# N-NITROSUCCINIMIDE AND N-NITROPHTHALIMIDE<sup>1</sup>

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The action of mixtures of acetic anhydride and concentrated nitric acid on imides, and the chemistry of N-nitroimides appear to have been neglected in the published literature. Several compounds containing the —CONHCO—group have been treated with nitric acid (d., 1.52) (1, 2) but have been reported either to remain unchanged, or to decompose with the evolution of nitrous oxide. This article is concerned with the structure and properties of the products obtained by the action of acetic anhydride and nitric acid on succinimide and phthalimide.

## N-NITRO DERIVATIVE OF SUCCINIMIDE

The compound from succinimide,  $C_4H_4N_2O_4$ , m.p. 92.5–94° appears to be N-nitrosuccinimide (I)<sup>3</sup> but the structure N-nitroisosuccinimide (II) cannot be excluded rigorously. Isosuccinimide (III) is apparently unknown although a tautomer, 2-amino-5-furanol possessing anomalous (3) properties for that formula has been reported (4). Our compound (I) was reduced catalytically to succinimide under very mild conditions.

The infrared absorption spectrum of I showed in the O—H region only a single sharp, strong peak at 3640 cm.<sup>-1</sup>. If this were interpreted as hydroxyl or unassociated N—H, unsaturated formulas such as 1-nitro-2,5-dihydroxypyrrole (IV) or 2-nitramino-5-hydroxyfuran (V) would have to follow. These structures have been excluded both spectroscopically and by the chemical properties of I.

The observed absorption band was too sharp and the frequency too high to be attributed readily to nitramino N—H (5) or hydrogen-bonded O—H. Moreover, all free, unhindered hydroxyls exhibit a shift in frequency as the carbon tetrachloride solution is progressively diluted (6, 7), but the position of the line at 3640 cm.<sup>-1</sup> was the same in concentrated as in very dilute carbon tetrachloride solution. The degree of hindrance of hydroxyl necessary to prevent the frequency shift on dilution exceeds that found in 2,4-di-*tert*-butylphenol (7). Bulky groups which might lead to this degree of hindrance are not present in IV or V or any of the other structural possibilities for our compound. Accordingly, the peak at 3640 cm.<sup>-1</sup> arises from something else besides hydroxyl or N—H. Similar absorption in this region has been reported recently by Barrow and Searles (8) for some tetrahydrofurans and trimethylene oxides which had no

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<sup>3</sup> Subsequent to our preparation and study of this compound, L. Goodman and L. W. Kissinger informed us privately that they had prepared the compound of melting point 92.5-94° by a similar method. They found that it did not react with cyclohexene and ascribed to it the structure I.

hydroxyl or amino groups, and for dioxane (9). A possible assignment of the frequency of I at 3640 cm.<sup>-1</sup> is that it is derived from a small heterocyclic ring. However, our infrared spectrum of succinimide did not show such a frequency unless it was masked by the N—H frequencies, and the peak at 3640 cm.<sup>-1</sup> is therefore left unassigned.



Absorption bands observed at 2800–3050 cm.<sup>-1</sup> and in the 1400–1440 cm.<sup>-1</sup> region are somewhat ambiguous but seem to favor the presence of methylene groups, as in I, and the absence of double-bonded C—H, as in IV and V. Other characteristics of the spectrum are the N-nitro absorption at 1600 cm.<sup>-1</sup> and the carbonyl peaks in the 1800–1900 cm.<sup>-1</sup> region comparable to those in succinimide itself.

Structure I is supported by many other properties. The substance did not react with bromine in carbon tetrachloride or chloroform and did not decolorize permanganate in acetone. This behavior is in contrast to that of substances to which the  $\alpha$ -hydroxypyrrole structure has been assigned (10, 11) as well as that of many pyrroles, of some furans, of enols, and of aromatic hydroxy derivatives in general. The compound did not give a color with ferric chloride solution. When treated with diazomethane, the substance did not react vigorously with the evolution of nitrogen as nitramines have been reported to do (12, 13); instead, an oil was obtained which evolved nitrogen only on subsequent hydrolysis. No evidence for the presence of hydroxyl groups could be obtained by attempted reaction of I under Schotten-Baumann conditions or with pyridine and acetyl chloride. Grob and Ankli (14) and Almström (15) have reported strong evidence in favor of assigning the  $\alpha$ -pyrrolone structure to several compounds which in their enolic forms would be  $\alpha$ -hydroxypyrroles.

Toward hydroxylic compounds N-nitrosuccinimide (I) showed reactivity

comparable to that of an acid anhydride or acyl halide. Aqueous solutions decomposed steadily on standing at room temperature, and when heated readily gave good yields of succinic acid and nitrous oxide. On long reflux with methanol or ethanol the corresponding dialkyl succinates were obtained.

Toward bases I was even more reactive. It decomposed rapidly in dilute aqueous caustic at room temperature. When heated with anhydrous 4-picoline, it gave 93% of the theoretical amount of nitrous oxide and 65% of succinic anhydride in a vigorous reaction. This represents a novel method of formation of an anhydride. While nitramide has been decomposed by tertiary bases (16, 17), and compounds of the acylnitramide type have often been split by ammonia and even by primary amines (18), the decomposition of I with 4-picoline appeared unique in that neither of the reactants had an N—H bond.

When N-nitrosuccinimide (I) was refluxed with anhydrous methanol for five hours, there was obtained in 39% yield a compound which had the composition of an adduct of the nitroimide and one molecule of methanol. It could be recrystallized from non-polar solvents but decomposed in aqueous alkali with the evolution of nitrous oxide. Titration with alkali at  $-10^{\circ}$  showed it to be a monobasic acid. Since prolonged methanolysis of I gave dimethyl succinate, and since this ester was also obtained in appreciable amount in the preparation of the methanol adduct from I, it seemed likely that the adduct was an intermediate in the complete methanolysis of I. It appeared to be methyl N-nitrosuccinamidate (VI), by analogy with the reaction product of a cyclic anhydride with an alcohol. The other principal structural possibilities were 1-nitro-5-methoxy-5-hydroxy-2-pyrrolidone (VII) and 5-methoxy-5-nitraminotetrahydro-2-furanone (VIII) which would be analogous to structures postulated in more or less similar cases (19-22).



Only one other derivative of the type  $RCONHNO_2$  encountered in VI seems to have been reported, namely, N-nitroacetamide, but this has been described as "quite unstable in the free state" (23). In VI the carbomethoxy group may be the stabilizing influence on our nitroamide.

In view of the well-known brominating action of N-bromosuccinimide in neutral solution it was hoped that I might be a nitrating agent in neutral media. However, it was found that the compound was ineffective for this purpose. Acenaphthene, cyclohexene, diethyl malonate, and 2-nitropropane all failed to react. Even toward phenol N-nitrosuccinimide did not exhibit useful nitrating action in the absence of a solvent. In concentrated sulfuric acid, I reacted with an equimolar amount of phenol to produce a 13% yield of *o*-nitrophenol, virtually no *p*-nitrophenol, and 0.7% of 2,4-dinitrophenol. Other acylnitramine-type compounds can also introduce nitro groups into nuclear positions of phenols and aromatic amines in concentrated sulfuric acid solution (24); we found that excess nitroguanidine converted phenol to picric acid in 30% yield under these conditions.

#### N-NITRO DERIVATIVE OF PHTHALIMIDE

An N-nitro derivative of phthalimide was obtained in 71% yield by nitration of phthalimide in acetic anhydride. The substance probably has the structure of N-nitrophthalimide (IX) although the N-nitroisophthalimide formula (X) again could not be excluded completely. Like the nitration product of succinimide,



its behavior toward water and alcohols was that of an acid anhydride or an acyl halide. Hydrolysis with warm dilute sodium hydroxide solution gave 83% of the theoretical amount of phthalic acid, and 97% of nitrous oxide. N-Nitrophthalimide appeared to be without useful activity for introducing nitro groups in neutral medium; twenty-two hours' boiling with cyclohexene in chloroform gave no more than a trace of a C-nitro derivative. Reduction with lithium aluminum hydride gave only o-bis(hydroxymethyl)benzene; the nitrogen was evidently lost by base-catalyzed decomposition to nitrous oxide. This is in contrast to the behavior of many amides and imides which on reduction with lithium aluminum hydride give at least small amounts of the corresponding amines.

On heating N-nitrophthalimide with ethanol, and with benzyl alcohol, respectively, stable crystalline adducts containing equimolar amounts of the components were formed. They could be recrystallized from benzene or chloroform, behaved as strong monobasic acids in aqueous ethanol, and decomposed on treatment with warm dilute alkali with the evolution of nitrous oxide. They were thus analogous to the methanol adduct of N-nitrosuccinimide, and on similar grounds appeared to be alkyl N-nitrophthalamidates (XI).

The principal ultraviolet spectral data of phthalimide, N-nitrophthalimide (IX), and ethyl N-nitrophthalamidate are given in Table I, along with literature data on other phthalic derivatives.

The absorption of IX in chloroform resembled that of phthalimide in chloroform and was reasonably close to that (20) of phthalic anhydride in dioxane. As expected, there was a decided parallel between the spectra of IX and its

| Substance                       | Solvent    | Concentration         | $\lambda_{max}$ , Å | •max     | $\lambda_{\min}, \rm \AA$ | emin     |
|---------------------------------|------------|-----------------------|---------------------|----------|---------------------------|----------|
| N-Nitrophthalimide (IX)         | Ethanol    | $1.4 \times 10^{-4}M$ | 2760                | 4656     | 2600                      | 3680     |
|                                 | Ethanol    | $3 \times 10^{-5}M$   | 2760                | 10195    | 2510                      | 6058     |
|                                 | Chloroform |                       | 2960                | 2581     | 2820                      | 2401     |
| Ethyl N-nitrophthalamidate      | Ethanol    | $1.4 \times 10^{-4}M$ | 2760                | 4419     | 2600                      | 3443     |
| (XIa)                           | Ethanol    | $3 \times 10^{-5}M$   | 2760                | 9867     | 2510                      | 5956     |
|                                 | Chloroform |                       | 2760                | 1699     | 2680                      | 1555     |
| Phthalimide                     | Ethanol    |                       | 2910                | 1812     | 2490                      | 689      |
|                                 | Chloroform |                       | 2930                | 2194     | 2480                      | 790      |
| Phthalic anhydride (18)         | Dioxane    |                       | 2860                | ca. 1700 | 2740                      | ca. 1400 |
|                                 | Ethanol    |                       | 2750                | ca. 1150 | 2640                      | ca. 870  |
| Phthalic acid (19)              | 0.1 N HCl  |                       | 2760                | 1450     |                           |          |
| Disodium phthalate (19)         | 0.1 N NaOH |                       | 2725                | 850      |                           |          |
| Ethyl phthalate (18)            | Ethanol    |                       | 2750                | ca. 1200 | 2540                      | ca. 840  |
| $\alpha$ -Methoxyphthalide (18) | Dioxane    |                       | 2810                | ca. 1300 | 2770                      | ca. 1200 |

| נ           | TABLE I    |         |
|-------------|------------|---------|
| ULTRAVIOLET | Absorption | Spectra |

ethanol adduct (XIa) on the one hand, and the spectra of phthalic anhydride and ethyl phthalate on the other hand.

The spectra of IX and ethyl N-nitrophthalamidate (XIa) in ethanol were so alike as to suggest that the ester was formed immediately when the nitroimide was dissolved in ethanol even at room temperature. Neither of these ethanol solutions followed Beer's Law. There was a regular progression of the spectral properties of XIa from those in chloroform through those in concentrated, to those in more dilute ethanol solutions. This was characterized by the absence of a change in the wave length of maximum absorption and by a marked increase in the apparent molar extinction coefficient in going from the chloroform solution to the more dilute ethanol solution.

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## EXPERIMENTAL<sup>4</sup>

*N-Nitrosuccinimide*. A mixture of 74.6 g. (0.753 mole) of succinimide and 285 ml. (6.12 moles) of acetic anhydride was cooled to  $-5^{\circ}$  and 285 ml. (6.12 moles) of 91% nitric acid was added with stirring over a period of 45 minutes at  $0-5^{\circ}$ . The reaction mixture was then warmed to 28°, maintained at *ca*. 30° for 12 hours, cooled to  $-10^{\circ}$ , and 1200 g. of ice and 720 ml. of ice-water were added with stirring over about 45 minutes. The precipitate was filtered, washed with 150 ml. of ice water, and dried *in vacuo*. The yield of glistening colorless plates was 62 g., m.p. 87-88.5°. Another 6.8 g. was obtained by extraction of the filtrate with ether; total yield, 63%. Crystallization from absolute ethanol, and from chloroform-petroleum ether raised the melting point to 92.5-94°.

<sup>4</sup> All melting points are corrected. Microanalyses by Clark Analytical Laboratories, Urbana, Illinois.

Anal. Calc'd for C<sub>4</sub>H<sub>4</sub>N<sub>2</sub>O<sub>4</sub>: C, 33.34; H, 2.80; N, 19.44.

Found: C, 33.68, 33.43; H, 2.53, 2.78; N, 19.43.

The substance was soluble in acetone, benzene, and ethyl acetate, and slightly soluble in cold water, ethanol, chloroform, boiling carbon tetrachloride, isoöctane, and petroleum ether. The aqueous solution immediately had pH about 4. The material decomposed at about 150-200° with the evolution of gas and the formation of an orange residue. It was only barely explosive on strong heating. It did not decolorize permanganate in acetone or bromine in carbon tetrachloride, chloroform, or glacial acetic acid, and gave no color with ferric chloride in water or ethanol. Boiling triethylamine converted it to a water-soluble, amine-insoluble black tar. A Franchimont test with  $\alpha$ -naphthylamine gave a pink color with impure samples while pure, old samples always gave only a pale yellow color. Diethylaniline gave a greenish-yellow color.

Hydrolysis. N-Nitrosuccinimide was hydrolyzed slowly by water on standing, or rapidly by 10% aqueous sodium hydroxide solution. No unchanged material was recovered when a cold sulfuric acid solution was poured into water. Formic acid (88%) on standing for 45 hours caused considerable decomposition but no nitramide could be detected.

When 0.1 g. of N-nitrosuccinimide was barely covered with water and heated at  $92^{\circ}$  for one hour, nitrous oxide was evolved rapidly (burning splinter test). On cooling, succinic acid crystallized out, m.p. 185-187°; no depression of a mixture melting point.

*Ethanolysis*. A solution of 5.0 g. of *N*-nitrosuccinimide in 20 ml. of anhydrous ethanol was refluxed for four days, the ethanol was removed, and the residue was dissolved in 15 ml. of ether; the ether solution was washed with 5% sodium bicarbonate solution and with water, dried, and distilled. A yield of 4.04 g. (67%) of diethyl succinate, b.p. 213° (751 mm.),  $n_{\rm p}^{20}$  1.4156 was obtained. [Literature data, b.p. 216.5° (25);  $n_{\rm p}^{14.6}$  1.42249;  $n_{\rm p}^{20}$  1.4201;  $n_{\rm p}^{21.6}$  1.4193 (27)].

Methanolysis. A solution of 5.0 g. of N-nitrosuccinimide in 25 ml. of anhydrous methanol was refluxed for 49.5 hours. Distillation at 60-100 mm. gave 2.69 g. (53%) of colorless dimethyl succinate which was purified by freezing, b.p. 195° (760 mm.), m.p. 17-18°,  $n_D^{20}$  1.4145.

Methanol adduct. A solution of 15.0 g. of N-nitrosuccinimide in 75 ml. of absolute methanol was refluxed for 4.8 hours, the solvent was removed with gentle warming under reduced pressure, 50 ml. of anhydrous benzene was added to the residue, and the mixture was allowed to crystallize in the cold. A yield of 5.35 g. (39% based on reacted starting material) of colorless needles, m.p. 105-108°, was obtained. Recrystallization from dry benzene or chloroform raised the melting point to 109-110°.

Anal. Calc'd for C<sub>5</sub>H<sub>8</sub>N<sub>2</sub>O<sub>3</sub>: C, 34.09; H, 4.58; Neut. equiv., 176.1.

Found: C, 34.57; H, 4.59; Neut. equiv., 178.9.

The material was soluble in ethanol, methanol, and ethyl acetate. No change in melting point occurred on storage in a desiccator. On treatment with aqueous base the substance rapidly evolved gas. In the Franchimont test,  $\alpha$ -naphthylamine gave a yellow color. Bromine and permanganate tests showed no sign of unsaturation. The titration for the neutral equivalent was carried out at 0°; only 20% of the titrated sample was recovered in pure form on vacuum evaporation of the re-acidified solution, but by far the greater part of the decomposition appeared to have taken place after reaching the end point.

The filtrates of the methanol adduct were worked up carefully and permitted recovery of 3.78 g. (25%) of unreacted N-nitrosuccinimide, and 2.91 g. (26%) of dimethyl succinate.

Reduction of N-nitrosuccinimide. By hydrogenating a solution of 1.00 g. of N-nitrosuccinimide in 15 ml. of dry dioxane in the presence of 75 mg. of Adams' catalyst at atmospheric pressure for 14 hours, 2.01 moles of hydrogen were absorbed. After filtration from the catalyst, concentration of the solution, and three crystallizations of the resulting solid from acetone, 0.270 g. (39%) of nearly colorless crystals, m.p. 120.5–126° was obtained. A mixture melting point with succinimide (m.p. 125–127°) was 123.5–126.5°. The melting point reported for 2-amino-5-furanol is 185° (4).

Reaction of N-nitrosuccinimide with 4-picoline. When 3.00 g. of N-nitrosuccinimide was

warmed gently with 4-picoline, an exothermic reaction took place and 485 ml. of nitrous oxide (756 mm., 23°, 93% conversion) was evolved. Extraction of the black residue with petroleum ether gave mostly 4-picoline; the insoluble residue was extracted with acetone, and the acetone solution was concentrated. The concentrate was decolorized in hot benzene-isoöctane and the solution cooled to give 1.36 g. (65%) of crude succinic anhydride, m.p. 108-145°. Exhaustive purification from benzene-isoöctane gave 0.44 g. of colorless needles, m.p. 114-120.5°, which did not depress the melting point of authentic succinic anhydride.

Nitrating action of N-nitrosuccinimide. A. In neutral medium. No nitration took place with diethyl malonate, cyclohexene, acenaphthene, or 2-nitropropane. Experiments with chloroform or sym-tetrachloroethane as solvents, or without a solvent, at temperatures of 80°, or 140°, with or without ultraviolet radiation, and at reaction times up to six days were unsuccessful in producing a detectable amount of a new C-nitro compound.

B. In sulfuric acid. To an ice-cold solution of 1.99 g. (21.2 millimoles) of phenol in 4 ml. of concentrated sulfuric acid was added, with occasional agitation, 3.14 g. (21.8 millimoles) of N-nitrosuccinimide over about one-half hour so that the temperature did not rise above 5°. After allowing the mixture to warm very gradually to 15° over a period of 2.25 hours, it was poured into 12 g. of ice. A precipitate formed; it was filtered at  $-10^{\circ}$  and steam-distilled. From the distillate there was recovered 0.40 g. (13%) of *o*-nitrophenol of which 0.27 g. was pure, m.p. 44-45° [Literature m.p., 44-45° (28)]. The  $\alpha$ -naphthylurethan melted at 109-111° [Literature, m.p. 112-113° (29)]. The residue from the steam-distillation was decolorized and worked up to give 20 mg. (0.7%) of 2,4-dinitrophenol, m.p. 108-110.5° which did not depress the melting point of an authentic sample.

Nitration of phenol with nitroguanidine. To a solution of 1.20 g. (12.8 millimoles) of phenol in 10 ml. of concentrated sulfuric acid was added in small portions with stirring and occasional cooling 5.00 g. (46.3 millimoles) of nitroguanidine. The temperature rose to 60–70°, and an additional 2.5 ml. of sulfuric acid was added to facilitate solution. The clear redbrown solution was allowed to stand at 27° for one day and then heated on a steam-bath until no more gas was evolved. It was poured into 35 ml. of water, cooled, and filtered. After further purification, 0.86 g. of picric acid, m.p. 121–122° was obtained and identified by a mixture melting point.

*N-Nitrophthalimide*. To 1 1. (22.8 moles) of colorless 96% nitric acid was added with stirring at 0-5°, 800 ml. (8.47 moles) of acetic anhydride, dry air being bubbled through rapidly in order to remove nitrogen oxides. The solution was cooled to  $-3^{\circ}$  and 250 g. (1.7 moles) of pure phthalimide was added. The material went into solution as the mixture was warmed to 16° with stirring, and stirring at 16-20° was continued for four hours with constant bubbling of dry air through the liquid. After standing at 6° for two days, the precipitate which had formed was collected on a sintered glass filter under positive pressure of dry air, and under these conditions was washed with three portions of fresh nitrating mixture, two portions of acetic anhydride, and three portions of carbon tetrachloride. The material was dried *in vacuo* over phosphorus pentoxide and soda lime and weighed 233.6 g. (71%), m.p. 202-206° (dec.). Purification by refluxing with 1500 ml. of dry chloroform for 17 hours, and further crystallization from chloroform gave 217 g. of fine colorless needles, m.p. 202-209° (dec.).

Anal. Calc'd for C<sub>8</sub>H<sub>4</sub>N<sub>2</sub>O<sub>4</sub>: C, 50.01; H, 2.10; N, 14.58.

Found: C, 49.85; H, 2.13; N, 14.67.

The substance was slightly soluble in acetone, sparingly soluble in chloroform, dioxane, and acetic anhydride, and nearly insoluble in most other organic solvents and in water. It sublimed at 146° (0.15–0.3 mm.) with only slight decomposition. The Franchimont test with  $\alpha$ -naphthylamine gave a red color. Treatment with warm dilute alkali gave 83% of phthalic acid (identified by mixture melting point) and 97% of nitrous oxide (splinter test).

Ethanol adduct. When 25.0 g. of N-nitrophthalimide was refluxed with 250 ml. of absolute ethanol for three hours, it went into solution. The solvent was removed under a vacuum, and 150 ml. of benzene and 75 ml. of isoöctane were added to the residue. The chunky crystals which formed on standing in the cold weighed 28.1 g. (91%), m.p. 97-100.5°. Recrystalliza-

tion from benzene and from carbon tetrachloride gave colorless crystals, m.p. 101-103.5°. Anal. Cale'd for C<sub>10</sub>H<sub>10</sub>N<sub>2</sub>O<sub>5</sub>: C, 50.42; H, 4.23; Neut. equiv., 238.2.

Found: C, 50.68; H, 4.40; Neut. equiv., 236.5.

The substance was soluble in dioxane, ethanol, ethyl acetate, 10% aqueous sodium hydroxide, and 5% sodium bicarbonate solution. It was nearly insoluble in water and petroleum ether. Boiling water liquefied but did not change it. On warming with 10% aqueous alkali, 99.7% of the theoretical amount of nitrous oxide was evolved. The Franchimont test with  $\alpha$ -naphthylamine gave a golden-yellow color, and a salmon-pink with diethylaniline.

Benzyl alcohol adduct. A suspension of 4.0 g. of N-nitrophthalimide in 8.6 ml. of benzyl alcohol and 10 ml. of chloroform was refluxed for three days. The solid went into solution during the third day. The solvents were removed, and the residue was taken up in 50 ml. of ether and extracted with three portions of ice-cold 5% sodium bicarbonate solution. The alkaline extracts were washed with 30 ml. of ether, acidified to Congo Red, the mixture was warmed gently to expel dissolved ether, and the precipitate was filtered. The yield was 5.69 g. (91%), m.p. 108-116°. Recrystallization from carbon tetrachloride and benzene-isoöctane raised the melting point to 116-117.5°.

Anal. Calc'd for C15H12N2O5: C, 60.00; H, 4.03; Neut. equiv., 300.

Found: C, 60.10; H, 4.09; Neut. equiv., 302.

The substance was soluble in ethanol, ethyl acetate, and benzene. The Franchimont test with  $\alpha$ -naphthylamine produced a yellow-red color. Although insoluble in cold 10% alkali, the compound decomposed on warming with this reagent with the evolution of gas.

Reduction of N-nitrophthalimide with lithium aluminum hydride. Into a refluxing mixture of 300 ml. of dry ether and 7.1 g. of lithium aluminum hydride, 7.2 g. of N-nitrophthalimide was extracted over a period of 31 hours from a Soxhlet thimble. After standing overnight, decomposition of the reaction mixture, and acidification, the aqueous layer was separated and extracted twice with ether. The ether extracts were washed with 15 ml. of 5% aqueous bicarbonate solution, concentrated to 30 ml., and extracted with three 50-ml. portions of water. From the evaporated water solution, 2.7 g. (52%) of o-bis(hydroxymethyl)benzene, m.p.  $61-65^{\circ}$ , was obtained on crystallization from a little ether. No amine could be detected in the acidic aqueous layer.

## SUMMARY

Nitration of succinimide and of phthalimide gives crystalline mononitro derivatives for which the structures of N-nitrosuccinimide, and of N-nitrophthalimide, respectively, have been made likely. Chemical reactions of these compounds are described.

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#### REFERENCES

- (1) FRANCHIMONT, Rec. trav. chim., 2, 329 (1883).
- (2) FRANCHIMONT AND KLOBBIE, Rec. trav. chim., 8, 283 (1889).
- (3) ELDERFIELD AND DODD, in Elderfield, Heterocyclic Compounds, Vol. I, p. 178, John Wiley and Sons, New York, 1950.
- (4) HODGSON AND DAVIES, J. Chem. Soc., 1013 (1939).
- (5) LOTHROP, HANDRICK, AND HAINER, J. Am. Chem. Soc., 73, 3581 (1951).
- (6) SMITH AND CREITZ, J. Research Natl. Bur. Standards, 46, 145 (1951).
- (7) COGGESHALL, J. Am. Chem. Soc., 69, 1620 (1947).
- (8) BARROW AND SEARLES, J. Am. Chem. Soc., 75, 1175 (1953).
- (9) MCKINNEY, LEBERKNIGHT, AND WARNER, J. Am. Chem. Soc., 59, 481 (1937).
- (10) FISCHER AND HARTMANN, Z. physiol. Chem., 226, 116 (1934).
- (11) FISCHER, YOSHIOKA, AND HARTMANN, Z. physiol. Chem., 212, 146 (1932).

- (12) HEINKE, Ber., 31, 1395 (1898).
- (13) DEGNER AND PECHMANN, Ber., 30, 646 (1897).
- (14) GROB AND ANKLI, Helv. Chim. Acta, 32, 2010, 2023 (1949).
- (15) Almström, Ann., 416, 279 (1918).
- (16) BELL AND WILSON, Trans. Faraday Soc., 46, 407 (1950).
- (17) BRÖNSTED AND PEDERSEN, Z. physik. Chem., 108, 185 (1924).
- (18) VAN ROMBURGH, Rec. trav. chim., 8, 273, 280 (1889); VAN ROMBURGH AND MAUREN-BRECHER, Verslag. Akad. Wettenschappen (Amsterdam), 15, 731 (1907).
- (19) ANDERSON AND KENYON, J. Am. Chem. Soc., 70, 3952 (1948).
- (20) HIRSHBERG, LAVIE, AND BERGMANN, J. Chem. Soc., 1030 (1951).
- (21) MCKAY AND WRIGHT, J. Am. Chem. Soc., 70, 3990 (1948).
- (22) MCKAY, PICARD, AND BRUNET, Can. J. Chem., 29, 746 (1951).
- (23) HINSBERG, Ber., 25, 1092 (1892).
- (24) LAMBERTON, Quart. Revs. (London), 5, 82 (1951).
- (25) PERKIN, J. Chem. Soc., 45, 515 (1884).
- (26) BRÜHL, J. prakt. Chem., (2) 50, 119, 140 (1894).
- (27) VOGEL, J. Chem. Soc., 2010, 2021 (1928).
- (28) DESVERGNES, Rev. chim. ind. (Paris), 36, 194, 224 (1927); Chem. Abstr., 21, 3607 (1927).
- (29) FRENCH AND WIRTEL, J. Am. Chem. Soc., 48, 1736 (1936).