colorless needles[18]; (c) 4.7 g. of almost colorless needles[18]; and (d) 18.6 g. of a dark red-brown pasty mass with some colorless needles.[18]

Subjecting crop a to a similar fractional crystallization procedure yielded following additional crops: (a1) 54.6 g. of mixed orange and yellow crystals; (a2) 9.7 g. of mixed orange and yellow crystals together with some colorless needles[18]; (a3) 5.5 g. of material which was visually identical with (a2); and (a4) 4.8 g. of a somewhat dark red residue which was obtained by evaporating the mother liquors.

A final fractional crystallization of crop a1 afforded 26.0 g. of lemon yellow crystals of the salt Vb and 18.6 g. of the salt IV (Y = $CONH_2$) as dichromatic orange crystals. The residues from this crystallization were combined with crops a2 and a3 and reworked to obtain an additional quantity of the two salts of somewhat lower purity.

Analytical samples of the salts Vb and IV (Y = $CONH_2$) were obtained by recrystallizing the previously obtained fractions from methanol–water.

Anal. of **potassium 4,4-dinitro-2-hydroxybutyramide (Vb).** Calcd. for $C_4H_6N_3O_6K$: C, 20.8; H, 2.6; N, 18.2; K, 16.9. Found: C, 20.7, 20.7; H, 2.6, 2.7; N, 18.2, 18.1; K, 16.9, 16.9. Drying the analytical sample 70° and 20 μ for 5 days did not change these analytical results.

Anal. of **potassium 4,4-dinitro-2-butenamide (IV,** Y = $CONH_2$). Calcd. for $C_4H_4N_3O_5K$: C, 22.5; H, 1.9; N, 19.7. Found: C, 22.4, 22.6; H, 2.1, 2.0; N, 20.3, 20.1.

Acid Hydrolysis of the Salts IV and Vb.—To 0.01 mole of IV (Y = $COOCH_3$) was added 20 ml. of 12 *N* hydrochloric acid, and the resulting mixture was refluxed for 18 hr. The resulting brown solution was concentrated to about 10 ml.[19] and extracted thoroughly with ether. The combined ether extracts were concentrated to about 5 ml. and 30 ml. of *n*-pentane was added. This caused the separation of a light tan solid which, after filtering and drying, had a melting point of 286–287° (sealed tube) (lit.[20] m.p. 293–295°). The yield was 0.1 g.

The crude fumaric acid was converted to its dimethyl ester by refluxing it with a solution of hydrogen chloride in methanol. Following the removal of the methanol and recrystallization from ether–pentane, the ester, obtained as glistening plates, melted at 100.8–102° and did not depress the melting point of an authentic sample of dimethyl fumarate prepared from fumaryl chloride.

In a similar manner, **potassium 4,4-dinitro-2-butenamide** and **potassium 4,4-dinitro-2-hydroxybutyramide** were converted to fumaric acid. Yields of the crude acid in these cases were about 0.5–0.7 g. In each case the acid was converted to the dimethyl ester for characterization.

Attempts were made to effect the acid hydrolysis of **potassium 4,4-dinitro-2-butenenitrile.** In each instance there was excessive carbonization of the organic material and it was not possible to extract fumaric acid from the resulting reaction mixture.

Alkaline Hydrolysis of the Potassium Salts IV.—Exactly 0.3598 g. of **potassium 4,4-dinitro-2-butenamide** was weighed into a 200-ml. volumetric flask and made up to volume with water. A 25-ml. aliquot of this solution was transferred to a 100-ml. volumetric flask, 10 ml. of 50% potassium hydroxide solution was added and, after mixing, the resulting solution was allowed to stand overnight. After diluting to volume, the following dilutions were made: 10 ml. to 100 ml., and 15 ml. of the resulting solution to 100 ml. with water. The optical density of the resulting solution was determined at 313 and 411 mμ.

O.D.$_{313}$ = 0.543, log ϵ_{313} 4.19; O.D.$_{411}$ = 0.288, log ϵ_{411} 3.92.

For the **dipotassium salt** of **4,4-dinitro-2-butenoic acid,** log ϵ_{313} 4.20, log ϵ_{411} 3.92.

Carrying out the previous procedure with **potassium 4,4-dinitro-2-butenenitrile** gave the following optical density and log ϵ values for a final concentration of 2.92×10^{-5} *M*.

O.D.$_{313}$ = 0.458, log ϵ 4.19; O.D.$_{411}$ = 0.244, log ϵ_{411} 3.92.

On a synthetic scale, 0.0044 mole (1.0 g.) of **potassium methyl 4,4-dinitro-2-butenoate** in 15 ml. of water was added to 2.0 g. of potassium hydroxide in 10 ml. of water. To the resulting solution was added 75 ml. of methanol and the solution cooled in ice. Since no precipitate formed, an additional 5.0 g. of potassium hydroxide was added. As soon as this had dissolved, a yellow precipitate began to form. This solid was filtered from the solution, washed with cold methanol and ether, and air dried. There was obtained 0.71 g. (71%) of the **dipotassium salt** of **4,4-dinitro-2-butenoic acid;** $\epsilon_{360}/\epsilon_{410}$ 0.438. Glover[3] reports $\epsilon_{360}/\epsilon_{410}$ 0.440. An analytical sample prepared by recrystallization from a large volume of methanol gave the following results.

Anal. Calcd. for $C_4H_2N_2O_6K$: N, 11.1. Found: N, 11.2, 11.6.

Hydrolysis of Potassium 4,4-Dinitro-2-hydroxybutyramide (Vb) to Dipotassium 4,4-Dinitro-2-hydroxybutyrate (VIIb).—To a solution of 0.0217 mole (5.01 g.) of the salt Vb in 30 ml. of warm water was added a solution of 0.0434 mole (2.44 g.) of potassium hydroxide in 20 ml. of methanol. The resulting solution was heated on the steam bath for 48 hr., at which time the evolution of ammonia had ceased. The resulting yellow solution was concentrated *in vacuo* until the mixture became pasty due to the separation of the dipotassium salt VIIb. The yellow salt was collected on a Büchner funnel and washed with 10 ml. of ice-water.[21] The material remaining on the funnel was then washed with 200 ml. of methanol, 50 ml. of ether, and sucked dry. After drying in the vacuum oven at 40° the following analytical results were obtained.

Anal. Calcd. for $C_4H_4N_2O_7K_2 \cdot H_2O$: C, 16.7; H, 2.1; N, 9.7; K, 27.1. Found: C, 16.6, 15.8; H, 2.0, 2.2; N, 10.2, 9.9; K, 28.9.

Since these results agreed fairly well with those calculated for a monohydrate of VIIb, it was decided to subject the material to vigorous drying at 70° and 20 μ in an Abderhalden pistol with phosphorus pentoxide. After 7 days under these conditions, the following analytical results were obtained.

Anal. Calcd. for $C_4H_4N_2O_7K_2$: C, 17.8; H, 1.5; N, 10.4; K, 28.9. Found: C, 17.4, 17.0; H, 1.8, 1.7; N, 10.3, 10.7; K, 27.3, 28.3.

6-Carbomethoxy-4,4-Dinitro-2-hydroxyhexanamide (IX).—A solution of 0.028 mole (6.65 g.) of the salt Vb was prepared in 100 ml. of water containing 0.03 mole (1.80 g.) of glacial acetic acid and 0.03 mole (2.46 g.) of sodium acetate. To this solution was added 0.06 mole (5.16 g.) of methyl acrylate and sufficient methanol to render the mixture homogeneous. The resulting solution was stirred for 7 days at room temperature. At the end of this time, a small amount of oil had separated. The mixture was thoroughly extracted with ether and the combined extracts were dried over magnesium sulfate, treated with Norit, and evaporated to dryness *in vacuo* to leave 6.5 g. of a pale yellow solid.

A portion of the crude material (4 g.) was purified for analysis by dissolving it in 1 l. of ether and treating the solution with Norit. The resulting colorless solution was concentrated to about 150 ml., whereupon the amide ester slowly crystallized in the form of fine white needles melting at 92.2–93°.

Anal. Calcd. for $C_7H_{13}N_3O_8$: C, 34.4; H, 4.7; N, 15.1. Found: C, 34.4, 34.4; H, 4.6, 4.4; N, 15.5, 15.0.

Infrared Spectrum.—$-$NH, 3180, 3280, 3450 cm.$^{-1}$; $-$OH, 1100, 3380 cm.$^{-1}$; $-C{=}O$, 1730 ($COOCH_3$), 1665, 1675 cm.$^{-1}$ $CONH_2$, possibly bonded and unbonded to OH; amide II, 1578 cm.$^{-1}$; $>C(NO_2)_2$, 1320, 1558 cm.$^{-1}$.

Hydrolysis of the Amide Ester IX.—Sixteen-thousandths of a mole (4.4 g.) of IX was refluxed with 60 ml. of concentrated hydrochloric acid and 20 ml. of water for 5.5 hr. The resulting solution was evaporated to near dryness *in vacuo* and the residual paste was extracted with 500 ml. of ether. The combined ether extracts were dried over magnesium sulfate, treated with Norit, and the solvent was removed *in vacuo*. The residual oil slowly crystallized on standing to yield 3.8 g. of a white solid melting at 137–139°. This product did not depress the melting point of an authentic sample of **4,4-dinitro-2-hydroxypimelic acid** and its infrared spectrum could be superimposed upon that of the authentic sample.

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[18] The colorless needles were shown to be potassium nitrate by comparison of the refractive index (1.506) and predominant crystal angle (78°) with that of an authentic sample.

[19] Some solid (potassium chloride) may separate at this point.

[20] E. H. Huntress and S. P. Mulliken, "Identification of Organic Compounds, Order I," John Wiley and Sons, Inc., New York, N. Y., 1941, p. 176.

[21] Although washing with water purified the salt VIIb, it also effected a considerable reduction in yield due to the extreme solubility of the salt in water at 0°.