

flask. The overall yield of 2-bromo-2,2-dinitroethyl acetate was 193.4 g. (75%), b.p. 70–71°/0.35 mm., n_D^{25} 1.4728.

Anal. Calcd. for $C_4H_5N_2O_6Br$: Br, 31.10; N, 10.90. Found: Br, 30.96; N, 10.59.

Potassium 2,2,4,4-tetranitrobutyl acetate (II). A solution of 25.7 g. (0.10 mole) of 2-bromo-2,2-dinitroethyl acetate in 100 ml. of methanol was cooled to 0° and a solution of 83 g. (0.50 mole) of potassium iodide in 150 ml. of 50% methanol was added dropwise. The purple reaction mixture was filtered and the yellow solid was washed thoroughly with ether to remove the iodine liberated in the reaction. The yield of potassium 2,2,4,4-tetranitrobutyl acetate was 24.0 g. (equivalent to 21.5 g. or 64.5% of dry salt). The salt was recrystallized 3 times from water, m.p. 174° explodes.

Anal. Calcd. for $C_8H_7N_4O_{10}K$: C, 21.56; H, 2.11; N, 16.76. Found: C, 21.89; H, 2.27; N, 16.67.

2,2,4,4-Tetranitrobutyl acetate (III). A slurry of 12 g. (0.035 mole) of potassium 2,2,4,4-tetranitrobutyl acetate and 150 ml. of water was cooled to 0° and a solution of 5 ml. of concentrated sulfuric acid in 30 ml. of water was added. At the end of the addition the reaction mixture turned from orange to yellow. Stirring was continued for another hour and the reaction mixture was filtered. The cream colored solid was collected, washed well with water, and air dried. The yield of 2,2,4,4-tetranitrobutyl acetate was 7.0 g. (67.5%), m.p. 57–58°. The product was recrystallized twice from ethyl chloride at –70° to give a white crystalline solid, m.p. 58–59°.

Anal. Calcd. for $C_6H_5N_4O_{10}$: C, 24.33; H, 2.72; N, 18.92; neut. equiv., 296. Found: C, 24.62; H, 2.89; N, 18.50; neut. equiv., 297, 298.

Potassium 1,1,3,3-tetranitrobutane (VIII). 1,1-Dinitroethane,⁸ 12.0 g. (0.10 mole), was cooled in an ice bath and a solution of 4.2 g. (0.10 mole) of 95% sodium hydroxide in 30 ml. of water was added. Then a solution of 12.85 g. (0.05 mole) of 2-bromo-2,2-dinitroethyl acetate in 25 ml. of methanol was added dropwise while the sodium 1,1-dinitroethane solution was maintained at 10°. Stirring was continued while the solution warmed to room temperature. The reaction mixture was extracted with ether to remove any starting material. The aqueous layer was cooled to 5° and treated with 8.0 g. (0.05 mole) of bromine. The solution was extracted with ether, dried, and concentrated to give 4.4 g. of 1-bromo-1,1,3,3-tetranitrobutane. One and seven-tenths g. of this orange liquid was dissolved in 3 ml. of methanol and cooled to 0°, then a solution of 1.78 g. of potassium iodide in 6 ml. of 50% methanol was added. The

purple reaction mixture was filtered and the yellow salt was washed with ether, wt. 1.0 g. The salt was recrystallized 3 times from ethanol, m.p. 137–138° dec.

Anal. Calcd. for $C_4H_5N_4O_8K$: C, 17.39; H, 1.83; N, 20.29. Found: C, 17.71; H, 1.83; N, 20.69.

2,2,4,4-Tetranitro-1-pentanol (VI). 1,1-Dinitroethane, sodium hydroxide, and 2-bromo-2,2-dinitroethyl acetate were treated in the same amounts and in the same manner as above. The reaction mixture was extracted with ether to remove any unreacted starting material. At room temperature, 4.1 g. of 37% formalin was added to the aqueous layer, the solution was stirred for 1 hr., and 3 g. of glacial acetic acid was added dropwise. The orange solution was extracted 3 times with ether, the ether extracts were combined, washed with water, dried, and concentrated leaving 2.5 g. of a yellow liquid. The liquid was heated in a bulb tube at 70–110° (1 micron), 0.5 g. of the liquid distilled leaving a viscous yellow liquid which solidified. This residue was recrystallized from carbon tetrachloride to give 0.3 g. of a white crystalline solid, m.p. 66–67°.

Anal. Calcd. for $C_5H_5N_4O_8$: C, 22.40; H, 3.01; N, 20.90. Found: C, 22.44; H, 2.87; N, 21.31.

Sodium 1,1-dinitro-2-phthalimidoethane (V). To a solution of 110.0 g. (0.65 mole) of sodium phthalimide in 500 ml. of 60% methanol, at room temperature, was added a solution of 83.7 g. (0.325 mole) of 2-bromo-2,2-dinitroethyl acetate in 150 ml. of methanol. A yellow solid separated in about 5 min.; stirring was continued for an additional 30 min. The yellow solid was collected, washed with ether, and air dried. The yield of sodium 1,1-dinitro-2-phthalimidoethane was 60.0 g. (64.3%), m.p. 238° explodes.

Methyl 4,4-dinitro-5-phthalimidopentanoate (VII). A mixture of 3.0 g. (0.01 mole) of sodium 1,1-dinitro-2-phthalimidoethane, 30 ml. of water, and 2.6 g. (0.03 mole) of methyl acrylate was heated at 50° for 3.5 hr.; the solid dissolved and an oil separated. On cooling, the oil solidified, and the tan solid was collected and dried. The yield of methyl 4,4-dinitro-5-phthalimidopentanoate was 1.7 g. (48.4%), m.p. 107–113°. The product was recrystallized 3 times from absolute ethanol to give a white crystalline solid, m.p. 113–115°.

Anal. Calcd. for $C_{14}H_{13}N_3O_8$: C, 47.87; H, 3.73; N, 11.96. Found: C, 47.95; H, 3.74; N, 12.12.

Acknowledgment. We are indebted to the Office of Naval Research for the financial support of this work.

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(8) E. ter Meer, *Ann.*, **181**, 1 (1876).

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

Derivatives of Nitromethylamine. II. Nitromethyl Imides¹

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N-Nitromethylphthalimide and *N*-nitromethylsuccinimide have been prepared from the corresponding *N*-bromomethyl imides and silver nitrite in acetonitrile. The new imides are crystalline solids which are stable at temperatures up to their melting points. They react with bases by displacement of the nitro group and decompose on heating with acids to mixtures from which nitromethylamine could not be isolated.

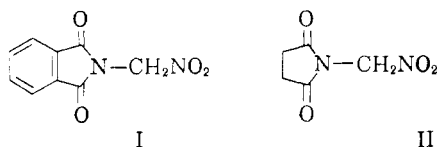
In the course of further investigations of nitromethylamine derivatives in this laboratory,² it

(1) (a) This work was performed under the auspices of the U. S. Atomic Energy Commission. (b) Presented before the Organic Section of the American Chemical Society at the 133rd Meeting, San Francisco, Cal., April 1958.

has been found that *N*-nitromethyl imides can be prepared in fairly good yield by the reaction of *N*-bromomethyl imides with silver nitrite in aceto-

(2) Paper I: H. E. Ungnade and L. W. Kissinger, *J. Org. Chem.*, **22**, 1662 (1957).

nitrile. In this fashion *N*-nitromethylphthalimide (I) and *N*-nitromethylsuccinimide (II) have been prepared from the corresponding *N*-bromomethyl compounds. Both are accompanied by the *N*-hydroxymethyl imides which are assumed to derive



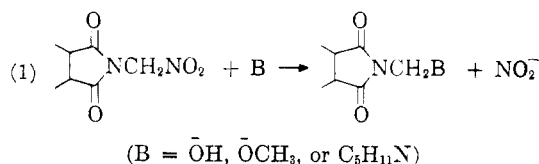
from the unstable nitrite esters, formed simultaneously with the nitro compounds by the action of silver nitrite on the *N*-bromomethyl imides. Under the usual conditions of the Victor Meyer reaction *N*-bromomethylphthalimide gives only a 2% yield of compound I. The reaction is heterogeneous in ether and furnishes as main products nitrogen oxides and bisphthalimidomethyl ether, arising from *N*-hydroxymethylphthalimide and unchanged bromo compound.

The spectral characteristics of the imides I and II agree well with the assigned structures. Two bands in the C=O stretching region, a strong band near 5.75μ and a band of medium intensity near 5.60μ correspond to similar bands in related imides³ (Table I). Additional bands near 6.30μ and 7.30μ are assigned to *asym.* and *sym.* stretching vibrations of the nitro group and fall within the ranges characteristic of mononitro compounds.⁴ In the ultraviolet, the nitromethyl imide I shows an increased absorption compared to phthalimide in the region of $260\text{--}280\text{ m}\mu$, where nitroparaffins absorb. In the case of *N*-nitromethylsuccinimide (II) a discrete band without fine structure is observed in ethanol ($\lambda_{\text{max}} 276\text{ m}\mu$, $\log \epsilon 1.57$), which is shifted

toward the blue in alcoholic hydrochloric acid ($\lambda_{\text{max}} 272\text{ m}\mu$, $\log \epsilon 1.57$), does not occur in succinimide, and is characteristic of nitroparaffins.⁵

Several attempts were made to hydrolyze these *N*-nitromethyl imides to nitromethylamine ($\text{NO}_2\text{-CH}_2\text{NH}_2$). Under conditions sufficiently mild to avoid the conversion of mononitro aliphatics to the corresponding hydroxamic or carboxylic acids,⁶ for example room temperature and aqueous or ethanolic 1 : 1 concentrated hydrochloric acid, no reaction is observed with I or II. On boiling, the same reagents rapidly decompose the imides to phthalic (and succinic) acid, ammonium chloride, oxides of nitrogen, and some formaldehyde. The alternate hydrolysis procedure for phthalimide with hydrazine⁷ yields, from I, formaldehyde and, after the hydrochloric acid treatment,⁷ phthalic acid.

Other bases react with the *N*-nitromethyl imides with elimination of nitrite ion, even under mild conditions. Thus I gives a quantitative yield of nitrite ion at 0° with sodium methoxide in methanol. Hydroxide ion and piperidine also displace nitrite ion from I and II and, in each case, the substituted methylimide is formed. This is pictured (Equation 1) as a nucleophilic displacement of a nitro group on carbon, which is rarely observed with mononitro compounds.



Anhydrous ammonia reacts only slowly with I in ether to form a complex which still contains the nitro group. On prolonged standing the complex decomposes with the formation of nitrite ion and other unidentified products. Attempts to brominate the complex have led only to degradation of the compound to phthalimide.

The *N*-nitromethyl imides are stable at their respective melting points, in boiling inert solvents and in boiling alcohols (in contrast with the corresponding bromomethyl imides which are solvolyzed by the alcohols).

EXPERIMENTAL⁸

N-Bromomethylphthalimide. *N*-Hydroxymethylphthalimide, prepared by heating of phthalimide and formalin,⁹ was converted to the bromo compound, m.p. $146\text{--}148^\circ$, by

(6) H. B. Hass and E. F. Riley, *Chem. Revs.*, **32**, 395 (1943).

(7) H. R. Ing and R. H. F. Manske, *J. Chem. Soc.*, 2348 (1926).

(8) All temperatures uncorrected. Analyses by M. J. Naranjo and C. A. Esquibel.

(9) M. B. Winstead and H. W. Heine, *J. Am. Chem. Soc.*, **77**, 1913 (1955).

TABLE I

INFRARED ABSORPTION BANDS FOR SUBSTITUTED IMIDES^a

| Compound | λ, μ | λ, μ |
|---------------------------------------|----------------|----------------|
| Phthalimide | 5.56 | 5.70 |
| <i>N</i> -Hydroxymethylphthalimide | 5.58 | 5.75 |
| <i>N</i> -Bromomethylphthalimide | 5.59 | 5.74 |
| <i>N</i> -Methoxymethylphthalimide | 5.57 | 5.76 |
| <i>N</i> -Ethoxymethylphthalimide | 5.56 | 5.74 |
| <i>N</i> -Nitromethylphthalimide | 5.60 | 5.73 |
| <i>N</i> -Piperidinomethylphthalimide | 5.62 | 5.81 |
| <i>N</i> -Acetylphthalimide | 5.50 | 5.62 |
| Succinimide | 5.63 | 5.78 |
| <i>N</i> -Hydroxymethylsuccinimide | 5.57 | 5.80 |
| <i>N</i> -Bromomethylsuccinimide | 5.52 | 5.78 |
| <i>N</i> -Methoxymethylsuccinimide | 5.62 | 5.83 |
| <i>N</i> -Ethoxymethylsuccinimide | 5.62 | 5.83 |
| <i>N</i> -Nitromethylsuccinimide | 5.57 | 5.75 |
| <i>N</i> -Piperidinomethylsuccinimide | 5.62 | 5.84 |

^a Determined in chloroform solution

(3) W. G. Roderick and W. A. Brown, *J. Am. Chem. Soc.*, **79**, 5196 (1957).

(4) N. Kornblum, H. E. Ungnade, and R. A. Smiley, *J. Org. Chem.*, **21**, 377 (1956) and references cited therein.

(5) H. E. Ungnade and R. A. Smiley, *J. Org. Chem.*, **21**, 993 (1956) and references cited therein.

refluxing with phosphorus tribromide and benzene;¹⁰ yield 82%.

N-Nitromethylphthalimide (I). A. *Victor Meyer procedure*.¹¹ A suspension of 24 g. (0.1 mole) of *N*-bromomethylphthalimide in 50 ml. of anhydrous ether was added slowly to a stirred mixture of 23.1 g. (0.15 mole) of silver nitrite and 50 ml. of ether at 0°. The bromo compound was completely transferred to the reaction flask by rinsing with 50 ml. of ether and the entire mixture was stirred at 0° for 17 hr., then at room temperature for 72 hr. The ether solution was filtered under nitrogen pressure and the remaining salts were washed with ether. Distillation of the combined ether solutions gave 6.5 g. of yellow oil which solidified on cooling. The oil was digested with ether. The ether-insoluble solid melted at 140–142° after crystallization from benzene-petroleum ether (yield 1.4 g., 8%), and was identified as hydroxymethylphthalimide by its infrared spectrum and mixed melting point with an authentic specimen. The ether digest was freed from solvent, taken up in benzene, and adsorbed on F-20 (Alcoa) alumina. The column was eluted successively with benzene and ether. The first 150 ml. of benzene eluate contained 0.8 g. (4%) of colorless solid, m.p. 75–80° (from benzene-petroleum ether), which was identified as *N*-ethoxymethylphthalimide by its infrared spectrum and mixed melting point (79–85°) with the authentic ether (m.p. 84–85°).^{12,13} The remaining 300 ml. of benzene eluate furnished *N*-nitromethylphthalimide, obtained as a yellow oil (0.45 g., 2%), which was crystallized from benzene-hexane to a constant m.p. of 110.5–111°. Its major absorption bands were: λ (C=O) 5.60, 5.73 μ ; λ (NO₂) 6.32, 7.33 μ ; λ_{max} (EtOH) 236 m μ (log ϵ 3.92); λ_{max} 294 m μ (log ϵ 3.27); shoulder 300 m μ (log ϵ 3.26).

Anal. Calcd. for C₈H₈N₂O₄: C, 52.44; H, 2.93; N, 13.59. Found: C, 52.70, 52.77; H, 2.86, 3.13; N, 13.51.

The main ether eluate yielded phthalimide (1.3 g., 9%) and the last portion 0.9 g. (5%) of bisphthalimidomethyl ether, m.p. 205–207° (lit. m.p. 207°).¹²

Anal. Calcd. for C₁₈H₁₂N₂O₈: C, 64.29; H, 3.59; N, 8.33. Found: C, 64.21; H, 3.49; N, 8.21.

Continued extraction of the silver salts with several portions of ether and with benzene gave a total of 8.7 g. (52%) of bisphthalimidomethyl ether, m.p. 205–207°, leaving 26.0 g. of silver salts (0.1 mole of silver bromide + 0.05 mole of nitrite = 26.5 g.).

B. *Reaction in acetonitrile*. *N*-Bromomethylphthalimide (24 g., 0.1 mole) in 130 ml. of acetonitrile was added slowly, with stirring, to a suspension of silver nitrite (16.9 g., 0.11 mole) in 50 ml. of acetonitrile. The mixture was stirred at 0° for 20 hr. and at room temperature for 20 hr. The precipitated silver bromide was filtered with suction, washed with acetonitrile, and dried, yield 19.0 g. (theory 18.8 g.). The filtrate was diluted with 3 volumes of water and the separated oil was taken up in ether. The ether solution was washed with water and distilled to remove the solvent. The residue was dried by adding 100 ml. of benzene and collecting the water in a Dean-Stark trap. The benzene-insoluble solid, m.p. 149–150°, weighed 1.6 g. (9%) and was identified as hydroxymethylphthalimide. The benzene solution was chromatographed on F-20 (Alcoa) alumina and the reaction products were eluted successively with benzene and ether. The fractions with similar infrared spectra were combined and recrystallized from benzene or benzene-hexane. In this fashion there was obtained 5.5 g. (27%) of *N*-nitromethylphthalimide, 6.8 g. (38%) of *N*-hydroxymethylphthalimide, and 1.3 g. (9%) of phthalimide.

(10) O. Mancera and O. Lemberger, *J. Org. Chem.*, **15**, 1253 (1950).

(11) N. Kornblum, B. Taub, and H. E. Ungnade, *J. Am. Chem. Soc.*, **76**, 3209 (1954).

(12) F. Sachs, *Ber.*, **31**, 1230 (1898).

(13) The formation of *N*-ethoxymethylphthalimide is accounted for by the reaction of the *N*-bromomethyl imide with the ethanol contained in the solvent ether.

N-Nitromethylphthalimide is a colorless solid which burns with luminous flame. It is stable in boiling methanol, from which it crystallizes in needles, and it is thermally stable at its melting point.

Hydrolysis of N-nitromethylphthalimide (I) with hydrochloric acid. *N*-Nitromethylphthalimide (1.6 g., 0.0078 mole) was unaffected by cold 1:1 hydrochloric acid (50 ml.). On refluxing of the mixture for one hr., the solid went partially into solution while oxides of nitrogen were evolved. The aqueous solution was allowed to cool. After shaking with benzene, phthalic acid [1.1 g., 85%, m.p. 226–227° (dec.)] crystallized, which was identified by its infrared spectrum. Evaporation of the benzene extract furnished unchanged starting material (0.2 g., 12%). The aqueous filtrate was distilled under reduced pressure into a Dry Ice trap. The distillate gave a positive test for formaldehyde with sodium 1,8-dihydroxynaphthalene-3,6-sulfonate. The solid residue (0.4 g.) contained ammonium chloride, identified as an ammonium salt, by adding 1 ml. of 50% potassium hydroxide, drying the gas over ascarite, and determination of its infrared spectrum.

Hydrolysis of N-nitromethylphthalimide (I) with hydrazine. *N*-Nitromethylphthalimide (1.5 g., 0.0072 mole), suspended in 10 ml. of 95% ethanol, was treated with hydrazine (64%, 0.1 ml., 0.02 mole). The imide went into solution with yellow color when the mixture was heated on the steam bath for 1 hr. A trace of starting material was filtered off, the filtrate was poured into excess water and extracted with benzene. On treatment with dimedone, the aqueous solution yielded formaldimethone (0.3 g., 14%), m.p. 191–193°. The benzene extract contained a yellow oil which gave phthalic acid (0.9 g., 75%) on hydrolysis with concentrated hydrochloric acid.

Reaction of N-nitromethylphthalimide (I) with sodium methoxide. A solution of *N*-nitromethylphthalimide (1.6 g., 0.0078 mole) in 100 ml. of methanol was added with ice cooling to a solution of sodium, (0.23 g., 0.01 g.-atom) in 50 ml. of methanol. Immediately after the addition, a 1-ml. sample was withdrawn, quenched with 5 ml. of glacial acetic acid, and treated with 5 ml. of a solution of sulfanilic acid (1.0 g.) in 1:10 aqueous hydrochloric acid (100 ml.). After 10 min., 5 ml. of a solution of α -naphthol (1.0 g.) and sodium acetate (1.0 g.) in 50% aqueous acetic acid (100 ml.) was added, the mixture was allowed to stand for 30 min., diluted, and its absorbance determined spectrophotometrically. Other samples, withdrawn after 0.5, 1.5, and 3.0 hr. at room temperature, all had the same absorbance at 475 m μ , corresponding to complete conversion of the nitro group to nitrite ion by comparison with a series of standard solutions.

When *N*-nitromethylphthalimide (0.8 g., 0.0039 mole) was allowed to stand with sodium methoxide (0.005 mole) in methanol (75 ml.) at 25° for 30 min., *N*-methoxymethylphthalimide was isolated in 82% yield. The solution was evaporated under reduced pressure, the residue extracted with hot benzene and crystallized from benzene-hexane. Melting point and mixed melting point with *N*-methoxymethylphthalimide 122–123°.

Reaction with ammonia. When ammonia gas was passed into a solution of 1.0 g. (0.0048 mole) of *N*-nitromethylphthalimide in 100 ml. of ethyl ether, an oil separated, which on standing solidified to a waxy solid, m.p. 100–150° (dec.). This material still contained a nitro group [λ (NO₂) 6.33 μ], had imide C=O bands, and was therefore regarded as an ammonia complex. It was dissolved in 50 ml. of ethanol and brominated with 0.9 g. of bromine. The mixture was diluted with 125 ml. of water and allowed to stand for 12 hr. The aqueous solution gave a positive test for formaldehyde and nitrite ion. Extraction with 5 \times 50 ml. of benzene gave 0.6 g. (84%) of phthalimide.

Reaction with piperidine. Piperidine (0.17 g., 0.002 mole) was added to a solution of *N*-nitromethylphthalimide (0.206 g., 0.001 mole) in 10 ml. of 95% ethanol and the mixture was refluxed for 1 hr. The yellow solution was evaporated to dryness leaving 0.35 g. of brown solid residue which was taken

up in methylene chloride, washed with water, dried, and freed from solvent. The aqueous washings gave a strong nitrite test. The organic residue was sublimed at 120° (7 mm.) and the sublimate digested with hexane-benzene. The insoluble portion (0.006 g.) was identified as phthalimide by mixed melting point and infrared spectrum. The digest deposited colorless needles (0.01 g.) which after vacuum sublimation gave *N*-piperidinomethylphthalimide, identical with authentic material (m.p. 117–118°)¹² in infrared spectrum and *R_f* value. A persistent oily impurity, believed to be bis-methylenepiperidine, lowered the m.p. to 108°.

N-Bromomethylsuccinimide. *N*-Bromomethylsuccinimide can be prepared in 92% yield by action of phosphorus tribromide on *N*-hydroxymethylsuccinimide,¹⁴ which in turn is available from succinimide in 52% yield. A much higher over-all yield (91%) was obtained by running these reactions without isolating the hydroxymethyl compound, as follows:

Succinimide (25 g., 0.25 mole) was refluxed with 25 ml. of 37% formalin for 4 hr. on a steam bath. Benzene (150 ml.) was then added and the water removed by distillation of the azeotrope. To the dry benzene solution was added 30.6 g. (0.11 mole) of phosphorus tribromide and the mixture was refluxed for 1.5 hr. The benzene solution was decanted and the residue was boiled with 25 ml. of benzene. The combined benzene solutions were distilled to remove the solvent. The residual oil (48 g.) was distilled under reduced pressure. The distillate, b.p. 128–130° (1 mm.), yield 44 g. (91%), solidified on cooling, m.p. 60–63° (lit. m.p. 63–64°).¹⁴

N-Nitromethylsuccinimide (II). A suspension of 33.8 g. (0.22 mole) of silver nitrite in 100 ml. of acetonitrile was added to a stirred solution of 38.4 g. (0.2 mole) of *N*-bromomethylsuccinimide and 2 g. of urea in 100 ml. of acetonitrile at 0°. The silver nitrite was completely transferred by use of another 100 ml. of acetonitrile, and the mixture was stirred at 0° for 22 hr. and at room temperature for 5 hr. The precipitated silver bromide was filtered, washed with acetonitrile, and dried, yield 36.9 g. (98%). The filtrate was distilled from a steam bath to remove acetonitrile, the last traces under reduced pressure. The oily residue was taken up in hot benzene (75 ml.) and the benzene solution was adsorbed on acid-washed alumina (Merck). The benzene eluates from the alumina column gave 17.3 g. (55%) of pale yellow oil which solidified on cooling, was crystallized from benzene-hexane, and melted at 86–87°. It had the following absorption bands: λ (NO₂) 6.34, 7.36 μ ; λ_{max} (EtOH) 276 m μ ; log ϵ 1.57.

Anal. Calcd. for C₅H₈N₂O₄: C, 37.99; H, 3.82; N, 17.72. Found: C, 38.57; H, 3.77; N, 17.48, 17.71.

When the alumina column was eluted successively with ether and acetone, viscous oils were obtained in yields of 7.2 g. (28%) with the infrared spectrum of *N*-hydroxymethyl-

succinimide. The combined oils were crystallized from benzene and melted at 60–65°, lit. m.p. 63–64°.¹⁴

Reaction of N-nitromethylsuccinimide with sodium methoxide. *N*-Nitromethylsuccinimide (0.40 g., 0.0025 mole) was dissolved in a solution of sodium (0.0644 g., 0.0028 g-atom) in methanol (7 ml.). The pale yellow mixture was allowed to stand at room temperature for 3 hr. Then it was evaporated under reduced pressure. The residual colorless oil which was extracted with methylene chloride weighed 0.25 g. (70%). It boiled at 70° (0.1 mm.) and was identical with authentic material prepared by reaction of *N*-bromomethylsuccinimide with sodium methoxide, b.p. 70° (0.1 mm.), n_D^{25} 1.4813.

Anal. Calcd. for C₅H₉NO₃: C, 50.35; H, 6.34; N, 9.78. Found: C, 50.73; H, 6.19; N, 9.52, 10.14.

Reaction of nitromethylsuccinimide with piperidine. A solution of piperidine (1.53 g., 0.0188 mole) in 95% ethanol (5 ml.) was added to a suspension of nitromethylsuccinimide (1.42 g., 0.00898 mole) in 25 ml. of ethanol. After 10 min. of mechanical shaking at room temperature, the imide had dissolved. The pale yellow solution was allowed to stand at 25° for 1 hr. and evaporated under reduced pressure. The crude yellow oil (3.39 g.) was dissolved in benzene and adsorbed on acid-washed alumina. The benzene and ether eluates contained only traces of product but the subsequent acetone eluate furnished 1.2 g. of yellow oil which gave a colorless solid, m.p. 95–97°, after two sublimations at 0.01 mm. Tenaciously adhering impurities were removed by crystallization from benzene-petroleum ether. The resulting colorless needles (m.p. 104–105°) did not depress the melting point of authentic *N*-piperidinomethylsuccinimide (m.p. 104–105°), prepared from *N*-bromomethylsuccinimide and piperidine, lit. value, m.p. 106–107°.¹⁴

Hydrogenation of N-nitromethylsuccinimide. *N*-Nitromethylsuccinimide (1.58 g., 0.01 mole), dissolved in 100 ml. of 95% ethanol, was shaken with platinum catalyst (0.2 g.) and hydrogen under 10-mm. pressure. The required amount of hydrogen (0.03 mole) was taken up in 13 hr. The colorless solution was filtered and evaporated, leaving 1.5 g. of oil which was identified as a mixture of starting material and phthalimide.

Absorption spectra. Ultraviolet absorption spectra were determined with a Beckman Model DR spectrophotometer, 1-cm. silica cells, and 1×10^{-3} to 1×10^{-5} molar solutions.

A solution of *N*-nitromethylsuccinimide (II) in 1:1 ethanol-concentrated hydrochloric acid was examined at 272 m μ as a function of time. The broad maximum decreased 0.7% in intensity after 6 hr. and 12% after 26 hr. at 25 ± 1°. At reflux temperature (75°/580 mm.) the decrease was 79% in 2 hr.

Infrared absorption spectra were obtained in solution in matched cells or in capillary films with a Perkin Elmer model 21 instrument.

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(14) E. Cherbuliez and G. Sulzer, *Helv. Chim. Acta*, **8**, 568 (1925).