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.

SCHOOL OF CHEMISTRY
UNIVERSITY OF MINNESOTA
MINNEAPOLIS, MINN.
RECEIVED JANUARY 30, 1943

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

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

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

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

Two greases were prepared as described above: one containing 20% lithium stearate, the other 20% commercial aluminum di-stearate, in a number 50 S.A.E. mineral oil. A lump of the lithium base grease retained its shape after two hours in an oven at 175°, while a similar sample of the aluminum base grease melted to a viscous liquid in less than twenty minutes. A small volume vacuum system containing a 14/35 ground glass joint lubricated with these greases and held thermostatically at a temperature of 170° showed a pressure increase of non-condensable gases from 10^{-5} mm. to 10^{-2} mm. in eighteen hours. Some oil distilled from the grease during the test, but, after cooling, the joint was easily taken apart. Although the aluminum base grease melts at a much lower temperature than that made with the lithium soap, the viscosity of the melted material is sufficient to give a good seal and it can also be used as a high temperature lubricant. It is noteworthy that the consistency of these greases does not increase greatly until cooled below the pour point of the oil used in their preparation.

These greases have been found to be very resistant to halogenation and have been used with success for about a year.

RECEIVED FEBRUARY 4, 1943

NEW COMPOUNDS

Xanthone 2,7-Dinitrile

This compound was required for investigation of its value as an insecticide.

Ten grams of 2,7-diaminoxanthone, prepared from xanthone by the method of Baeyer,[1] was dissolved in 25 g. of concentrated hydrochloric acid and 75 cc. of water, cooled in ice, a cold solution of 15 g. of sodium nitrite in 60 cc. of water slowly added, the reaction product diluted with 250 cc. of ice water and filtered. The filtrate was added gradually to a potassium cuprous cyanide solution prepared by mixing a solution of 25 g. of cupric sulfate in 100 cc. of water with a solution of 27.5 g. of potassium cyanide in 50 cc. of water and cooling in ice. The reaction product was allowed to stand overnight at room temperature, after which the precipitate was filtered off, washed thoroughly with water and dried at 100°. Sublimation *in vacuo* yielded 5.3 g., or 48%, of bright yellow crystals. The nitrile dissolved in concentrated sulfuric acid to give a colorless solution with a bright blue fluorescence. It was almost completely insoluble in all the common solvents. For analysis a portion was twice recrystallized from benzonitrile, washed thoroughly with alcohol and dried at 100°. The recrystallized product was a cream-colored microcrystalline powder.

Anal. Calcd. for $C_{15}H_6O_2N_2$: N, 11.38. Found: N, 11.34, 11.27.

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[1] Baeyer, *Ann.*, **372**, 138 (1910).

CONNECTICUT AGRICULTURAL EXPERIMENT STATION
NEW HAVEN, CONN. HARRY J. FISHER

RECEIVED MARCH 16, 1943

t-Butyl Benzoyldimethylacetate

This compound was prepared by a modification of the procedure for the synthesis of ethyl benzoyldimethylacetate.[1] *t*-Butyl isobutyrate[2] (0.158 mole) was added to an ether solution of sodium triphenylmethyl (0.158 mole), the mixture was shaken and allowed to stand at room temperature for forty minutes when the color had become light orange. Benzoyl chloride (0.158 mole) was then added with shaking. After standing for several hours, 10 cc. of acetic acid was added and the mixture was extracted with water, followed by sodium carbonate solution. After removing the solvent from the dried ether solution, the material boiling up to 160° at 15 mm. was collected. Refractionation of the material yielded *t*-butyl benzoyldimethylacetate boiling at 146–148° at 15 mm., and melting at 64–65° after recrystallization from methanol; yield, 50%.

Anal. Calcd. for $C_{15}H_{20}O_3$: C, 72.55; H, 8.12. Found: C, 72.89; H, 8.32.

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[1] Hauser and Renfrow, "Organic Syntheses," **19**, 43 (1939).

[2] Abramovitch, Shivers, Hudson and Hauser, THIS JOURNAL, **65**, 986 (1943).

DEPARTMENT OF CHEMISTRY
DUKE UNIVERSITY J. C. SHIVERS
DURHAM, NORTH CAROLINA CHARLES R. HAUSER

RECEIVED MARCH 8, 1943

1-Phenylethylidenemalonitrile

This compound was prepared by a method analogous to that used by Cope[1] for ethyl 1-phenylethylidenecyanoacetate: 33 g. (0.5 mole) of malononitrile, 60 g. (0.5 mole) of acetophenone, 4 g. of ammonium acetate and 12 g. of acetic acid were refluxed with 100 cc. of benzene under a condenser equipped with a device for constant removal of water. After twenty hours the solution was cooled, washed with water and dried over anhydrous sodium sulfate. The benzene solution was warmed and diluted with technical hexane just short of turbidity. Upon cooling with ice water a large crop of orange crystals separated. Four recrystallizations from dilute ethanol gave 60 g. (56%) of colorless prisms, m. p. 94° (uncor.).

Anal. Calcd. for $C_{11}H_8N_2$: C, 78.5; H, 4.79; N, 16.65. Found: C, 78.27, 78.71; H, 5.03, 4.97; N, 16.40, 16.28.

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[1] Cope, Hofmann, Wyckoff and Hardenbergh, THIS JOURNAL, **63**, 3452 (1941).

CENTRAL RESEARCH LABORATORIES
MONSANTO CHEMICAL COMPANY
DAYTON, OHIO DAVID T. MOWRY

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