Anal.[9] (On compound prepared in first experiment). Calc'd for $C_{27}H_{26}Si$: Si, 7.43; C, 85.65; H, 6.92. Found: Si, 7.66, 7.61; C, 86.61, 85.91; H, 7.16, 7.24.

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1-Phenyl-4-methyl-6-pyridazone-3-carboxylic-Acid Derivatives

Richard H. Wiley and C. H. Jarboe, Jr.[1]

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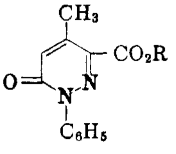
1-Phenyl-4-methyl-6-pyridazone-3-carboxylic acid (Ia), which has been made available for the first time by the rearrangement of γ-keto-β-methylglutaconic anhydride phenylhydrazone,[2] has been converted to its methyl ester (Ib), ethyl ester (Ic), N,N-diethylamide (Id), and anilide (Ie). The preparation and properties of these derivatives are recorded in this Note. All were prepared from the acid chloride which was in turn prepared from the acid.



I

a, R = H
b, R = CH_3
c, R = C_2H_5
d, R = $N(C_2H_5)_2$
e, R = NHC_6H_5

EXPERIMENTAL

1-Phenyl-4-methyl-6-pyridazone-3-carboxylic acid chloride. One gram of 1-phenyl-4-methyl-6-pyridazone-3-carboxylic acid was warmed one hour with 15 ml. of thionyl chloride. The yellow residue remaining after removal of the excess thionyl chloride under a vacuum was recrystallized from carbon tetrachloride to give 1.1 g. of white needles melting at 135°. This chloride was used in the following reactions.

Methyl 1-phenyl-4-methyl-6-pyridazone-3-carboxylate (Ib). The acid chloride (0.5 g.) was refluxed one hour with absolute methanol. Evaporation of the solvent left a solid which was recrystallized from petroleum ether to give 0.4 g. (76.3%) of the methyl ester as white needles, m.p. 125°.

Anal. Calc'd for $C_{13}H_{12}N_2O_3$: N, 11.47. Found: N, 11.16.

Ethyl 1-phenyl-4-methyl-6-pyridazone-3-carboxylate (Ic). The acid chloride (0.5 g.) was refluxed 2.5 hours with 15 ml. of absolute ethanol. Dilution with water precipitated a solid which was recrystallized from ethyl acetate to give 0.5 g. (83.5%) of the ethyl ester as white needles, m.p. 102°.

Anal. Calc'd for $C_{14}H_{14}N_2O_3$: N, 10.85. Found: N, 10.65.

N,N-Diethyl-1-phenyl-4-methyl-6-pyridazone-3-carboxamide (Id). To a solution of 0.5 g. of the acid chloride in 25 ml. of hot toluene was added 2 ml. of diethylamine. After 0.5 hour at reflux the mixture was filtered hot to separate the amine hydrochloride and was cooled. Addition of 25 ml. of petroleum ether precipitated a crude product. On recrystallization from petroleum ether 0.4 g. (66%) of the N,N-diethylamide, m.p. 54°, was obtained.

Anal. Calc'd for $C_{16}H_{21}N_3O_3$: N, 13.85. Found: N, 13.75.

1-Phenyl-4-methyl-6-pyridazone-3-carboxanilide (Ie). To a solution of 0.5 g. of the acid chloride in 25 ml. of hot toluene was added 2 ml. of freshly distilled aniline. After one hour at reflux, the mixture was filtered hot to separate the aniline hydrochloride. On cooling the crude product precipitated. Recrystallization from a mixture of equal parts of toluene and petroleum ether gave 0.4 g. (70%) of the anilide as white needles, m.p. 259°.

Anal. Calc'd for $C_{18}H_{15}N_3O_2$: N, 13.76. Found: N, 13.89.

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[1] The authors wish to acknowledge support of this research through a grant (NSF-G55) from the National Science Foundation.

[2] Wiley and Jarboe, Jr., *J. Am. Chem. Soc.*, **77**, 403 (1955).

A Wayward Prevost Oxidation

Robert I. Meltzer and Arnold D. Lewis

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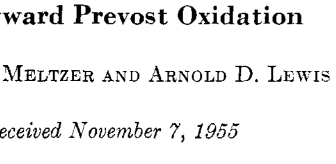
In connection with our study of central nervous system depressants, we were interested in some derivatives of 5-isopropyl-5-(2′,3′-dihydroxypropyl)barbituric acid. A likely approach to the dibenzoate of this compound appeared to be through a Prevost[1] oxidation of the commercially available 5-isopropyl-5-allylbarbituric acid using the silver benzoate-iodine complex. The product we obtained, however, did not analyze for the expected compound. It gave a blue color with alcoholic cobalt nitrate and potassium hydroxide [Mohrschulz[2] test for barbituric acid], but unlike this test for the starting material, the color disappeared with continued addition of the alcoholic potassium hydroxide. Rather the analysis corresponded to the formula



This structure can be explained by the action of the silver benzoate-iodine complex to give 5-

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[1] Prevost, *Compt. rend.*, **196**, 1129 (1933); **197**, 1661 (1933); Prevost and Lutz, *Compt. rend.*, **198**, 2264 (1934); Prevost and Wiemann, *Compt. rend.*, **204**, 700, 989 (1937).

[2] Mohrschulz, *Munchen med. Wochschr.*, **81**, 672 (1934).

isopropyl-5-(3′-iodo-2′-benzoyloxypropyl)barbituric acid followed by the elimination of the elements of hydrogen and iodine under the influence of silver benzoate. The isolation of halo acyloxy compounds from Prevost oxidations has been previously reported.[3]

Not only did elemental analysis for carbon, hydrogen, and nitrogen support the structure, but also the amount of ammonia evolved on basic digestion corroborated this structure assignment. The fact that only one nitrogen appeared as ammonia indicates that one of the nitrogen atoms in the newly formed compound is now involved in a linkage (*i.e.*, amine linkage) which is not split by heating with 30% alkali. The isolation of 92.5% of the theoretical benzoic acid on hydrolysis of the compound using 4 *N* sodium hydroxide is also in accord with the indicated structure.

EXPERIMENTAL[4,5]

Silver benzoate. This was prepared by the addition of the calculated amount of 10% silver nitrate to a 1 *N* solution of sodium benzoate. The resulting precipitate was washed repeatedly with water, absolute alcohol, and finally ether.

2,4,9-Triketo-7-benzoyloxy-5-isopropyl-1,3-diazabicyclo-[3,3,1]nonane. To 23 g. (0.1 mole) of silver benzoate in 200 ml. of dry benzene was added rapidly with stirring, 12.7 g. (0.05 mole) of iodine in 200 ml. of dry benzene. The reaction mixture became thick and yellow in color. After stirring for an additional few minutes, there was rapidly added with stirring 10.5 g. (0.05 mole) of 5-allyl-5-isopropylbarbituric acid in 100 ml. of hot dry benzene. The reaction mixture was heated to reflux and kept at reflux for 75 minutes and then was allowed to stand overnight at room temperature. Filtration through a layer of Super-Cel gave a clear filtrate which was concentrated to dryness at atmospheric pressure on a steam-bath. The residual oil solidified on cooling. Extraction with 50 ml. of hot absolute alcohol gave after filtration and cooling 6.2 g. (38%) of material melting at 172–173.5°. Additional product could be obtained on concentration of the mother liquor. The material was purified for analysis by recrystallization from absolute ethanol.

Anal. Calc'd for $C_{17}H_{18}N_2O_5$: C, 61.81; H, 5.49; N, 8.48; N as ammonia, 4.24. Found: C, 61.88; H, 5.48; N, 8.52; N as ammonia, 4.25.

In a previous experiment it was found that the residue from the ether evaporation could be taken up in hot benzene and precipitated by cooling. It was attempted to recrystallize the material from benzene but just prior to complete solution, that material which had already dissolved precipitated and could then be recrystallized only from absolute alcohol as above. The material which was obtained by cooling the benzene melted over a range at about 85°.

Hydrolysis of 2,4,9-triketo-7-benzoyloxy-5-isopropyl-1,3-diazabicyclo-[3,3,1]nonane. A solution of 3.5 g. of Prevost oxidation product in 50 ml. of 4 *N* sodium hydroxide was kept at reflux for two and one half hours during which time the solution was concentrated by 50%. The solution was diluted to its original volume and acidified with 4 *N* hydrochloric acid. Filtration gave 1.7 g. of material. On extraction twice with 50-ml. portions of absolute ether and evaporation to dryness, 1.1 g. of benzoic acid melting point 121–122.5° was obtained. On standing the filtered acidified aqueous solution deposited an additional 0.1 g. of benzoic acid, m.p. 122–123°.

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[3] Birckenbach, Goubeau, and Berninger, *Ber.*, **65**, 1339 (1932); Bockemuller and Hoffman, *Ann.*, **519**, 165 (1935); Uschakow and Tchistow, *Ber.*, **68**, 824 (1935); Halperin, Donahoe, Kleinberg, and Vanderwerf, *J. Org. Chem.*, **17**, 623 (1952).

[4] Melting points are uncorrected.

[5] Analyses were carried out by Miss Linda Einstein.

The Decomposition of Picric Acid Complexes with Potassium Chloride[*]

DAVID TABER AND ALVIN I. KOSAK

Received November 8, 1955

The conventional method of composing amine complexes of picric acid by means of aqueous ammonia suffers from the limitation that extensive decomposition sometimes occurs with base-sensitive materials, *e.g.*, 3,3′-dihydroxybenzidine.[1] Having at one time noted that an attempt to salt out an alkaloid picrate from aqueous solution with sodium chloride had resulted in the precipitation of sodium picrate, we investigated the use of potassium chloride (which would give the less soluble potassium picrate) as a dissociative agent for both amine and polynuclear hydrocarbon picrates.

In a typical case, *e.g.*, β-naphthol picrate, a solution of the picrate in alcohol at its boiling point was treated with an excess of a saturated aqueous solution of the chloride, and after cooling, the potassium picrate which deposited was removed by filtration. Evaporation of the filtrate gave a quantitative recovery of the desired material which then was purified by standard procedures. Because one is concerned here with relative solubilities, the situation is not always as straightforward as this, and the proportion of water to alcohol in the system is sometimes of critical importance, as in the case of pyrene picrate. This solvent dependence has the undesirable effect of sometimes requiring trials with different solvent proportions before acceptable yields are obtained. Although the experiments with the picrates of pyrene and 3,3′-dihydroxybenzidine gave recoveries (63 and 52% respectively) which were far from quantitative, in the case of the latter compound the procedure appears to be superior to the use of ammonia water.[1] Except in such special cases, the standard methods of decomposing picrates are preferable.

EXPERIMENTAL

Melting points are uncorrected; micro melting points were taken with a Fisher-Johns apparatus.

β-Naphthol from the picrate. A mixture of 0.50 g. (0.134 mmole) of β-naphthol picrate (m.p. 154–155°), 6 ml. of 95% ethanol, and 1 ml. of a saturated (25°) aqueous solu-

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[*] Aided by grants from the American Cancer Society and the Damon Runyon Memorial Fund.

[1] H. Weinfeld, this laboratory, unpublished results.