gravity at 15/15, 0.7954, optical rotation, −0.7°, and refractive index at 20°, 1.4705. These figures are close to those recorded for myrcene.

This fraction boils at 164–166° at atmospheric pressure with partial polymerization.

Oxidation with permanganate gave succinic acid, m. p. 186°. Reduction with sodium in alcohol yielded dihydromyrcene (tetrabromide m. p. 89–90°), and hydration with acetic acid and 50% sulfuric acid at low temperature gave myrcenol, having a lavender odor and giving a phenylurethan melting at 71–72°. (Enklaar[2] reported a melting point of 68° for myrcenol phenylurethan.) The phenylurethan from the myrcenol gave sharp depressions in melting point when mixed with both *l*-linalool and *i*-linalool phenylurethans.

The small higher boiling fraction remaining after distillation of the myrcene was redistilled at 10 mm. from a small flask provided with a Vigreux column yielding the following products: (1) a very small fraction, 85–90°; (2) a small fraction, 90–100°; (3) the main fraction, 100–110°; (4) a small fraction, 110–140°; leaving a thick, viscous residue in the flask.

Fraction 1 gave a negative reaction for alcohols on treatment with phenyl isocyanate, but gave a positive reaction for the carbonyl group on treatment with semicarbazide, as did also fractions 2 and 3, which gave copious yields of semicarbazone. On decomposition of the semicarbazones an odor suggesting methyl nonyl ketone was observed.

The semicarbazone from fraction 1 melted at 114.5°. The semicarbazones from fractions 2 and 3 melted at 123–124°, and gave no depression in melting point when mixed with the semicarbazone of methyl *n*-nonyl ketone. While indices of refraction were not measurable in either case, optical crystallographic examination showed identical crystalline form and interference figures.[3]

Fraction 3, boiling at 100–110°, had an odor suggesting geraniol. When a portion of this fraction was oxidized with potassium dichromate, an odor of citral was detected. However, attempts to isolate geraniol as the diphenylurethan, or the semicarbazone of citral, were unsuccessful, due no doubt to the predominance of methyl *n*-nonyl ketone.

From the distillation residue a non-volatile oil was extracted which gives a lasting tingling sensation to the tongue and lips. Alkaloidal material was found only in traces, so this physiological effect is not due to aconitine. This substance is being further investigated.

Summary

The volatile oil of Amur cork tree fruit contains over 92% of the aliphatic terpene, myrcene.

The higher boiling portion of the oil contains methyl *n*-nonyl ketone, with possibly a small amount of a lower homolog such as methyl *n*-heptyl ketone.

Evidence was obtained of the presence of a small amount of geraniol in the fraction boiling at 100–110° at 10 mm.

The slight optical activity of the myrcene fraction is probably due to a small amount of an optically active terpene.

WASHINGTON, D. C.

RECEIVED FEBRUARY 1, 1938

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[2] Enklaar, "Over Ocimeen en Myrceen," Inaugural Dissertation, Utrecht, 1905.

[3] Optical crystallographic examination was made by G. L. Keenan of the Food and Drug Administration, U. S. Department of Agriculture.

[CONTRIBUTION FROM THE NAVAL STORES RESEARCH DIVISION, BUREAU OF CHEMISTRY AND SOILS, UNITED STATES DEPARTMENT OF AGRICULTURE]

On the Nature of Pyroabietic Acids

BY ELMER E. FLECK AND SAMUEL PALKIN

The pyroabietic acids[1] have been known for some time as highly stable conversion products of pine resin and rosin acids. Although the experimental data available on the structure of these acids are rather meager, these acids have, up to the present time, been universally regarded as isomeric with abietic and other resinic acids.

Thus assuming two double bonds, Greth[1c] believes that the difference in reactivity between abietic and pyroabietic acids can be explained on the basis of the relative position of the bonds, and proposes for the less reactive pyroabietic acid, structure I, in which he assumes that one of the bonds is common to two rings (B and C), whereas for abietic acid, he assumes structure II, the earlier form proposed by Ruzicka.[2a] Recently Fieser and Campbell[3] have obtained substantial evidence in support of structure III. Sandermann[4] also has proposed the latter structure as one of two possibilities, while Ruzicka and Bacon[2b] have proposed a structure involving distribution of the bonds between the two rings B and C, but with the position of one of the bonds (in ring C) uncertain.

As will be shown later, inferences heretofore regarding the degree of unsaturation and the assumed isomeric character of pyroabietic acid

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[1] (a) Dupont-Dubourg, *Bull. inst. pin.*, 181 (1928); (b) Fanica, *ibid.*, 155, 181 (1933); (c) Greth, *Z. angew. Chem.*, **47**, 827 (1934).

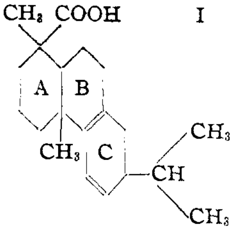
[2] (a) Ruzicka, DeGraaf and Muller, *Helv. Chim. Acta*, **15**, 1300 (1932); (b) Ruzicka and Bacon, *ibid.*, **20**, 1542 (1937).

[3] Fieser and Campbell, THIS JOURNAL, **60**, 159 (1938).

[4] Sandermann, *Bull. inst. pin*, **30**, 138 (1937).

have been erroneous because the latter is not in reality a single compound, but a complex of several compounds difficult to resolve.

I



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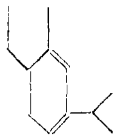

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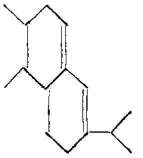

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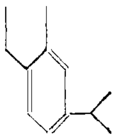

Prior to the publication of our catalytic method for preparing "α-pyroabietic acid,"[5] the only means available for the preparation of these acids was that of subjecting rosin acids or rosins to drastic and prolonged heat treatment (usually one hundred hours at 250°). The extensive pyrolysis[1] which accompanied the supposed isomerizing action and the difficulty of separating the "pyroabietic acid" from the reaction mixture rendered the interpretation of the reaction mechanism difficult. By the catalytic method, not only is the conversion greatly expedited (reaction shown to be practically complete in fifteen minutes), but the resulting acid in terms of the assumed compound "pyroabietic acid" as reported in the literature[1] appeared to be of high purity. The fact, however, that this conversion takes place so readily under conditions which may be regarded as typically those of dehydrogenation (palladium-carbon catalyst, relatively high temperature, without the use of hydrogen) raised some question in our minds as to whether or not this catalytic action was in fact one of isomerization, and not dehydrogenation, and whether or not the reported "pyroabietic acid," with which our catalytic product agreed in every particular, was indeed an isomer of abietic acid.

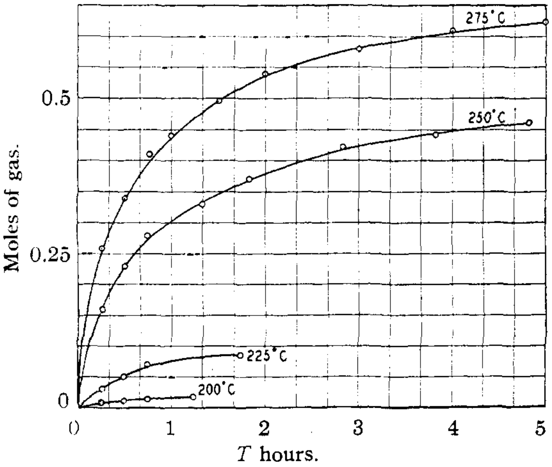

Fig. 1.—Rate of gas evolution in catalytic treatment of *l*-abietic acid.

Data obtained with the pyro acid on hydrogenation with platinum oxide at ordinary pressure, on titration with perbenzoic acid (this showed equivalence of 0.4 of one double bond) and on condensation with maleic anhydride, gave no helpful clues to the degree of unsaturation, except to indicate the low reactivity or high stability already known to characterize the "pyroabietic acids." Its behavior toward tetranitromethane, however, showed the α-pyroabietic acid to be definitely unsaturated. Similar marked difference in stability and resistance to saturation exhibited between the isomeric resin acids is not unknown, as is evidenced in the well-known difference in behavior between the very stable *d*-pimaric acid and the labile *l*-pimaric and *l*-abietic acids.[6]

A series of experiments carried out in a closed system (see Fig. 1) showed that gas was evolved in appreciable quantity at temperatures of 250–275°, and analysis of the acid resulting at the higher temperatures showed it to conform best to the dehydroabietic acid formula ($C_{20}H_{28}O_2$). This obvious indication of dehydrogenation is to be more or less expected, in view of the close approach to the high temperatures normally used for dehydrogenation of the resin acids (300° and up), with this difference, however, that under the more drastic conditions, decarboxylation, loss of the angular methyl group, and more extensive dehydrogenation generally follow, with production of the well-known retene.[7]

At the low temperature (225°), on the other hand, relatively little gas was evolved, and analysis of the product so obtained, as well as that after purification through the ammonium salt, showed it to conform best to the isomer formula ($C_{20}H_{30}O_2$). This latter product, which also

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[5] (a) Fleck and Palkin, *Science*, **85**, 126 (1937); (b) Fleck and Palkin, THIS JOURNAL, **59**, 1593 (1937).

[6] Palkin, *J. Chem. Education*, **12**, 35 (1935), and citations given.

[7] Ruzicka and Waldmann, *Helv. Chim. Acta*, **16**, 842 (1933).

conforms in its properties to those of α-pyroabietic acid described by Fanica, *et al.*,[1] behaves as a homogeneous compound in that resolution by means which have been found effective with other resin acids, was not found possible.[8]

The inferential deduction, however, which would exclude dehydrogenation as the dominant reaction involved at low temperatures, is contradicted by the isolation of tetrahydroabietic acid from the crude products prepared at 225°,[9] unless dehydrogenation and hydrogenation, by way of disproportionation, was the mechanism.

In the meantime, Fieser and Campbell,[3] while working on dehydroabietic acid (structure IV), obtained the first tangible evidence, particularly spectroscopic data, that α-pyroabietic acid contained, or consisted in part, of dehydroabietic acid, the absorption maxima obtained on the pyro and dehydro acid being the same, except that the maxima of the pyroabietic acid were very much lower in intensity.

The α-pyroabietic acid, which behaved as a homogeneous compound, has now been separated into three compounds, dehydro-, dihydro-, and tetrahydroabietic acids.

By esterification with diazomethane, a crystalline methyl ester, m. p. 62–63°, $[\alpha]^{20}_D + 60°$, was isolated from the semicrystalline reaction product. This methyl ester proved to be identical with the methyl ester obtained from the dehydroabietic acid of Fieser and Campbell;[3] furthermore, the free acid, m. p. 172–173°, $[\alpha]^{20}_D +62°$, formed by hydrolysis of the methyl ester in 10% *n*-butyl alcoholic potassium hydroxide, also proved to be identical with the dehydroabietic acid of Fieser and Campbell.[10]

From the non-crystalline portion of the methyl ester, the dihydroabietic acid, m. p. 129–130°, $[\alpha]^{20}_D -3°$, was isolated by partial sulfonation at room temperature and subsequent hydrolysis of the unsulfonated methyl ester.

It therefore becomes apparent that formation of pyroabietic acid is essentially a disproportionation reaction, as suggested by Fieser and Campbell, particularly so when carried out at temperatures about 225°, where the liberation of hydrogen is at a minimum.

The principal products are dehydroabietic and dihydroabietic acids, with a small amount of tetrahydroabietic acid also being formed. Such a mixture would give analytical data corresponding to the $C_{20}H_{30}O_2$ (isomer) formula, and has doubtless led to the belief in the past that pyroabietic acid was isomeric with abietic acid.

At the higher temperatures, but below decarboxylation temperatures, the main product of reaction is dehydroabietic acid, the original abietic acid having sustained a loss of 1 mole of hydrogen.

Experimental Part

Preparation of Pyroabietic Acid.—The *l*-abietic acid used in this preparation was made by the method previously described.[8b] The abietic acid was stored as the quarter salt and freed from alcoholic solution by the addition of dilute hydrochloric acid just before use. Freshly prepared *l*-abietic acid was found necessary, as oxidation of the free abietic acid, which takes place rapidly even at ice-box temperatures, gave a partially oxidized abietic acid which yielded an α-pyroabietic acid of poor quality.

Fifty grams of *l*-abietic acid and 1 g. of palladium-carbon catalyst were heated in an oil-bath held at 225° (inside temperature 215–220°) for one and one-half hours. The product was stirred mechanically. The reaction mass was allowed to cool until 200 cc. of alcohol could be added. The solution was filtered hot and the filtrate was diluted with water to the point of crystallization. The cooled mass was filtered and washed with 100 cc. of 50% alcohol, and dried at 80° in vacuum. The yield was 46 g. of a crude acid product that melted at 169–170° and showed a rotation of $[\alpha]^{20}_D +62°$ in absolute alcohol.

The crude acid was dissolved in 150 cc. of hot alcohol and converted to the ammonium salt by addition of 290 cc. of 0.5 *N* ammonium hydroxide. The crystalline ammonium salt that separated on standing overnight was filtered off and converted into the free "mixed acids" by drying in vacuum at 80°. This product was used for the isolation of tetrahydroabietic acid.

The filtrate was acidified by the addition of dilute hydrochloric acid and the solids collected by filtration. This product was dissolved in ether, the ether solution, after washing with water, was evaporated, and the residue recrystallized successively from ligroin and alcohol, and finally ligroin. The yield was 17 g. of a product that melted at 169–170°; $[\alpha]^{20}_D +67°$ in absolute alcohol, *c* 2.034. *Anal.* Calcd. for $C_{20}H_{30}O_2$: C, 79.41; H, 10.01. Found: C, 79.42, 79.23, 79.69; H, 10.00, 9.90, 9.90.

Isolation of the Methyl Ester of Dehydroabietic Acid.—Six grams of the above "pyroabietic" acid, $[\alpha]^{20}_D +67°$, was esterified with diazomethane in the usual manner. The residue was dissolved in methyl alcohol at 0°, and water was added to incipient crystallization. Rods separated on prolonged standing at 0°. The product was

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(8) Balas, *Časopis Českoslov. Lékárnictva*, **7**, 220 (1927); (b) Palkin and Harris, THIS JOURNAL, **56**, 1935 (1934).

(9) The tetrahydroabietic acid, m. p. 183–184°; $[\alpha]^{20}_D +6°$, obtained by subjecting the reaction product to repeated fractional crystallization, as the ammonium salt, in alcohol gave no yellow color with tetranitromethane, and yielded a crystalline methyl ester, m. p. 44–45°.

(10) During the progress of this investigation there was an exchange of information and samples, in which Professor Fieser kindly made available to us spectroscopic, and other data, and some of their dehydroabietic acid prepared by way of hydroxyabietic acid.

recrystallized from methyl alcohol to constant melting point. When dried at 30° in vacuum, it melted at 62–63°; $[\alpha]^{20}\text{D}$ +60°, c 2.000 in absolute alcohol. *Anal.* Calcd. for $C_{21}H_{30}O_2$: C, 80.20; H, 9.62; OCH_3, 9.88. Found: C, 79.99; H, 9.82; OCH_3, 10.10.

The refractive indices as determined by the immersion method are: n_α 1.542 (common and shown lengthwise on the rods); n_γ 1.574 (also common and shown crosswise on the rods); n_β not determined due to solubility of material in oils. The double refraction is rather strong, $n_\gamma - n_\alpha$ = 0.032.

The methyl ester of dehydroabietic acid was prepared by the above procedure from a sample of dehydroabietic acid kindly supplied by Professor Fieser. It melted at 62–63° after one recrystallization, and showed no lowering of melting point when mixed with a sample of methyl ester obtained from pyroabietic acid. Refractive indices of the respective methyl esters were found to be identical, as also those of regenerated acids.

Hydrolysis of Dehydroabietic Methyl Ester.—A solution of 0.4 g. of dehydroabietic methyl ester, obtained from the pyroabietic acids, was refluxed for two hours with 10 cc. of 10% *n*-butyl alcoholic potassium hydroxide. The solution was acidified with dilute hydrochloric acid, and the butyl alcohol was removed by a current of steam. The dehydroabietic acid was extracted with ether, the ether solution washed with water and then evaporated to dryness. The residue separated as triangular crystals from dilute alcohol. When dried at 80° in vacuum, it melted at 172–173°; $[\alpha]^{20}\text{D}$ +62°, c 1.940 in absolute alcohol. *Anal.* Calcd. for $C_{20}H_{28}O_2$: C. 79.94; H, 9.40. Found: C, 79.87, 79.62, 79.77; H, 9.45. 9.52, 9.46: R. I. n_α 1.513, n_γ 1.595.

Dihydroabietic Acid.—Successive crops of crystalline dehydroabietic methyl ester were obtained by gradual addition of water. When the point was reached where further addition of water caused an oil to deposit, the supernatant liquid was evaporated to dryness and distilled at 1 mm. at 165–170°. The yield was 2.2 g. of an oil which could not be induced to crystallize. Analyses showed C. 79.99; H, 9.99; which indicated admixture with dehydromethyl ester.

One gram of this material was dissolved in 10 cc. of concentrated sulfuric acid, and the solution was allowed to stand at room temperature for ten minutes. The solution was poured on ice and neutralized with sodium hydroxide. The neutral material was extracted with ether and the ether solution was shaken with 0.25 *N* sodium hydroxide, washed with water, and then evaporated to dryness. The yield was 0.5 g. of an oil.

When this methyl ester was hydrolyzed with *n*-butyl alcoholic potassium hydroxide as outlined above, it yielded an acid that crystallized in rectangular plates from dilute alcohol and melted at 129–130°; $[\alpha]^{20}\text{D}$ −3°, c 0.979 in absolute alcohol.[11] *Anal.* Calcd. for $C_{20}H_{32}O_2$: C. 78.88; H, 10.60. Found: C, 79.10; H, 10.70.

The Isolation of Tetrahydroabietic Acid.—One part of the "mixed acids" was dissolved in four parts of hot alcohol, and to this was added the calculated amount of aqueous 0.5 *N* ammonium hydroxide. The crystals that separated on standing overnight were filtered and recrystallized immediately, without drying, from hot alcohol. Three recrystallizations were completed before it was necessary to regenerate the unstable ammonium salt. A total of nine recrystallizations was carried out before the optical rotation of the acid freed from the crystalline ammonium salt was identical with that of the acid obtained from the mother liquor. The acid was finally recrystallized from alcohol. It melted at 183–184° and did not give a yellow color with tetranitromethane; $[\alpha]^{20}\text{D}$ +6° in absolute alcohol, c 2.056. *Anal.* Calcd. for $C_{20}H_{34}O_2$: C, 78.36; H, 11.19. Found: C, 78.42, 78.29; H, 11.34, 11.35.

Tetrahydroabietic Methyl Ester.—Tetrahydroabietic acid was esterified with diazomethane. When recrystallized from methyl alcohol, it separated as needles, which melted at 44–45°. *Anal.* Calcd. for $C_{21}H_{36}O_2$: C, 78.68; H, 11.33; OCH_3, 9.69. Found: C, 78.51; H, 11.60; OCH_3, 9.67.

The Catalytic "Isomerization" of *l*-Abietic Acid in a Closed System.—A 200-cc. three-necked distilling flask was fitted with a mercury sealed stirrer, a thermometer, and a delivery tube that was connected with a gas buret. The apparatus was flooded with nitrogen and a mixture of 25 g. of *l*-abietic acid and 0.5 g. of palladium–carbon catalyst was heated in an oil-bath held at 275–280, 250–255, 225–230, and 200–205° on successive runs. The rate at which gas was evolved is shown in Fig. 1. Analysis of the gas collected from the 250° run showed: CO_2, 0.97; O_2, 0.88; H_2, 59.56; CO, 1.30; N_2, 37.29.[12] Analysis of the crude crystalline product from the 250° run showed: C, 79.26; H, 9.84, and at 225°, analysis showed: C, 79.29; H, 9.95.

The Action of Palladium–Carbon Catalyst on *l*-Abietic Acid at 275°.—A mixture of 25 g. of *l*-abietic acid and 0.5 g. of palladium–carbon catalyst was heated for five hours in an oil-bath whose temperature was held at 275 ± 5°. The product was isolated as outlined above. The yield was 21.9 g. of a product that melted at 160–162°. Since this product contained some neutral material, it was dissolved in ether, and the acid portion removed by extraction with 0.25 *N* sodium hydroxide. The aqueous solution was shaken with ether to remove last traces of neutral material, and then the acid was freed with dilute hydrochloric acid. The acid was recrystallized from alcohol by addition of water. When dried at 80° in vacuum, the product melted at 169–171°; $[\alpha]^{20}\text{D}$ +56°, c 2.005 in absolute alcohol. *Anal.* Calcd. for $C_{20}H_{28}O_2$: C, 79.96; H, 9.39. Found: C, 80.05, 79.47, 79.89; H, 9.75, 9.53, 9.71. A total of 1.3 g. of neutral product was obtained.

Summary

α-Pyroabietic acid, heretofore regarded as an isomer of abietic acid, has been resolved, by way of the methyl ester, into dehydroabietic,

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(11) While the combustion data are in good agreement with those calculated for dihydroabietic acid, the melting point and rotation do not conform with those of the several isomeric dihydro-compounds reported in the literature. The Biot relationship [*Ann. chim. phys.*, [3] **59**, 206 (1860)] indicates the presence of another dihydroabietic acid of high positive rotation, which we have not been able to isolate.

(12) We are indebted to Dr. E. J. Hoffman, of the Chemical Engineering Research Division, Bureau of Chemistry and Soils, for the gas analysis, and to Mr. G. L. Keenan, of the Food and Drug Administration, for the crystallographic data.

dihydroabietic, and tetrahydroabietic acids.

This affords conclusive evidence that so-called α-pyroabietic acid is not an isomer of abietic acid, but a product of dehydrogenation and disproportionation.

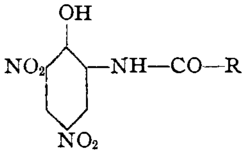
Washington, D. C. Received February 23, 1938

[Contribution from the Chemistry Laboratory of the University of Washington]

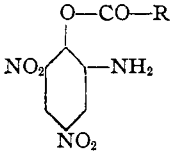
Derivatives of Picramic Acid and Some of their Rearrangements

By Irwin A. Pearl and William M. Dehn

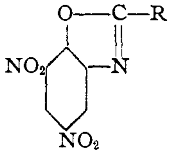
Picramic acid yields two types of acetyl derivatives.[1] We have obtained both (I) and (II) in acetylation of picramic acid. Our investigation has revealed that a product, reported by Schiff as (II),[2] is in reality a benzoxazole (III), a type previously known to synthesis.[3]



(I)



(II)



(III)

Our analytical data and the insolubility of the Schiff compound in dilute acids confirm the assigned structure. As might be expected, either acid or caustic hydrolysis yields picramic and acetic acids.

From the acetylation products of picramic acid we have isolated the O-acetyl compound (II), the structure of which was confirmed by its dissolving in dilute acids and by alkaline hydrolysis to picramic and acetic acids.

This derivative melts at 160–161°; the N-acetyl derivative, at 201°; and the benzoxazole, at 193°.

Acetyl-benzoylpicramic acids were investigated and data substantiating the conclusions of Pollard and Nelson[4] and others on the rearrangements of diacyl derivatives of 2-aminophenols were obtained.

By treating N-acetylpicramic acid with benzoyl chloride in benzene solution we obtained an acetyl-benzoylpicramic acid melting at 119.5–120.5° (IV). On warming N-benzoylpicramic acid with acetic anhydride we obtained an acetylbenzoylpicramic acid melting at 170–171° (V). On hydrolysis with dilute alkali, both of these compounds yielded N-acetylpicramic acid melting at 204–205°.[5] These facts indicate that rearrangement takes place on hydrolysis and that compound (IV) is 4,6-dinitro-2-acetylaminophenylbenzoate, and that compound (V) is 4,6-dinitro-2-benzoylaminophenylacetate.

A number of other new derivatives of picramic acid have been prepared. All are given in Table I and are indicated in the experimental part by asterisks.

In addition to these new derivatives, the following compounds have been prepared in increased yields by improved processes: 3,5-dinitro-2-hydroxyphenylurethan, 1-phenyl-4,6-dinitrobenzoxazole, 4,6-dinitro-2-acetylaminophenol, and 4,6-dinitro-2-benzoylaminophenol.

Experimental

1-Methyl-4,6-dinitrobenzoxazole.*—A mixture of 100 g. of picramic acid,[6] 250 g. of acetic anhydride, and one drop of sulfuric acid was heated in a liter flask on the steam-plate for six hours. The initial precipitate redissolved after a few minutes. On cooling, slightly brownish, transparent needles separated. A yield of 100 g. melting at 192–193° was obtained. Recrystallization from alcohol or xylene gave white needles melting at 193°. When dissolved in nitric or sulfuric acids and then poured into water, or when boiled with dilute alkali, it yielded N-acetylpicramic acid melting at 204–205°.

4,6-Dinitro-2-acetylaminophenol.—The filtrate from above was poured into water and allowed to stand. A yield of 25 g. of 4,6-dinitro-2-acetylaminophenol (N-

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[1] Meldola and Wechsler, *Chem. News*, **82**, 254 (1900); Cassella and Company, German Patent 161,341 (1903).

[2] Schiff, *Ann.*, **239**, 366 (1887).

[3] Ladenburg, *Ber.*, **9**, 1525 (1876); Hubner and Haarhaus, *Ann.*, **210**, 394 (1881). These authors prepared the phenyldinitrobenzoxazole.

[4] Pollard and Nelson, This Journal, **53**, 996 (1931). This article gives a complete bibliography.

[5] Although the melting point for N-acetylpicramic acid is given in the literature as 201°, we have found that repeated crystallizations from xylene, benzene, toluene, or alcohol give shiny yellow needles melting at 204–205°.

[6] Ammonium picramate was prepared by the method of Dehn [U. S. Patent 1,472,791 (1923)]. The ammonium salt was dissolved in water and neutralized with dilute acetic acid. The free picramic acid separated as dark red needles melting at 169°.