a 2-hr. period. After an additional 2 hr. at this temperature the resulting mixture was extracted with four 150-ml. portions of ether. The ether was dried and distilled *in vacuo* leaving a residue of 85 g. of product. The solid was recrystallized from chloroform giving 35 g. (yield 35%) of white 2,2,4,4-tetranitro-1,5-pentanediol; m.p. 97–99° dec.

Anal. Calcd. for $C_5H_8N_4O_{10}$: C, 21.13; H, 2.84; N, 19.07. Found: C, 21.55; H, 3.26; N, 19.02.

Methyl potassium aci-4,4,6,6-tetranitrohexanoate (XI). To a solution of 100 g. of damp (20%) methanol) dipotassium *aci*-1,1,3,3-tetranitropropane in 200 ml. of water was added 80 g. of methyl acrylate at room temperature. After 2 hr. at 45–50° the mixture was refluxed (70–72°) until all the starting material disappeared. The mixture was allowed to stand overnight and the crystals which separated were filtered, washed with ice water, 50% methanol and methanol giving 47 g. (yield 49%) of salt; m.p. 140° dec.

Anal. Calcd. for $C_7H_9N_4O_{10}K$: C, 24.14; H, 2.61; N, 16.09. Found: C, 23.79; H, 2.62; N, 17.02.

Methyl 4,4,6,6-tetranitrohexanoate (XII). To 4 g. of XI in 50 ml. of water at 60° was added 30% sulfuric acid to a *p*H of 2. The resulting suspension was extracted with methylene chloride. Evaporation of the solvent gave 3.2 g. of a resinous residue which was crystallized from isopropyl ether at Dry Ice-acetone temperature; m.p. 36–37°.

Anal. Calcd. for $C_7H_{10}N_4O_{10}$: C, 27.10; H, 3.25; N, 18.06; equiv. wt., 310. Found: C, 27.75; H, 3.58; N, 17.90; equiv. wt., 317.

Methyl 6-bromo-4,4,6,6-tetranitrohexanoate (XIII). Bromine was added dropwise to a suspension of 1 g. of XI in 30 ml. of water until the bromine color persisted. A yellow oil precipitated, which soon crystallized. Extraction with ether gave a crude product which was recrystallized from hexane at −70°. The bromide, 0.8 g. (yield 72%), m.p. 65–66°, exhibited a depression when mixed with authentic 1,3-dibromo-1,1,3,3-tetranitropropane (m.p. 66–67°) to 45°.

Anal. Calcd. for $C_7H_9N_4O_{10}Br$: C, 21.06; H, 2.31; N, 14.04; Br, 20.60. Found: C, 21.07; H, 2.24; N, 14.35; Br, 19.79; 19.68.

Reaction of XI *with aqueous potassium hydroxide.* Methyl potassium *aci*-4,4,6,6-tetranitrohexanoate (10.5 g.) was dissolved in 105 ml. of water, heated to 70°, and 25 ml. of 20% aqueous potassium hydroxide was added. The color changed from yellow to deep red and after 2.5 hr. the color turned orange. Upon cooling to room temperature and acidification with 30% sulfuric acid, a vigorous gas evolution occurred (carbon dioxide, nitric oxide, nitrogen dioxide and probably nitrous oxide were liberated). The solution was extracted with ether for 7 hr. and the residue (2.6 g.) from the ether extract, m.p. 188–189°, was sublimed *in vacuo*. Succinic acid, 2.4 g. (yield 67%), was obtained which did not show a depression when mixed with authentic succinic acid, m.p. 188–189°.

Anal. Calcd for $C_4H_6O_4$: equiv. wt. 59.05. Found: equiv. wt. 59.01.

AZUSA, CALIF.

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

Reactions of Polynitroalkanes with Hot Mineral Acids

MORTIMER J. KAMLET, LLOYD A. KAPLAN, AND JOSEPH C. DACONS

Received April 24, 1961

On refluxing with constant boiling hydrochloric acid, 1-nitroalkanes and 1,1-dinitroalkanes are converted to carboxylic acids with the same carbon skeleton. The internal *gem*-dinitro function is stable to these conditions as is the terminal trinitromethyl group except when alpha to an activated methylene group. With compounds of the latter type the chain is degraded by one carbon atom and a carbonyl group is formed.

Hot mineral acids convert primary nitroalkanes to hydroxamic acids and thence to the corresponding carboxylic acids. The transformation is known as the Victor Meyer reaction.[1] Secondary nitroalkanes are generally stable to hot mineral acids in their *normal*-forms, but may readily be hydrolyzed to carbonyl compounds under substantially milder conditions if first converted to the *aci*-forms by formation and neutralization of their alkali salts (Nef reaction[2]). We wish now to describe the effect of Victor Meyer reaction conditions on terminal and internal *gem*-dinitroalkanes and on terminal trinitroalkanes and their derivatives.

We have observed that when 1-(2,4-dinitrophenyl)-3-nitropropane or 1,1-dinitro-3-(2,4-dinitrophenyl)propane was suspended in constant boiling hydrochloric acid and the mixture heated to reflux, complete solution ensued within several hours. In either case the same product, 2,4-dinitrohydrocinnamic acid precipitated in fair yield when the solution was cooled.

In the former instance hydroxylamine hydrochloride could be isolated from the mother liquor; this represents a typical example of the Victor Meyer reaction. The latter case, however, exemplifies a new type of chemical transformation. Although the eventual product is the same as with the mononitro compound, the hydroxamic acid is not an intermediate, and a somewhat different mechanism probably applies.

The reaction appears to be general for 1,1-dinitro compounds and their salts. Thus, in refluxing hydrochloric acid, α,α,m-trinitrotoluene was converted to *m*-nitrobenzoic acid (80%), potassium 4,4-dinitrobutyramide to succinic acid (80%), potassium methyl 4,4-dinitrobutyrate to succinic acid (73%), potassium 4,4-dinitro-2-butenamide to fumaric acid (34%), and potassium methyl 4,4-dinitro-2-butenoate to fumaric acid (10%). With 1,1-dinitro-3-phenylpropane the anticipated hydrocinnamic acid was not obtained. Instead 1-indanone, which

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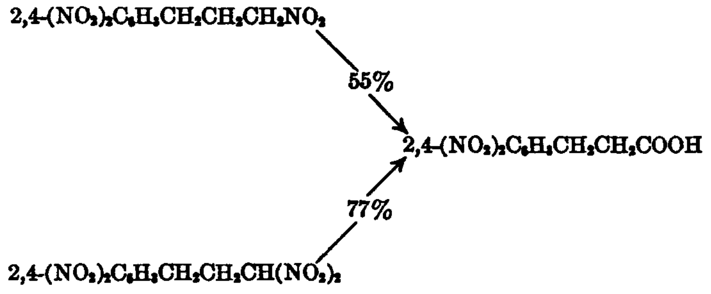
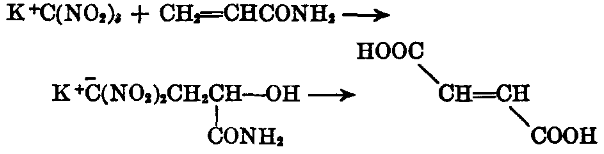
[1] T. W. J. Taylor and W. Baker, *Sidgwick's Organic Chemistry of Nitrogen*, Clarendon Press, Oxford, 1945, pp. 230–236.

[2] For an excellent review of the Nef reaction see W. E. Noland, *Chem. Revs.*, **55**, 137 (1955).



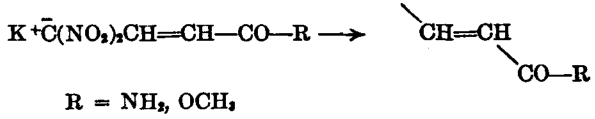
may have resulted from cyclization of the latter compound or an intermediate, was the only product isolated (72%).

The method has been useful in proof of structure.[3] A reaction product of potassium nitroform with acrylamide in anhydrous methanol showed ultraviolet and infrared spectra characteristic of saturated dinitroalkane salts which are not substituted alpha to the *gem*-dinitro group. Conversion to fumaric acid suggested the presence of a substituent which, under these conditions, was readily eliminated with formation of a double bond. The structure thus indicated, potassium 4,4-dinitro-2-hydroxy butyramide, was later confirmed by conversion to a known derivative.



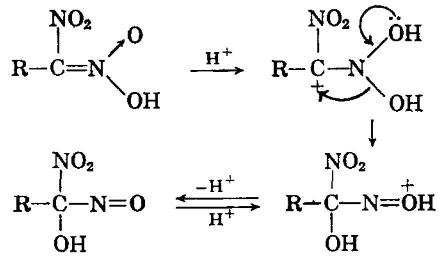
Less success was achieved in another instance. Under a variety of conditions, two salts, later identified as potassium 1,1,3-trinitropropane and potassium 1,1,3-trinitro-2-propene,[4] were both degraded to mixtures of not readily isolable fragments.

The low yields encountered when fumaric acid was the product and the simultaneous hydrolysis of ester and amide linkages led us to seek milder conditions wherein degradation of the dinitromethyl function would be the only reaction taking place. Such selectivity was achieved by dissolving the salts in a cold sulfuric acid–fluosulfonic acid mixture and pouring the solution over ice. In this way potassium 4,4-dinitro-2-butenamide was converted to fumaramic acid in 80% yield and potassium methyl 4,4-dinitro-2-butenoate to monomethyl fumarate in 75% yield.

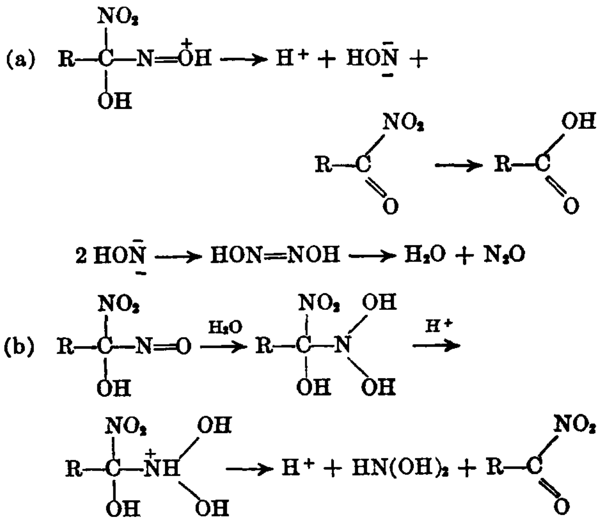


R = NH$_2$, OCH$_3$

No conclusive evidence is available regarding the mechanism, but the failure of internal *gem*-dinitro compounds to react (*vide infra*), and the appearance of a transient deep blue color in several cases suggest that, as in the Victor Meyer reaction, the *aci*-form is the reactive species and that a pseudonitrole is an early intermediate.



Subsequent steps may resemble either (a) the mechanism suggested by Hawthorne[5] or (b) that of van Tamelen and Thiede[6] for the Nef reaction.



In contrast with the terminal *gem*-dinitromethyl group, the internal *gem*-dinitromethyl group appears to be quite stable to the action of hot mineral acids. Hydrochloric acid hydrolyses of dimethyl 4,4-dinitroheptanedioate to 4,4-dinitroheptanedioic acid[7] and of methyl 4,4-dinitropentanoate to 4,4-

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(3) L. A. Kaplan and M. J. Kamlet, Abstracts Papers Am. Chem. Soc., 137, 56-O (1960).

(4) M. J. Kamlet, J. C. Dacons, and J. C. Hoffsommer, *J. Org. Chem.*, *in press.*

(5) M. F. Hawthorne, *J. Am. Chem. Soc.*, **79**, 2510 (1957).

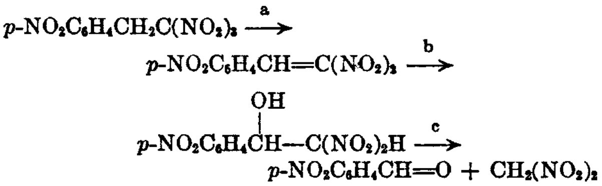
(6) E. E. van Tamelen and R. J. Thiede, *J. Am. Chem. Soc.*, **74**, 2615 (1952).

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

dinitropentanoic acid[8] have been reported. The reaction conditions described resembled quite closely those used in converting the 1,1-dinitro compounds to carboxylic acids. In both instances the yields were better than 95%, and there was no evidence that the nitro functions had been affected. The analogous acid hydrolysis of methyl 4,4-dinitrohexanoate is recorded in the experimental section.

The situation regarding terminal trinitromethyl compounds is more involved. Methyl 4,4,4-trinitrobutyrate was readily converted to 4,4,4-trinitrobutyric acid (>95%) by refluxing with 18% hydrochloric acid, and on prolonged refluxing the nitro groups remained unaffected.[9] Similarly, 1-(2,4-dinitrophenyl)-3,3,3-trinitropropane was recovered 90% unchanged after twenty-four hours of reflux.

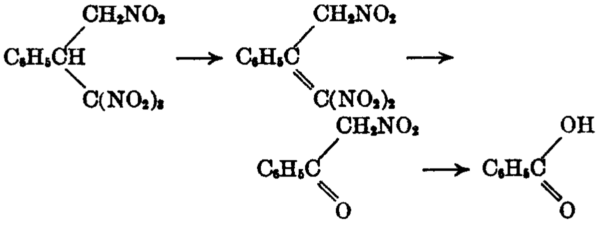
With 1-(4-nitrophenyl)-2,2,2-trinitroethane, however, only 15% of the starting material could be recovered after an overnight reaction. The remaining 85% had been converted quantitatively to *p*-nitrobenzaldehyde. This transformation may have involved (a) thermal denitrosation of the trinitro compound to 1,1-dinitro-2-(4-nitrophenyl)ethylene, (b) hydration of the olefin, and (c) reversal of carbonyl addition yielding the aldehyde and dinitromethane. The fact that the hydrogen atom alpha to the trinitromethyl group was also alpha to the ring and was further labilized by the *p*-nitro substituent may have contributed to the facile thermal denitrosation.



$$p\text{-}NO_2C_6H_4CH_2C(NO_2)_3 \xrightarrow{a} p\text{-}NO_2C_6H_4CH{=}C(NO_2)_2 \xrightarrow{b} p\text{-}NO_2C_6H_4\overset{\overset{OH}{|}}{C}H\text{—}C(NO_2)_2H \xrightarrow{c} p\text{-}NO_2C_6H_4CH{=}O + CH_2(NO_2)_2$$

2-Phenyl-1,1,1,3-tetranitropropane resembles the previous compound in that the hydrogen atom alpha to the trinitromethyl group is also alpha to the ring, but the inductive activating effect of a neighboring nitromethyl group is weaker than was the electromeric effect of the *p*-nitro substituent. The neighboring nitromethyl group is, of course, itself potentially capable of undergoing the Victor Meyer reaction. When this compound was refluxed for twenty-two hours with hydrochloric acid, 65% of the starting material was recovered unchanged together with traces of benzoic acid. After an additional twenty-four hours the yield of benzoic acid had risen to 46%.

This degradation cannot easily be explained on the basis of a Victor Meyer reaction on the primary nitro group, but is readily rationalized if one assumes that the reaction took the same course as in the previous instance with the product, α-nitroacetophenone, cleaving further to benzoic acid.



The cleavage involved in the last step has been reported as occurring quite readily under similar conditions of acidity with α-nitroacetophenone[10] and α,*p*-dinitroacetophenone.[11]

The structure of the mixed-acid nitration product of 2-phenyl-1,1,1 3-tetranitropropane was established by a similar degradation. The product was *m*-nitrobenzoic acid (65%) indicating that substitution had occurred in the *meta* position.

The action of hot mineral acids on mono- and polynitroalkanes may be summarized as follows:

Nitroalkane	Product
RCH_2NO_2	RCOOH
$RR'CHNO_2$	No reaction
$RR'C{=}NO_2H$	RR'C=O
$RR'C(NO_2)_2$	No reaction[12]
$RCH(NO_2)_2$	RCOOH
$RR'CHC(NO_2)_3$, CH not activated	No reaction[9]
$RR'CHC(NO_2)_3$, CH activated	RR'C=O

The stability of nonactivated 1,1,1-trinitroalkanes to strong acid conditions does not preclude the use of the reactions discussed above in their proof of structure. They may first be reduced to the corresponding 1,1-dinitroalkane salts with potassium iodide[13] or alkaline hydrogen peroxide[14] and thence converted to the carboxylic acids. This method may be exemplified by the sequence: 4,4,4-trinitrobutyramide to potassium 4,4-dinitrobutyramide[13] to succinic acid.

EXPERIMENTAL[15] (CAUTION[16])

Materials. The following compounds, first synthesized by Dr. Charles Plummer,[17] were kindly supplied to us by

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[8] H. Shechter and L. Zeldin, *J. Am. Chem. Soc.*, **73,** 1276 (1951).

[9] Trinitrobutyric acid may be converted to succinic acid by simply heating a neutral aqueous solution, however. Other soluble trinitromethyl compounds act analogously. H. Feuer, E. H. White, and S. M. Pier, *J. Org. Chem.*, **26,** 1639 (1961).

(10) J. Thiele and S. Haeckel, *Ann.*, **325,** 1 (1902).

(11) A. I. Yacubovich, *J. prakt. Chem.*, **142,** 37 (1935).

(12) No examples were available of compounds with internal *gem*-dinitro groups alpha to activated methylene groups, so we cannot exclude the possibility that they react analogously to the terminal trinitro compounds.

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

(14) D. J. Glover, *Tetrahedron, in press.*

(15) Melting points are uncorrected. Microanalyses by Prof. Mary H. Aldridge, Dept. of Chem., American University, Washington, D. C.

(16) Many of the compounds herein described are explosive in nature. Appropriate precautions should be taken in their handling.

(17) C. Plummer, Ph.D. thesis, University of Maryland, 1953.

Prof. Nathan L. Drake, University of Maryland: 1-(2,4-dinitrophenyl) - 3 - nitropropane, 1,1 - dinitro - 3 - (2,4-dinitrophenyl)propane, 1 - (2,4 - dinitrophenyl) - 3,3,3-trinitropropane, 1,1-dinitro-3-phenylpropane, and α,α,*m*-trinitrotoluene.

The reactions leading to potassium methyl 4,4-dinitro-2-butenoate, potassium 4,4-dinitro-2-butenamide, and potassium 4,4-dinitro-2-hydroxybutyramide have been reported in a preliminary fashion.[3] Details regarding their synthesis and physical properties will appear in a forthcoming paper. Potassium methyl 4,4-dinitrobutyrate and potassium 4,4-dinitrobutyramide were derived by potassium iodide reduction of the corresponding 4,4,4-trinitro compounds.[13]

The preparation of 2-phenyl-1,1,1,3-tetranitropropane from nitroform and β-nitrostyrene has been described by Hine and Kaplan.[18] Nitration of 4.0 g. of this material in 25 ml. of 15% oleum with 15 ml. of 100% nitric acid added dropwise at 5–15° gave 2.60 g. (57%) of a crude product, m.p. 86–105°. On recrystallization from ether-hexane there was obtained 1.78 g. (39%) of *2-(3-nitrophenyl)-1,1,1,3-tetranitropropane*, m.p. 102.5–103°.

Anal. Calcd. for $C_9H_7N_5O_{10}$: C, 31.50; H, 2.03; N, 20.30. Found: C, 32.22, 32.24; H, 2.15, 2.17; N, 20.09, 20.38.

1-(4-Nitrophenyl)-2,2,2-trinitroethane, m.p. 133.5–134.5° was prepared in 38% yield by the procedure of Reich, Rose, and Wilson.[19] An attempt to recover additional product by concentrating the deep red mother liquor resulted in a *violent fume-off*.

The procedure described by Shechter and Zeldin for methyl 4,4-dinitropentanoate[8] was followed in the preparation of methyl 4,4-dinitrohexanoate from 1,1-dinitropropane and methyl acrylate. The product boiled at 107–108.5° (35 mm.).

Standard procedure. In the preferred procedure about 1 g. of the nitroaliphatic compound was suspended in 25 ml. of constant boiling hydrochloric acid and the mixture refluxed for 16–24 hr. The solution was cooled to room temperature and, if necessary, concentrated and extracted with two 100-ml. portions of ether. The combined ether extracts were washed with water, dried over Drierite, and concentrated *in vacuo*. Variations from the standard procedure, yields and melting points of crude products, recrystallization solvents, and melting points of purified products are given below.

Action of hot hydrochloric acid on (a) *1-(2,4-dinitrophenyl)-3-nitropropane.* Charcoal was added and the reaction mixture filtered hot. 2,4-Dinitrohydrocinnamic acid (55%) precipitated directly on cooling. The product had a m.p. of 125.5–126.5° (lit.,[20] m.p. 126.5°).

(b) *1,1-Dinitro-3-(2,4-dinitrophenyl)propane.* The reaction mixture, treated as in (a), yielded 77% of 2,4-dinitrohydrocinnamic acid, m.p. 123–125°, no depression in melting point on admixture with product from (a).

(c) *α,α-m-Trinitrotoluene.* On cooling the reaction mixture, *m*-nitrobenzoic acid (80%) precipitated directly; m.p. 139–140°, no depression with authentic sample, m.p. 142°.

(d) *1,1-Dinitro-3-phenylpropane.* After 3 hr. of reflux charcoal was added and the mixture filtered hot. The charcoal was washed with ether, and the standard procedure was then followed to yield 72% of 1-indanone, m.p. 35–37°. Recrystallization from carbon tetrachloride raised the m.p. to 39–41° (lit.,[21] m.p., 40°).

(e) *1-(2,4-Dinitrophenyl)-3,3,3-trinitropropane.* Ninety per cent of starting material was recovered by filtering the cooled reaction mixture; m.p. 106–107°, no depression with original material, m.p. 108–108.5°.

(f) *1-(4-Nitrophenyl)-2,2,2-trinitroethane.* After 20 hr. of reflux there was still some insoluble material in the hot mixture. On filtering hot, 15% of impure starting material, m.p. 115–125° was recovered. Recrystallization from carbon tetrachloride raised the m.p. to 131–132°, and there was no depression with the original sample, m.p. 133.5–134.5°.

On cooling the mother liquor, *p*-nitrobenzaldehyde, m.p. 102–104°, precipitated (85% conversion, 100% yield). After one recrystallization from carbon tetrachloride the melting point was raised to 103.5–104.5°, and there was no depression with an authentic sample, m.p. 104–106°. *p*-Nitrobenzaniline, obtained by treating the aldehyde with aniline in ethanol containing a drop of sulfuric acid, melted at 90–92° (lit. m.p., 93°) after two recrystallizations from hexane.

(g) *2-Phenyl-1,1,1,3-tetranitropropane.* After 24 hr. of reflux 64% of the starting material and only traces of benzoic acid were recovered. When reflux was continued for 46 hr., benzoic acid (46%), m.p. 114–118° precipitated directly on cooling. A single recrystallization from water raised the m.p. to 121–122°, no depression with authentic sample.

(h) *2-(3-Nitrophenyl)-1,1,1,3-tetranitropropane.* The standard procedure gave 65% of *m*-nitrobenzoic acid, m.p. 139–141°, no depression with sample from (c).

(i) *Potassium 4,4-dinitro-2-hydroxybutyramide.* One gram in 7.5 ml. of hydrochloric acid, refluxed for 18 hr., concentrated, and cooled in ice gave 24% of fumaric acid, m.p. (sealed tube) 295–300° (lit. m.p., 293–295°). On refluxing with methanolic hydrogen chloride the latter product was converted to the dimethyl ester, m.p. 100.6–102°, no depression with authentic sample of dimethyl fumarate, m.p. 101–102.4°.

(j) *Potassium 4,4-dinitro-2-butenamide.* Procedure as in (i) gave 34% of fumaric acid, m.p. (sealed tube) 285–290°; dimethyl ester, m.p. 101–102.5°.

(k) *Potassium methyl 4,4-dinitro-2-butenoate.* Procedure as in (i) gave 10% of fumaric acid, m.p. (sealed tube) 286–287°.

(l) *Potassium 4,4-dinitrobutyramide.* Procedure as in (i) gave 73% of succinic acid, m.p. 180–183°, *no* depression with authentic sample, m.p. 185°.

(m) *Potassium methyl 4,4-dinitrobutyrate.* Procedure as in (i) gave 80% of succinic acid, m.p. 183–185°, no depression with sample from (l).

(n) *Methyl 4,4,4-trinitrobutyrate.* By separating the product which precipitated on cooling and working up mother liquor as in the standard procedure, 4,4,4-trinitrobutyric acid, m.p. 62–64°, was obtained in 98% yield.

(o) *Methyl 4,4-dinitrohexanoate.* One gram refluxed for 4 hr. with 7.5 ml. of hydrochloric acid, the mixture cooled and the product filtered and recrystallized twice from chloroform-hexane gave 77% of *4,4-dinitrohexanoic acid*, m p. 72.5–73.4°.

Anal. Calcd. for $C_6H_{16}N_2O_6$: N, 13.60. Found: N, 13.34, 13.18.

Conversion of potassium methyl 4,4-dinitro-2-butenoate to monomethyl fumarate. Four milliliters of fluosulfonic acid was added dropwise to a cooled solution of 1.0 g. of potassium methyl 4,4-dinitro-2-butenoate in 4 ml. of concd. sulfuric acid. The resulting solution was allowed to stand overnight at room temperature then added dropwise to 40 g. of cracked ice with cooling so that the temperature did not exceed 20°. The mixture was extracted with two 50-ml. portions of ether, the combined ether extracts washed with water and dried, and the solvent stripped *in vacuo*

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

(19) W. S. Reich, C. G. Rose, and W. Wilson, *J. Chem. Soc.*, 1234 (1947).

(20) S. Gabriel and W. Zimmermann, *Ber.*, **13**, 1680 (1880).

(21) S. Gabriel and J. Hausmann, *Ber.*, **22**, 2017 (1889).

to yield 0.43 g. (75%) of crude monomethyl fumarate, m.p. 133–138°. A single recrystallization from ether-hexane afforded 0.37 g. (65%) as white prisms melting at 144–146° (lit., m.p., 144.5°), neutral equivalent 128 (calcd. 130).

By a similar procedure potassium 4,4-dinitro-2-butenamide was converted in 85% yield to fumaric acid, m.p. 214.5–216° dec. (lit., m.p., 217° dec.), neutral equivalent 112 (calcd. 115).

SILVER SPRING, MD.

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

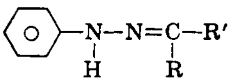
Tautomerism in Phenylhydrazones[1]

ROD O'CONNOR[2]

Received March 6, 1961

A study of the infrared, visible, ultraviolet, and NMR spectra of a series of phenylhydrazones, methylphenylhydrazones, and benzeneazoalkanes has been made. It is found that freshly prepared phenylhydrazones of aliphatic aldehydes and ketones exist as the hydrazone tautomer. These phenylhydrazones tautomerize rapidly in solution to benzeneazoalkanes. No detectable concentration of the ene-hydrazine tautomer is found in solutions of phenylhydrazones in neutral nonpolar organic solvents.

The problem of isomerism of phenylhydrazones among the hydrazone (I), azo (II), and ene-hydrazine (III) forms has been the subject of considerable investigation during the past half century. In addition to the general interest in this tautomerism, with the added potential of *cis-trans* isomers for each tautomer, further interest has been stimulated by the use of phenylhydrazones as analytical derivatives of carbonyl compounds and by considerations of the mechanism of the Fischer indole synthesis, for which phenylhydrazones are starting materials.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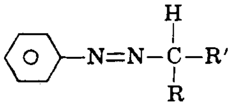
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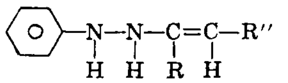
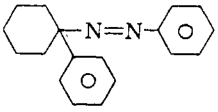

III

Tautomerism in phenylhydrazones was first investigated by Freer[3] in 1893. For the next forty years, there was considerable controversy concerning attempts to determine the structures of various phenylhydrazone tautomers and their relative stabilities.[4–8] By the late 1930's it was generally agreed[9] that the hydrazone tautomer was the most stable form and that it was resistant to tautomeric change. In 1947, Grammaticakis[10] recognized a serious flaw in all the earlier work on this problem. There had, as yet, been no study using any one tautomer which might not contain equilibrium amounts of other forms. Grammaticakis prepared the azo compound (IV) to be used as a standard for the ultraviolet and visible spectrum of a benzeneazoalkane. From a comparison of the ultraviolet and visible spectra of phenylhydrazones with that of compound IV, he concluded that phenylhydrazones in solution exist in equilibrium with small quantities of the azo tautomer.[11] He did not report any study of spectra as a function of time and thus failed to establish that equilibrium had been reached (if, indeed, an equilibrium were involved). No serious attempt was made to verify Grammaticakis' conclusions until 1957. At that time, Arbuzov and Kitayev[12] concluded


IV

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(1) The work described in this paper was included in the Ph.D. thesis of the author at the University of California, August, 1958.

(2) National Science Foundation Fellow, 1955–1957, Procter and Gamble Fellow 1957–1958; present address, Montana State College, Bozeman, Mont.

(3) P. C. Free, *J. prakt. Chem.*, **47**, 238 (1893); *Ann.*, **283**, 391 (1894).

(4) E. Fischer, *Ber.*, **29**, 793 (1896).

(5) J. Thiele and K. Heuser, *Ann.*, **290**, 1 (1896).

(6) E. C. C. Baly and W. B. Tuck, *J. Chem. Soc.*, **89**, 982 (1906).

(7) K. V. Auwers and H. Wunderling, *Ber.*, **64**, 2748 (1931).

(8) Taku Uemura and Y. Inamura, *Bull. soc. chim. Japan*, **10**, 169 (1935).

(9) P. Ramart-Lucas, J. Hoch, and M. Martynoff, *Pull. soc. chim. France* **4**, 481 (1937).

(10) P. Grammaticakis, *Bull. soc. chim. France*, 438 (1947).

(11) Recently, Grammaticakis' work has been interpreted as evidence for the existence of the ene-hydrazine tautomer [*cf.* K. H. Pausacker and C. I. Schubert, *J. Chem. Soc.*, 1384 (1949), and H. Plieninger, *Ber.*, **83**, 273 (1950)]. Although Grammaticakis did, at one time, believe such a form might exist [*Compt. rend.*, **223**, 804 (1946)], the work in question (ref. 10) showed no evidence of the presence of any ene-hydrazine form in neutral solutions in organic solvents.

(12) A. E. Arbuzov and Y. B. Kitayev, *Doklady Akad. Nauk SSSR*, **113**, 577 (1957).