tions differed only in that lavender crystals of nickel(II) chloride 6-ammonate[7] were obtained.

Anal. Calcd. for $Ni(NH_3)_6Cl_2$: Ni, 25.3; NH_3, 44.1; Cl, 30.6. Found: Ni, 25.6; NH_3, 44.2; Cl, 30.4.

Reactions with Potassium Amide.—Nickel(II) oxide was recovered unchanged after treatment with a liquid ammonia solution containing an excess of potassium amide for seventy-two hours at 25 or 100°. By similar treatment, nickel(II,III) oxide was converted to an intractable mixture of insoluble products. Essentially the same conversion resulted from treatment of this oxide with liquid ammonia solutions of potassium at 25°. At either 25 or 100°, iron(III) oxide reacted with liquid ammonia solutions of potassium amide to form mixtures of iron(II) oxide and elemental iron in relative quantities dependent upon the quantity of potassium employed.

Reduction by Liquid Ammonia Solutions of Potassium.—At 0°, nickel(II) oxide was reduced to elemental nickel by liquid ammonia solutions of potassium to an extent dependent upon the concentration of potassium used. With 2, 4, 8 and 12 equivalents of potassium, reduction occurred to the extent of 0.3, 0.5, 1.4, and 4.3%, respectively. The weights of potassium amide formed concurrently[2] (as shown by analysis), agreed closely with corresponding values calculated on the basis of (a) the volumes of hydrogen liberated, and (b) the quantities of elemental nickel produced.

The catalytic activity of nickel(II,III) and iron(III) oxides (or that of very small quantities of their reduction products) toward the conversion of potassium to potassium amide was so pronounced that appreciable reduction of these oxides (by ammonia solutions of potassium) could not be accomplished. The decreasing order of catalytic activity is $Fe_2O_3 > Ni_3O_4 > NiO$.

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(7) Rose, *Pogg. Ann.*, **20**, 155 (1830).

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RECEIVED FEBRUARY 23, 1943

The Nitration of Methyl α-Naphthoate and Related Compounds[1]

BY C. F. KOELSCH AND DONALD O. HOFFMAN

Because the nitration of methyl benzoate takes place so much more smoothly than does that of benzoic acid,[2] it was hoped that the nitration of methyl α-naphthoate might yield methyl 3,8-dinitronaphthoate among the dinitration products. It has been found, however, that the main product of this reaction is methyl 4,5-dinitronaphthoate, a substance which is also formed when methyl 5-nitronaphthoate is nitrated. The nitration of methyl 8-nitronaphthoate yields a dinitro ester which appears to be methyl 4,8-dinitronaphthoate. In none of the naphthoic ester nitrations does the reaction take place smoothly; oily by-products are formed, and unless the temperature is kept close to 0°, gas is evolved and much hydrolysis occurs. This is not similar to the behavior of methyl benzoate, where neither hydrolysis nor by-product formation is important at 15° or higher.

In the nitration of α-naphthoic acid there is formed a small amount of an acid not previously reported, which is probably 6,8-dinitronaphthoic acid. A stable molecular compound of naphthoic acid with 5-nitronaphthoic acid has also been isolated.

Experimental

Methyl α-Naphthoate.—The ester (b. p. 167–169° at 20 mm.) was obtained in 89% yield by passing methanol vapor (600 g.) at 85–100° during ninety minutes through 113 g. of α-naphthoic acid mixed with 10 ml. of concd. sulfuric acid and 300 ml. of methanol.[3]

To a solution of 10 g. of methyl α-naphthoate in 33 ml. of concd. sulfuric acid, a solution of 10 ml. of nitric acid (d. 1.2, 3 eq.) in 10 ml. of concd. sulfuric acid was slowly added at 0–10°. The mixture became red-black almost at once, and much heat was evolved during the addition of the first two-thirds of the nitric acid. After the addition was completed, the mixture was allowed to stand at 0° for ten minutes and then poured on ice. The sticky product was washed with dilute sodium carbonate (which removed 5- and 8-nitro- and a small amount of 4,5-dinitro-naphthoic acids) and then with ether–ligroin. The insoluble material (4.0 g., m. p. 140–185°) was crystallized from toluene and then from acetic acid, giving 2.12 g. of **methyl 4,5-dinitronaphthoate** which formed nearly colorless needles that melted at 194–195°.

Anal. Calcd. for $C_{12}H_8N_2O_6$: C, 52.2; H, 2.9. Found: C, 52.2; H, 2.9.

The ester was identified by hydrolysis (acetic acid, water and sulfuric acid); the resulting 4,5-dinitronaphthoic acid melted at 266–267° (reported[4] 265°), and on boiling for fifteen minutes in quinoline containing a little copper acetate yielded 1,8-dinitronaphthalene, m. p. 170–172°.

Oily material and about 3 g. of crystalline material were present in the ether–ligroin washings of the crude nitration product, but no pure substance could be isolated from these.

Duplicate experiments and others in which up to five equivalents of nitric acid in sulfuric acid was used gave results quite similar to those described. However, when less nitric acid was used, less dinitronaphthoic ester and more 5- and 8-nitronaphthoic acids were obtained. Nitration in the absence of sulfuric acid, using fuming nitric acid, gave mainly a mixture of methyl 5- and 8-nitronaphthoates, little hydrolysis or dinitration taking place.

Methyl 5-Nitronaphthoate.—The ester, prepared in 70% yield by boiling 5-nitronaphthoic acid (5.1 g.) with methanol (50 ml.) and sulfuric acid (1 ml.) for five hours,

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(1) From the M.S. thesis of D. O. Hoffman, March, 1941.

(2) Kamm and Segur, "Organic Syntheses," Coll. Vol. I, 1932, p. 364.

(3) *Cf.* Corson, Adams and Scott, "Organic Syntheses," **10**, 48 (1930).

(4) Ekstrand, *J. prakt. Chem.*, **38**, 256 (1888).

melted at 107–109° (reported[5] 109–110°). No nitration took place when the ester was heated with an excess of fuming nitric acid in acetic acid. When it was dissolved in concd. sulfuric acid (2 g. in 10 ml.) and treated at 0° with 0.6 ml. of nitric acid (d. 1.42), there was formed 1.3 g. (52%) of methyl 4,5-dinitronaphthoate, and only a small amount of starting material was recovered. In this nitration almost no acidic products were formed.

Methyl 8-Nitronaphthoate.—The ester was prepared in about 50% yields by the action of methyl sulfate on 8-nitronaphthoic acid in aqueous sodium hydroxide. It separated from 70% acetic acid in the form of nearly colorless prisms that melted at 97–98°.

Anal. Calcd. for $C_{12}H_9NO_4$: C, 62.3; H, 3.9. Found: C, 61.9; H, 4.0.

Nitration with an excess of fuming nitric acid in acetic acid gave a solid product from which no pure material could be isolated. Nitration in sulfuric acid with 1.1 equivalents of concd. nitric acid at 0–10° gave a solid product from which a pure dinitro ester was obtained only by repeated crystallization from 70% acetic acid and then from ethanol.

Anal. Calcd. for $C_{12}H_8N_2O_6$: C, 52.2; H, 2.9. Found: C, 51.9; H, 2.9.

This ester melted at 189–190° and was probably **methyl 4,8-dinitronaphthoate.** Heated on a steam-bath overnight with 90% sulfuric acid, the ester gave a small amount of an acid that melted at 236–238° and a small amount of 1,5-dinitronaphthalene, m. p. 218°.

Nitration of α-Naphthoic Acid.—A number of experiments were made, but the best results were obtained by the method of Ekstrand[6] using fuming nitric acid in acetic acid. The crude mixture of nitro acids (81 g. from 100 g. of α-naphthoic acid) was boiled with alcohol for four hours while a stream of hydrogen chloride was led into the solution. Most of the alcohol was then distilled, and the residue was taken up in ether and treated with dilute sodium carbonate. The mixture was filtered and then separated; the ether contained ethyl 5-nitronaphthoate and the aqueous solution contained sodium 8-nitronaphthoate. The insoluble solid consisted of sodium 6,8(?)-dinitronaphthoate; it was recrystallized from sodium carbonate solution, and the acid was then liberated with hydrochloric acid and crystallized twice from acetic acid giving small tan plates that melted with decomposition at 267–268° or at 274–276° when heated rapidly.

Anal. Calcd. for $C_{11}H_6N_2O_6$: C, 50.4; H, 2.3. Found: C, 50.5; H, 2.3.

Mixed with 4,5-dinitronaphthoic acid, the **6,8(?)-dinitronaphthoic acid** melted at 245–250°. When it was heated in quinoline with copper acetate, it gave 1,3-dinitronaphthalene, m. p. 145–147°.

On boiling for twelve hours with methanol containing a little sulfuric acid, the acid gave **methyl 6,8(?)-dinitronaphthoate,** colorless needles that melted at 179–180°.

Anal. Calcd. for $C_{12}H_8N_2O_6$: C, 52.2; H, 2.9. Found: C, 52.0; H, 2.8.

A **1:1 molecular compound** of α-naphthoic acid with 5-nitronaphthoic acid was isolated in one experiment on the nitration of α-naphthoic acid, and later was synthesized by mixing the components in alcohol. Recrystallized from alcohol, it formed pale yellow platelets that melted at 198–200°.

Anal. Calcd. for $C_{22}H_{15}NO_6$: C, 67.6; H, 3.8. Found: C, 67.4; H, 3.7.

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RECEIVED JANUARY 30, 1943

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(5) Graeff, *Ber.*, **16**, 2252 (1883).

(6) Ekstrand, *J. prakt. Chem.*, **38**, 154 (1888).

A Note on the Preparation of High Temperature Stopcock Greases[1]

BY I. E. PUDDINGTON

Although metallic soaps have been incorporated into mineral oils in the preparation of lubricating greases for years, little appears in the literature regarding their use as stopcock lubricants. The most promising greases for this purpose appear to be those made with the stearates of lithium or aluminum. Both of these materials give products having good stability and high temperature characteristics. They are also water resistant, an essential property for some uses.

These lubricants may be made conveniently from any commercial lubricating oil of good quality and suitable vapor pressure. Depending on the consistency required, a cold dispersion containing 15–25% soap in the oil should be prepared and the mix then carefully heated until complete solution occurs. This will take place in the vicinity of 200°. If the product forms a hard gel on cooling, it should be mechanically worked to a smooth paste. This may be done with a spatula and a glass plate or by forcing the gel through a small orifice several times.

Measurements of the vapor pressure of the stearates of lithium and aluminum lead to the conclusion that the vapor pressure of the grease itself is due almost entirely to the oil from which it is made. The rate of evaporation of the soaps in a heated, evacuated space indicate a vapor pressure in the vicinity of 10^{-5} mm. at 170° for commercial aluminum stearate and less than 10^{-8} mm. for lithium stearate. This difference may be due to the fact that aluminum stearate almost invariably contains some free stearic acid. The production of low vapor pressure oils has already been described.[2] Except where very high vacua are required, however, stripping the oil by vacuum distillation will probably render it sufficiently nonvolatile.

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(1) N. R. C. No. 1113.

(2) C. R. Burch, *Proc. Roy. Soc.* (London), **A123**, 271 (1929).