Duplicate experiment on a 0.016-mole scale: yield 0.82 g. (30%), n_D^{17} 1.5335, α_D^{14} −0.21°, $[\alpha]_D^{14}$ −2.6° (*c* 8.23).

Reduction of the partially active ethyl (+)-β-methyl-β-phenylglycidate with lithium aluminum hydride. Reduction of the ethyl glycidate obtained by ethanolysis of (−)-menthyl β-methyl-β-phenylglycidate gave on a 0.021-mole scale 1.2 g. (35%) of (−)-3-phenylbutane-1,3-diol, n_D^{18} 1.5310, α_D^{17} −0.74°, $[\alpha]_D^{17}$ −6.2° (*c* 11.89). Duplicate experiment on a 0.015-mole scale: yield 1.0 g. (41%) n_D^{20} 1.5240 α_D^{12} −0.62°, $[\alpha]_D^{12}$ −6.4° (*c* 9.71).

Reduction of the ethyl glycidate obtained by ethanolysis of (+)-bornyl β-methyl-β-phenylglycidate afforded on a 0.046-mole scale 1.3 g. (17%) of 3-phenylbutane-1,3-diol, n_D^{17} 1.5290, α_D^{14} −0.25°, $[\alpha]_D^{14}$ −1.9° (*c* 13.29). Duplicate experiment on a 0.024-mole scale: yield 1.6 g. (40%), n_D^{18} 1.5329, α_D^{12} −0.28°, $[\alpha]_D^{12}$ −1.8° (*c* 15.88).

The infrared spectra of these products were completely identical with those of racemic 3-phenylbutane-1,3-diol and of the partially active samples described above. The diol gave correct analyses for carbon and hydrogen.

Addendum. According to the private communication of Professors M. Ohno and H. M. Walborsky, which has reached to us after completion of writing this paper, the Darzens condensation of (−)-menthyl chloroacetate with acetophenone and the following hydride reaction have been investigated independently in their laboratories. The formation of a mixture of glycols consisting of 95% 3-phenylbutane-1,3-diol and 5% 3-phenylbutane-1,2-diol was observed. Removal of the 1,2-glycol by periodate oxidation yielded the pure 1,3-glycol, $[\alpha]_D^{24}$ −9.1° (*c* 4.2, chloroform).[20] The possibility of the 1,3-diol samples obtained in our experiments being contaminated by the 1,2-diol was excluded by periodate titration. Apparently the 1,2-diol had been eliminated by chromatographic purification of the glycol over silica-gel column.

KYÔTO, JAPAN

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(20) Y. Inouye, S. Inamasu, M. Ohno, T. Sugita, and H. M. Walborsky, *J. Am. Chem. Soc.*, **83**, 2962 (1961).

[CONTRIBUTION FROM THE ORGANIC CHEMISTRY DIVISION, U. S. NAVAL ORDNANCE LABORATORY]

Reaction of 1,1,1,3-Tetranitropropane with Bases

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A product obtained in the reaction of the title compound with bases, reported by previous workers to be the potassium salt of 1,1,3-trinitropropane (II), is shown to be the potassium salt of 1,1,3-trinitro-2-propene (IV). Authentic II was synthesized by two independent methods. Evidence bearing on the mechanisms of the reactions is presented.

Novikov and co-workers[1] have recently reported that the reaction of 1,1,1,3-tetranitropropane (I) with dimethylamine in aqueous alcohol yielded as the main product a dimethylammonium salt which, on subsequent treatment with aqueous potassium chloride, was converted to a monopotassium salt. For this compound the Russian workers suggested the structure of the potassium salt of 1,1,3-trinitropropane (II), offering as evidence elemental analyses for potassium and nitrogen. The over-all yield in the transformation of I to the potassium salt was 74%. I was also purported to yield II as the main product on treatment with potassium acetate in acetone-ethanol.[2]

With aqueous ethanolic ammonia the reaction took a different course.[1] The major product obtained after treatment with aqueous potassium chloride was the dipotassium salt of 1,1,3,3-tetranitropropane (III), and only minor amounts of monopotassium salt were isolated. With the two higher homologs of I and dimethylamine, potassium acetate or potassium methoxide, only the potassium salts of 1,1,3,3-tetranitrobutane and 1,1,3,3-tetranitropentane were isolated and no trinitro derivatives corresponding to II were reported.[2]

We wish now to record the synthesis by two independent methods of the authentic potassium salt of 1,1,3-trinitropropane (II) whose properties differed markedly from those of the compound thought by Novikov to be II. We wish also to suggest evidence that the latter compound has the structure of the potassium salt of 1,1,3-trinitro-2-propene (IV).

$C(NO_2)_3CH_2CH_2NO_2$
I

$K^+ \bar{C}(NO_2)_2CH_2CH_2NO_2$
II

$K^+ \bar{C}(NO_2)_2CH_2C(NO_2)_2^- K^+$
III

$K^+ \bar{C}(NO_2)_2CH{=}CHNO_2$
IV

Our separate preparations of authentic II involved (a) the direct reduction of I with potassium iodide in methanol and (b) the reaction of the potassium salt of 2,2-dinitroethanol with nitroethylene in absolute methanol containing a slight excess of acetic acid. The products in both instances showed comparable ultraviolet and infrared spectra and similar crystal habits and melting behavior. Elemental analyses for both samples corresponded to II (Table I).

Method (a) is general for the conversion of 1,1,1-trinitroalkanes to salts of the corresponding 1,1-dinitro compounds. Under similar conditions, for example, methyl 4,4,4-trinitrobutyrate may be

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(1) S. S. Novikov, A. A. Feinsil'berg, S. A. Shevelev, I. S. Korsakova, and K. K. Babievskii, *Doklady Akad. Nauk S.S.S.R.*, **124**, 589 (1959).

(2) S. S. Novikov, A. A. Feinsil'berg, S. A. Shevelev, I. S. Korsakova, and K. K. Babievskii, *Doklady Akad. Nauk S.S.S.R.*, **132**, 846 (1960).

TABLE I

PROPERTIES OF II AND IV

	K, %	C, %	H, %	N, %	Melting Behavior[a]	Ultraviolet Spectrum	
						Solvent	λ_{max} (log ε)
Calcd. for $KC_3H_4N_3O_6$ (II)	18.02	16.58	1.84	19.35			374 mμ[c]
Calcd. for $KC_3H_2N_3O_6$ (IV)	18.18	16.75	0.93	19.54			
Found for authentic II	17.99	16.44	2.10	19.00	118–120°	H_2O[b]	374 mμ (4.25)
(Method a)		16.70	2.06	19.19	dec.		
(Method b)	17.47	16.55	1.91	19.13	122–124°	H_2O[b]	374 mμ (4.24)
		16.84	2.03	19.30	dec.		
Found for monopotassium salt	18.33	—	—	19.65	211–213°		
(Novikov's values)	17.99			19 84	dec.		
(Present investigation, Novikov's	—	16.40	1.09	19.34	195°	Dil. KOH	228 mμ (3.97)
$(CH_3)_2NH$ method)		16.89	1.15	19.17	(expl.)		394 (4.33)
(Potassium hydroperoxide method)	—	16.49	1.24	19.16	193°	Dil. KOH	228 mμ (3.96)
					(expl.)		394 (4.32)

[a] The temperatures at which these compounds decompose or explode depend strongly on impurities, particle size, and rate of heating. [b] It is our practice to determine spectra of 1,1-dinitroalkane salts in dilute alkali. The spectrum of II fades in dilute alkali, but is reasonably constant in neutral solution. [c] See text and reference 10.

transformed to the potassium salt of methyl 4,4-dinitrobutyrate in 77% yield, 5,5,5-trinitro-2-pentanone to the potassium salt of 5,5-dinitro-2-pentanone in 41% yield.[3] The yield in the conversion of I to authentic II was 33%.

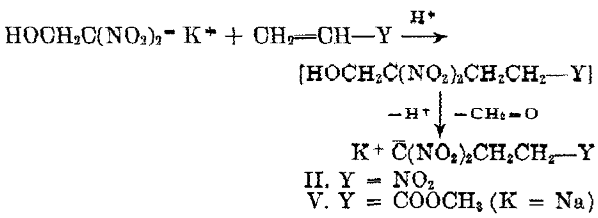
$$\mathrm{C(NO_2)_3CH_2CH_2{-}X + 2KI \longrightarrow K^+\,\bar{C}(NO_2)_2CH_2CH_2{-}X + KNO_2 + I_2}$$

$X = NO_2$ (II), $COOCH_3$, $COCH_3$

Analogous reductions of 1-bromo-1,1-dinitroalkanes to salts of the corresponding 1,1-dinitroalkanes have been reported.[4]

Method (b) was a modification of Klager's procedure for the preparation of the sodium salt of methyl 4,4-dinitrobutyrate (V) by the deformylation of methyl 4,4-dinitro-5-hydroxyvalerate.[5] In treating the potassium salt of 2,2-dinitroethanol with nitroethylene we had hoped to form the normal Michael adduct, 2,2,4-trinitro-1-butanol. Our reaction conditions were evidently insufficiently acidic, however, so that deformylation took place spontaneously and the only product isolated was authentic II. Although the yield was low (13%), we accomplished in the single step what we had hoped to accomplish in two.

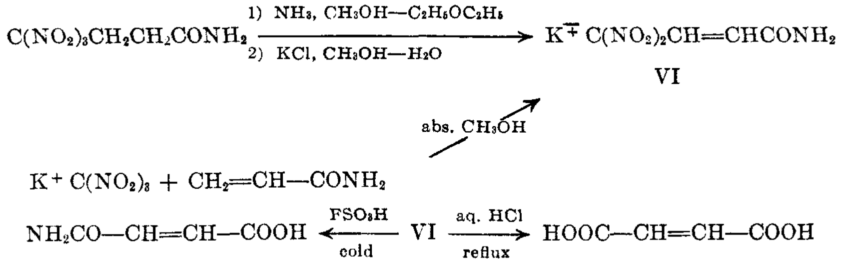
Prior to the Russian group's publication, we had treated I with potassium hydroxide and hydrogen peroxide in aqueous methanol and isolated two products which we had tentatively identified as III and IV. We have since repeated the reaction of I with dimethylamine, following exactly the procedure described by Novikov and co-workers. We have found that the products which we considered to be IV and which they reported as II were identical in ultraviolet and infrared spectra, crystal form, and melting behavior. Elemental analyses (Table I) favor structure IV.



$$\mathrm{HOCH_2C(NO_2)_2^-\,K^+ + CH_2{=}CH{-}Y \xrightarrow{H^+} [HOCH_2C(NO_2)_2CH_2CH_2{-}Y] \xrightarrow[-CH_2=O]{-H^+} K^+\,\bar{C}(NO_2)_2CH_2CH_2{-}Y}$$

II. $Y = NO_2$
V. $Y = COOCH_3$ ($K = Na$)

An exact analogy to the conversion of I to IV has been found in the reaction of 4,4,4-trinitrobutyramide with ammonia in methanol-ether. The only product isolated was an ammonium salt (64% yield) which, on treatment with potassium chloride in aqueous methanol, was converted to the potassium salt of 4,4-dinitro-2-butenamide (VI). The latter compound has been reported by Kaplan and Kamlet[6] to be an unexpected product in an



$$\mathrm{C(NO_2)_3CH_2CH_2CONH_2 \xrightarrow[2)\ KCl,\ CH_3OH{-}H_2O]{1)\ NH_3,\ CH_3OH{-}C_2H_5OC_2H_5} K^{\mp}\,C(NO_2)_2CH{=}CHCONH_2}$$

VI

$$\mathrm{K^+\,C(NO_2)_3 + CH_2{=}CH{-}CONH_2 \xrightarrow{abs.\ CH_3OH} VI}$$

$$\mathrm{NH_2CO{-}CH{=}CH{-}COOH \xleftarrow[cold]{FSO_3H} VI \xrightarrow[reflux]{aq.\ HCl} HOOC{-}CH{=}CH{-}COOH}$$

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[3] D. J. Glover and M. J. Kamlet, *J. Org. Chem.*, **26**, 4734 (1961).

[4] K. Klager, *Anal. Chem.*, **23**, 534 (1951); J. Meisenheimer, *Ber.*, **36**, 434 (1903).

[5] K. Klager, *J. Org Chem.*, **16**, 161 (1951).

[6] L. A. Kaplan and M. J. Kamlet, *Abstracts Papers Amer. Chem. Soc.*, **137**, 56-O (1960).

attempted Michael reaction of potassium trinitromethide with acrylamide. It was characterized as an olefinic species by acid hydrolysis to fumaric and fumaramic acids under conditions which with the potassium salt of 4,4-dinitrobutyramide gave succinic and succinamic acids.[7]

Final confirmation of the olefinic nature of Novikov's monopotassium salt and the paraffinic nature of authentic II was derived from the infrared and ultraviolet spectra. Details of the infrared spectra of authentic II, IV, and VI are given in Table II together with pertinent band assignments.

TABLE II

INFRARED SPECTRA
(Nujol mull)

Band Assignment	Authentic II	IV	VI	"Normal Position"
C═C str.	Absent	1607	1589	1630–1660[a]
NO_2 asym. str.	1540	1499	—	1520–1580[a]
NO_2 sym. str.	1340	1302	—	1310–1380[a]
$C(NO_2)_2^-$	1275	1254	1260	1248[b]
$C(NO_2)_2^-$	1188	1187	1176	1187[b]
H—C═C—H wag	Absent	972	970	950–960[a]
Other bands	1425	1412	1673[c]	
	1380	1375	1638[d]	
	1312	1298	1630[d]	
	1298	887	1410	
	1140		1340	
	1120		1267	
	920		1130	
			1112	
			952	
			878	
			860	

[a] Reference 8. [b] Position of band in potassium 1,1-dinitropentane. [c] C═O (amide). [d] Amide-II band.

The bands at 972 and 1607 cm.$^{-1}$ in the spectrum of IV may be attributed to the carbon-carbon double bond. The shifts of these bands from the "normal" positions are in the directions predicted by Brown[8] and of magnitudes such as would be expected for a highly conjugated olefin. Compound IV also showed an increase from normal intensity of the C═C stretching band such as has been described by Brown for α-nitroolefins. The corresponding bands of VI appear at 970 and 1589 cm.$^{-1}$ while the potassium salts of methyl 4,4-dinitro-2-butenoate[6] and 4,4-dinitro-2-butenonitrile[6] show similar band systems at 983 and 1608 cm.$^{-1}$ and at 972 and 1595 cm.$^{-1}$, respectively. As was the case with authentic II, neither band appeared in the spectra of the potassium salts of 1,1-dinitropentane, 4,4-dinitrobutyramide, 4,4-dinitro-2-hydroxybutyramide[6] or 3,3-dinitropropionitrile.[9] It is further noteworthy that, while authentic II showed its NO_2 symmetric and antisymmetric stretching bands at about the midpoints of the ranges observed by Brown[8] for unconjugated nitroparaffins, these bands in the case of IV were also shifted in the directions expected for conjugated nitro compounds.

Kamlet and Glover[10] have suggested an equation relating the positions of maximal absorption in the ultraviolet charge-resonance spectra of anions of the type $RC(NO_2)_2^-$ with Taft's substituent constant of R,

$$\lambda_{\max} = (381.6\text{–}15.25\,\sigma^*\text{–}8.5\gamma) \pm 0.5 \text{ m}\mu$$

where γ is 1.0 or 0.0 depending on the presence or absence of nonbonded electrons on the atom *beta* to the charged carbon. Based on a value of + 0.50 for σ^* of the $NO_2CH_2CH_2$ grouping,[11] II would be expected to absorb maximally at 373.5–374.5 mμ. The observed $\lambda_{\max}$ for authentic II was 374 mμ. Compound IV, on the other hand, showed $\lambda_{\max}$ = 394 mμ and its characterization as a salt of 1,1,3-trinitro-2-propene conformed with the observation that the only compounds of the type $RC(NO_2)_2^-\ M^+$ thus far discovered to show maxima above 385 mμ are the 3-substituted 1,1-dinitro-2-propene derivatives.[12]

In addition to the reaction of I with potassium hydroperoxide mentioned above, Novikov's other product, the dipotassium salt III, has been reported as a by-product with the dipotassium salt of bis(2,2-dinitroethyl)amine in the reaction of 2,2-dinitroethylamine with potassium hydroxide.[13] It may also be synthesized by treating equimolar potassium dinitromethide and potassium 2,2-dinitroethanol[14] or most conveniently by refluxing an aqueous solution of the latter compound.[15] The close similarity of physical properties of a sample prepared by Novikov's ammonia method[1] with those of samples prepared by all four of the above methods and nondepression in the mixture

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

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

(9) The latter band was also absent in the case of the potassium salt of methyl 4,4-dinitrobutyrate, but this compound showed two weak maxima at 972 and 980 cm.$^{-1}$ whose presence we cannot now explain. Maxima at 1580 and 1605 cm.$^{-1}$, respectively, for salts of 4,4-dinitro-2-hydroxybutyramide and 4,4-dinitrobutyramide may probably be ascribed to the amide-II band since VI also shows a band in this region for which no other assignment is possible. Details of these comparison spectra will be described in a forthcoming paper by Kaplan and Kamlet.

(10) M. J. Kamlet and D. J. Glover, *Tetrahedron Letters*, No. 27, 17 (1960).

(11) R. W. Taft in M. S. Newman, ed., *Steric Effects in Organic Chemistry*, John Wiley and Sons, New York, 1956, Chap. 13.

(12) M. J. Kamlet and D. J. Glover, *in press.*

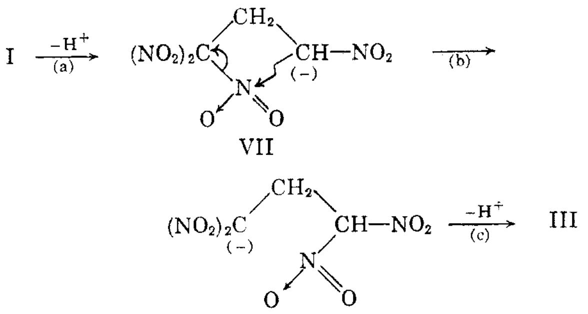
(13) M. J. Kamlet and J. C. Dacons, *J. Org. Chem.*, **26**, 3005 (1961).

(14) Private communication, Dr. Karl Klager, Aerojet-General Corp.

(15) R. B. Kaplan and H. Shechter, *Symposium on Nitroaliphatic Chemistry*, Purdue University, Lafayette, Ind., May 25–26, 1961.

melting points of dibromo derivatives confirmed that III had the suggested structure.

Mechanism. The transformation I→III may be described as an intramolecular alkaline nitration, mechanistically analogous to base-catalyzed nitrations of active methylene compounds by alkyl nitrates.[16] The successive steps are probably (a) abstraction of a proton *alpha* to the mononitro group by the base, (b) intramolecular nucleophilic displacement on nitro nitrogen of dinitroalkane anion by mononitroalkane anion, and (c) a second proton abstraction. The very much greater ability of the dinitroalkane moiety to delocalize the negative charge than the mononitroalkane moiety would supply the driving force in step (b).


VII

From their observation that the *aci*-forms of 1,1,1,3-tetranitrobutane and 1,1,1,3-tetranitropentane are more rapidly isomerized than the *normal*-forms to the corresponding 1,1,3,3-tetranitro compounds, Novikov and co-workers concluded that the isomerization of the *normal*-1,1,1,3-tetranitroalkanes proceeds *via* the prior formation of the *aci*-compounds.[2] We cannot concur in this conclusion on the basis that the base catalyzed *normal* →*aci* tautomerism would require as an intermediate an anion corresponding to VII. A more satisfactory rationalization of the relative reactivities would derive from the fact that removal of the first proton is probably the rate-determining step and proton abstraction from *aci*-nitroalkanes is far faster than from *normal*-nitroalkanes.[17]

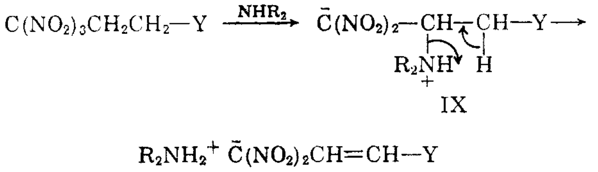
It is of interest that 2-phenyl-1,1,1,3-tetranitropropane reacts with bases to form the 2-phenyl analog of VII which then undergoes reversal of Michael addition with quantitative formation of trinitromethide ion and *β*-nitrostyrene.[18]

Zeldin and Shechter[19] and Kamlet and Dacons[13] have described reactions of 1,1,1-trinitroethane with a number of amines to yield zwitterionic derivatives of 2,2-dinitroethylamine.

$$C(NO_2)_3CH_3 + 2\,B\!: \longrightarrow \bar{C}(NO_2)_2CH_2{-}B^+ + BH^+\,NO_2^-$$

VIIIa. B = NH_3
b. $NH(CH_3)_2$
c. NHC_5H_{10} (piperidino)
d. $NH{=}C(NH_2)_2$

These reactions offer analogy for the preferred mechanism in the formation of IV and VI by the ammonia and dimethylamine reactions. This mechanism involves as a first step the formation of a zwitterionic intermediate corresponding to VIII and as a subsequent step the spontaneous elimination of ammonium or substituted ammonium ion with extension of the conjugated system supplying the driving force.


IX

Y = NO_2, $CONH_2$

Evidence that the conversion of 4,4,4-trinitrobutyramide to VI may have gone by way of IX (R = H, Y = $CONH_2$) was derived from ultraviolet spectra of the reaction mixture. VIIIa, VIIIb, and VIIIc show maxima at 362, 357, and 357 mμ respectively. Since the CH_2CONH_2 group should not affect the chromophore, IX would be expected to show maximal absorption in the same region. The ammonium salt of 4,4-dinitro-2-butenamide, on the other hand, shows a sharp maximum at 322 mμ and a broad band at 401–405 mμ, $\epsilon_{322}/\epsilon_{402}$ = 1.84. The latter compound is only slightly soluble in 60% methanol–40% ether.

When ammonia was bubbled into a solution of trinitrobutyramide in this solvent mixture, reaction was instantaneous as evidenced by heat evolution and coloration of the solution. The spectrum of the solution, taken just before precipitation started, showed a single maximum at 359 mμ with only inflections to mark the positions of the maxima of the eventual product. Precipitation was then allowed to continue until almost complete, the solid filtered, a portion of the mother liquor immediately diluted, and the spectrum redetermined. Again there was observed a single band with λ_{max} = 360 mμ. A further crop of precipitate was then taken. Both crops of precipitate showed spectra with sharp maxima at 322 mμ and diffuse maxima at 385–405 mμ, $\epsilon_{322}/\epsilon_{402}$ = 1.60–1.77.

These observations imply the formation of a soluble intermediate with λ_{max} near 360 mμ which was then transformed to the ammonium salt of 4,4-dinitro-2-butenamide. The latter precipitated immediately as formed, thereby contributing little to the solution spectrum. The intermediate could be precipitated by adding an excess of ether-hexane, but attempts to dry it for analysis were unsuccessful as it spontaneously decomposed to a

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(16) For a general review see R. Boschan, R. T. Merrow, and R. W. Van Dolah, *The Chemistry of Nitrate Esters, Chem. Revs.*, **55**, 485 (1955).

(17) R. Pearson and R. Dillon, *J. Am. Chem. Soc.*, **75**, 2439 (1953).

(18) J. Hine and L. A. Kaplan, *J. Am. Chem. Soc.*, **82**, 2915 (1960).

(19) L. Zeldin and H. Shechter, *J. Am. Chem. Soc.*, **79**, 4708 (1957).

gummy tar. If immediately dissolved in methanol it showed $\lambda_{max} = 362$ mμ.

Since VIIIa reacts rapidly with bromine to give 2-bromo-2,2-dinitroethylammonium bromide,[13] an attempt was made to effect an analogous reaction with the intermediate. Bromine was rapidly decolorized when added to a suspension of the intermediate in ether, but attempts to dry the product for analysis again led to spontaneous decomposition.[20] Both the spectrum and the behavior on bromination are consistent with the formulation of the intermediate as IX ($R = H$, $Y = CONH_2$).

We have tested the obvious possibility that half-neutralized III might be the intermediate leading to IV in the reactions of I with potassium acetate or potassium hydroperoxide by dissolving III in a number of buffer systems and monitoring the solutions spectrophotometrically. Although III did decompose in weak acid media, we were never able to discern evidence of the characteristic spectrum of IV.

$$\bar{C}(NO_2)_2CH_2CH(NO_2)_2 \not\longrightarrow \bar{C}(NO_2)_2CH{=}CH{-}NO_2 + HNO_2$$

EXPERIMENTAL,[21] CAUTION[22]

Potassium salt of 1,1,3-trinitropropane (II). *Method* (*a*). Solutions of 4.0 g. (0.017 mole) of 1,1,1,3-tetranitropropane (I) in 20 ml. of methanol and 8.0 g. (0.048 mole) of potassium iodide in 100 ml. of methanol were mixed and allowed to stand overnight. Crude II separated as dirty yellow-orange crystals which were filtered off, washed with 15 ml. of cold methanol, then with excess ether and air dried. The product, 1.22 g. (33%), had a m.p. of 118–119° (frothing), $\lambda_{max}^{H_2O}$ (log ε) = 373.5 mμ (4.23). Recrystallization from 100 ml. of methanol containing a few drops of water gave the analytical sample (0.89 g., 23%, Table I) as flat yellow-orange blades.

Method (*b*). A solution of 4.5 g. (0.062 mole) of freshly prepared nitroethylene in 20 ml. of methanol was added dropwise at 4–7° to a suspension of 10.0 g. (0.057 mole) of potassium 2,2-dinitroethanol[23] in 50 ml. of methanol containing 10.0 ml. of glacial acetic acid. After standing overnight at room temperature the insoluble product was filtered off and washed with cold methanol and ether. The crude II (brownish yellow platelets, 1.64 g., 13%) showed $\lambda_{max}^{dil.\ KOH}$ (log ε) = 373 mμ (4.22). Recrystallization from absolute methanol afforded the analytical sample (Table I) similar in crystal form to material prepared by method (a).

The reddish black mother liquor was diluted with water and extracted with ether whereupon much of the color went into the organic phase. Attempts to recover 2,2,4-trinitro-1-butanol from the ether extract by crystallization techniques were to no avail. Concentration gave an intractable oil from which no solid product could be isolated.

Dipotassium salt of 1,1,3,3-tetranitropropane (III) *by potassium hydroperoxide method*. To a stirred solution of 2.5 g. of I in 40 ml. of methanol was added 8 ml. of 30% hydrogen peroxide and then dropwise a solution of 5.0 g. of potassium hydroxide in 25 ml. of methanol, the temperature being kept below 10°. After stirring for an additional 15 min. the yellow precipitate was filtered, washed with methanol (CAUTION—not dried at this stage[24]) and the damp filter cake taken up for recrystallization in 65 ml. of 2% potassium hydroxide solution. Two crops, totaling 1.30 g. (39%) of pure III were collected as well formed bright yellow equant crystals, $\lambda_{max}^{dil.\ KOH}$ (log ε) = 367.5 mμ (4.41, photosensitive) [lit.[13] 367 mμ (4.41, photosensitive)]. Occasional samples melted with decomposition between 225° and 235°, but purified III when slowly heated began to discolor at 120°, turned gun-metal grey at 220° and black at 240° without melting sharply (lit.[1] m.p. 225°). The product is quite sensitive to a hammer blow.

Treatment of the material with bromine according to our previously described procedure[13] gave *1,3-dibromo-1,1,3,3-tetranitropropane*, m.p. 66–67.5°. The product showed no change in melting point after recrystallization from petroleum ether (b.p. 60–80°); no depression in melting point on admixture with previously described product,[13] m.p. 67–69°; no depression with dibromide, m.p. 66–68° from III prepared by Novikov's ammonia method[1]; no depression with dibromide, m.p. 65–68°, from III prepared by refluxing an aqueous solution of potassium 2,2-dinitroethanol.[15]

Potassium salt of 1,1,3-trinitro-2-propene (IV) *by potassium hydroperoxide method*. The product (IV) was obtained accidentally in trying to effect the Michael reaction of III with methyl acrylate. Six grams of potassium hydroxide in 50 ml. of water was added dropwise to a solution of 10.0 g. of I in 150 ml. of methanol containing 10 ml. of 30% hydrogen peroxide. The damp filter cake of crude III was fortunately not recrystallized, but was suspended in 65 ml. of water. A solution of 5.0 ml. of methyl acrylate in 30 ml. of methanol was then added, followed by 6.0 g. of acetic acid in 10 ml. of water. The temperature rose to 50° and the material all dissolved. The solution was held at 45° for 2 hr., then cooled to 0°, causing the precipitation of a yellow salt. This product, washed with cold methanol and with ether, 1.40 g. (15%), was recrystallized from methanol to give the analytical sample of IV (Table I). The expected Michael adduct of III with 2 moles of methyl acrylate could not be isolated from the mother liquors.

This sample of IV was compared with a sample of Novikov's monopotassium salt obtained by following Novikov's dimethylamine procedure exactly. Our yield was 63%. Melting point behavior, ultraviolet spectra (Table I), and X-ray diffraction patterns were similar.

In later attempts to effect the Michael reaction of *recrystallized* III with methyl acrylate we were similarly unable to obtain an adduct, nor could we find any IV, and recovery of unchanged III was almost nil. Our inadvertent discovery of IV had evidently resulted from its being formed as a by-product with III in the reaction of I with potassium hydroperoxide. It was carried over with III in the crude filter cake and separated by virtue of the fact that it was unaffected by warm acetic acid which decomposed III.

4,4,4-Trinitrobutyramide. A mixture of 45.3 g. of nitroform (0.30 mole), 42.6 g. of acrylamide (0.6 mole), and 40.8 g. of sodium acetate trihydrate (0.3 mole) was stirred for 144 hr. at room temperature, then concentrated to half volume under reduced pressure to yield 60 g. of crude trinitrobutyramide, m.p. 91–94°. Further concentration of the mother liquors gave a product, m.p. 80–83°, which was mainly acrylamide. Recrystallization of the initial product from 800–1000 ml. of chloroform gave two crops, totalling 55.0 g. (63%) of pure *4,4,4-trinitrobutyramide*, m.p. 95–96°, as off-white crystals.

Potassium salt of 4,4-dinitro-2-butenamide (VI). Anhydrous ammonia was bubbled into a solution of 4.0 g. of 4,4,4-trinitrobutyramide in 50 ml. of 60:40 methanol-ether at

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(20) In contrast, a suspension of the ammonium salt of 4,4-dinitro-2-butenamide in dry ether decolorized bromine only very slowly.

(21) Melting points were uncorrected. Microanalyses were by Prof. Mary Aldridge, Dept. of Chemistry, American University, Washington, D. C.

(22) All the compounds herein described are highly explosive in nature. Appropriate precautions should be taken in their handling.

(23) H. Feuer, G. B. Bachman, and J. P. Kispersky, *J. Am. Chem. Soc.*, **73**, 1360 (1951).

25°. There was a temperature rise to 35° (reflux) as the colorless solution turned yellow, orange, and finally orange-red. After 15 min. a precipitate began to form and the temperature began to fall; after 30 min. the flow of ammonia was discontinued. Ten milliliters of ether was added to replace material carried off in the ammonia stream and the mixture was refluxed for an additional 15 min. The first crop of the crude ammonium salt of 4,4-dinitro-2-butenamide weighed 2.35 g.; an additional 100 mg. was recovered by allowing the mother liquor to stand for several hours (total 64%).

Two grams of the ammonium salt was dissolved at 75° in a minimal amount of an aqueous solution which was saturated with respect to potassium chloride at 10°, and the solution was allowed to cool slowly. There precipitated 1.35 g. (43%) of pure VI as lath-shaped orange crystals $\lambda_{max}^{dil. KOH}$ (log ϵ) = 322, 402 mμ (4.23, 3.96). The ultraviolet and infrared spectra (Table II) as well as the X-ray diffraction pattern were identical with those of a sample previously described[8] as an abnormal Michael reaction product of potassium trinitromethide with acrylamide for which elemental analyses were as follows.

Anal. Calcd. for $KC_4H_4N_3O_5$: C, 22.5; H, 1.88; N, 19.7. Found: C, 22.4; 22.6; H, 2.06; 2.00; N, 20.3, 20.1.

The ultraviolet spectra of intermediate crops and of mother liquors in a similar run have been described in the mechanisms section of the discussion.

Spectra. Infrared spectra were determined with a Beckman model IR-4, ultraviolet spectra with a Cary model 14 spectrophotometer. Previously described precautions were taken in measuring all spectra[25] and in the case of III showed the compound to be photosensitive.

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[24] Although pure III was stable for several years at ambient temperatures, crude samples dried at this stage have ignited spontaneously.

[25] M. J. Kamlet and L. A. Kaplan, *J. Org. Chem.*, **22**, 576 (1957).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF OKLAHOMA]

An Improved Method of Ketimine Synthesis

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A general method for the synthesis of ketimines has been developed. The process, involving the decomposition of nitrile-Grignard reagent complexes by anhydrous methanol, has given better yields than those previously reported and has made possible the preparation of ketimines hitherto unobtainable.

A variety of methods have been used to prepare the many ketimines described since the first of the series, diphenyl ketimine,[3] was reported. Until now, however, no one method of preparation has been general. Previously, the best and most general procedure was that of Pickard and Vaughan,[4] which involves the formation of a complex between a Grignard reagent and a nitrile, followed by decomposition of the complex with anhydrous ammonia. Use of this method has resulted in moderate to good yields of a large number of ketimines. However, certain characteristics of the decomposition reaction either have prevented isolation of the more reactive, water-sensitive imines or have severely lowered their yields.

It has been found that by modifying the method of Pickard and Vaughan, the problems of isolation can be eliminated, while retaining its advantages. Decomposition of the Grignard-nitrile complex by anhydrous methanol, rather than by anhydrous ammonia, produces higher yields of imine and requires considerably less time. Several alkyl, aryl, and heterocyclic ketimines have been prepared by this new method which cannot be satisfactorily prepared by an earlier method.

The improvements offered by decomposition with methanol result from the production of an easily handled, insoluble by-product, a methoxymagnesium halide. This salt is a readily filtered, crystalline solid, while the by-product of the earlier procedure is a gummy material which is often so difficult to handle that the major portion of the imine is lost. An additional advantage of using methanol is that the by-product precipitates immediately, giving a faster, more controlled decomposition and showing clearly when reaction is complete.

The methanol modification has resulted in improved yields over earlier methods in every case tried. Four new ketimines have been prepared in this way: diethylketimine, propyl isopropyl ketimine, ethyl 2-pyridyl ketimine, and 2-thienyl-5-acridyl ketimine. Table I summarizes the yields and the physical constants obtained for all the imines prepared in this study. An attempt to prepare methyl ethyl ketimine was unsuccessful.

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[3] A. Hantzsch and F. Kraft, *Ber.*, **24**, 3511 (1891).

[4] P. L. Pickard and D. J. Vaughan, *J. Am. Chem. Soc.*, **72**, 876–878 and 5017–5019 (1950).