in a thermostat in the customary manner, and analysis of the clear solution obtained. The results were also checked over the range 37.6 to 74.6° by a technique involving the growth or solution of a thin crystal film.[4] In a few of these determinations, technical grade material was used, but no significant difference was noted. The accuracy of this work is of the order of 0.4° and 0.2% in dichromate content.

The transition temperature, $Na_2Cr_2O_7 \cdot 2H_2O \leftrightharpoons Na_2Cr_2O_7$, was determined by allowing a sample of about 1 kg. weight, containing a considerable quantity of suspended sodium dichromate, to cool with agitation through the transition range. The change in cooling rate was noted, and a pronounced break at the transition point measured with a calibrated thermometer with an accuracy of 0.2°.

TABLE I

EXPERIMENTAL VALUES FOR EQUILIBRIUM CONDITIONS IN THE SYSTEM SODIUM DICHROMATE–WATER

% $Na_2Cr_2O_7$ by weight	Temp., °C.	% $Na_2Cr_2O_7$ by weight	Temp., °C.
0.00	0.0	66.06	32.2
22.05	− 5.0	67.52[b]	37.6[b]
26.45	− 5.4	67.98	40.6
37.47	−10.6	69.21	46.1
48.50	−19.7	71.38	57.2
57.32	−35.7	71.76	60.0
58.90	−39.0	72.15[b]	60.9[b]
59.96	−44.0	73.82[b]	67.9[b]
60.54	−47.1	73.76	68.3
60.77[a]	E −48.2[a]	75.65	74.4
60.84	−45.4	75.43[b]	74.6[b]
61.73	− 8.0	78.41	82.2
62.17	0.0	79.18[a]	T84.6
62.49	5.0	79.65	90.1
65.01	25.0	80.01	95.0

[a] Interpolated. [b] These values obtained by film solution technique. E Eutectic. T Transition: $Na_2Cr_2O_7 \cdot 2H_2O \longrightarrow Na_2Cr_2O_7$.

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(4) This work was performed by I. Levin of this Laboratory, using an unpublished technique developed by R. B. Peet.

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The Oxidation of Acyloins

BY BERNARD KLEIN

For several years, these laboratories have been interested in reactions conducted in glacial acetic acid.[1,2,3] The present communication is an examination of the action of ammonium nitrate in glacial acetic acid on benzoin and similar acyloins.

It was found that benzoin, in the presence of excess ammonium nitrate, at the temperature of boiling glacial acetic acid, will be oxidized to benzil in almost quantitative yield. This reaction, upon further investigation, was found to be a general one for the oxidation of acyloins. Thus, anisoin, *p*-toluoin and furoin were converted smoothly to the corresponding diketones[4]

$$RCH(OH)COR \longrightarrow RCOCOR$$
$$NH_4NO_3 \longrightarrow NH_4NO_2 \longrightarrow N_2 + H_2O$$

The above equations are substantiated by the following observations. (a) There is a copious evolution of a colorless, odorless, neutral gas, insoluble in water, immediately upon mixing the reactants. No gas is evolved when the reactants are heated independently in boiling glacial acetic acid. (b) Neither lophine[2] nor amarone[3] is produced. Hence, in the course of the reaction no ammonium acetate is formed by metathesis in any appreciable quantity. Ammonium nitrate, therefore, acts merely in the capacity of a mild oxidizing agent and can be used to oxidize sensitive α-hydroxy ketones to diketones.

Experimental

Preparation of Benzil.—To 2.12 g. (0.01 *M*) benzoin in 15 ml. of boiling glacial acetic acid, 3.2 g. (0.04 *M*) ammonium nitrate was added in one portion and the solution, once the vigorous gas evolution had subsided, was gently refluxed for one and one-half to two hours and then poured while hot into 50 ml. of cold water and placed in a refrigerator overnight. The precipitated material was collected on a filter and washed well with cold water.

Recrystallization from 80% acetic acid yielded 2.04 g. of yellow needles melting 95–96° (uncor.) A mixed melting point with an authentic sample of benzil[5] showed no depression.

No color was produced when a small amount of benzil thus made was heated with alcoholic potassium hydroxide. Benedict's qualitative reagent was not reduced.

Preparation of Anisil and *p*-Tolil.—These compounds were prepared as above (see Table I).

Preparation of Furil.—1.1 Grams of furoin, m. p. 135°, was dissolved in 10 ml. of boiling glacial acetic acid; 3.2 g. of ammonium nitrate was added in small portions as the reaction is extremely vigorous. When the evolution of gas ceased, the solution was gently refluxed for two hours. The solution was then evaporated to dryness under diminished pressure. The dry material was thoroughly extracted with butanol and the solvent evaporated to dryness under diminished pressure. The residue was crystallized from methanol (2 ml.) and then recrystallized from 80% acetic acid; yield, 0.5 g. of pale yellow needles melting at 160° (uncor.) No depression was produced when a sample was melted with an authentic sample of furil prepared by another method.[5]

Preparation of Isatin from Dioxindole.—To 0.55 g. of dioxindole[6] in 10 ml. of glacial acetic acid 3.0 g. of ammon-

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(1) D. Davidson, THIS JOURNAL, **58**, 1821 (1936).

(2) D. Davidson, M. Jelling and M. Weiss, *J. Org. Chem.*, **2**, 319 (1937).

(3) D. Davidson, M. Weiss and M. Jelling, *ibid.*, **2**, 328 (1937).

(4) In concentrations above 0.5 *M* benzoin is converted to mixtures of benzil and unreacted benzoin—private communication, Mr. Lester Weil, Columbia University.

(5) "Organic Syntheses," Coll. Vol. I., p. 80.

(6) Marschalk, *Ber.*, **45**, 583 (1912).

ium nitrate was added and the solution gently refluxed. The color of the solution changed quickly from pale yellow to orange, at the end of one minute. The solution was refluxed thirty minutes longer and diluted with cold water. The red precipitate was collected and recrystallized from 80% acetic acid; yield, 0.35 g. of isatin, melting at 199°. A mixed melting point with pure synthetic isatin[7] showed no depression.

TABLE I

Substance	Used, g.	Product	M. p., °C.	Yield, g.
Benzoin	2.12	Benzil	95–96	2.04
Anisoin[8]	1.2	Anisil	132–133	0.8
p-Toluoin	1.9	*p*-Tolil	102	.9
Furoin	1.1	Furil	160	.5
Dioxindole[6]	0.5	Isatin	199	.35

I am deeply indebted to Prof. David Davidson, of Brooklyn College, for his interest and suggestions and to Dr. M. Jacobi, Director of Laboratories, Beth-El Hospital.

(7) "Organic Syntheses," Coll. Vol. I, p. 321.

(8) Bosler, *Ber.*, **14**, 423 (1881).

CHEMICAL LABORATORIES
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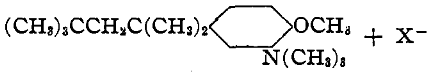
Invert Soaps. Quaternary Ammonium Salts of Derivatives of Long Chain Phenols

BY JOSEPH B. NIEDERL AND MARTIN I. DEXTER[1]

Some of the previously reported "invert soaps" involve long chain ethers of *o*-, *m*- and *p*-aminophenol.[2] It has now been found that invert soaps can also be obtained by using short chain ethers of the long chain substituted phenols as follows: $\alpha,\alpha,\gamma,\gamma$-tetrametho-butylphenol ("diisobutylphenol"), prepared by condensing diisobutylene with phenol,[3] was methylated and the resulting methyl ether (I) was subsequently nitrated to yield the mono nitro derivative of *p*-($\alpha,\alpha,\gamma,\gamma$-tetrametho)-butyl-anisole (II). This compound in turn was reduced to the respective amine (III), which was then converted into the tertiary dimethylamine (IV), from which, then, water soluble "invert soaps" were prepared by converting this tertiary amine into the respective ammonium salts, the 2-trimethylammonium-4-($\alpha,\alpha,\gamma,\gamma$-tetrametho)-butylphenol methyl ether iodide (V) and methosulfate (VI), using methyl iodide and dimethyl sulfate, respectively.

The structure of these salts is



($X = I$; CH_3OSO_2O-)

Experimental

Nitration.—Fifty grams of the methyl ether (I) was dissolved in 300 cc. of a mixture of equal parts of acetic acid and acetic acid anhydride. The mixture was then placed in an ice-bath, and 50 cc. of concentrated nitric acid (sp. gr. 1.42) was then added cautiously in small amounts, while the reaction mixture was kept at a temperature not exceeding 10°. After the completion of the addition, the reaction mixture was allowed to come to room temperature gradually and to stand for thirty minutes; 500 cc. of water was added to hydrolyze the acetic anhydride and the nitrated ether (II) precipitated at the same time. It was crystallized from methyl alcohol, in large, yellow plates, possessing a faint floral odor.

The same product may also be obtained by nitrating first the phenol and methylating the mononitrodiisobutylphenol afterward.

Reduction.—Thirteen grams of the above nitro compound (II) was dissolved in 50 cc. of ethyl alcohol. To this solution were added 15 g. of tin and 27 cc. of hydrochloric acid over a period of two hours. During this period the mixture was refluxed. Complete reduction was indicated when all color had disappeared, and when a small sample withdrawn from the reaction mixture dissolved completely in water. The mixture was then cooled, and 50% sodium hydroxide solution was added until the precipitated tin hydroxide had dissolved. From this the amine (III) was extracted with ether, and the ether extract dried over anhydrous sodium sulfate. The ether was then distilled off and the amino compound redistilled *in vacuo* under reduced pressure.

The hydrochloride of the amine (IIIa) was prepared by passing dry hydrogen chloride gas through a solution of the amine in petroleum ether. The benzoate (IIIb) was prepared by employing the usual Schotten–Baumann procedure, using 0.5 cc. of the amine, 2 cc. of benzoyl chloride, and 5 cc. of 20% sodium hydroxide solution.

Methylation.—Eight grams of the above primary amine (III), and 8.5 g. of the dimethyl sulfate contained in a stoppered Erlenmeyer flask, were heated in a steam-bath for two hours. The reaction mixture was then cooled and treated with 50 cc. of 2 *N* sodium hydroxide solution.

The mixture was then extracted with ether and the ether dried over sodium sulfate. The ether was then distilled off and the tertiary amine (IV) redistilled at reduced pressure.

Methiodide.—Two cc. of the above tertiary amine (IV) was dissolved in 20 cc. of methyl iodide and, after a short period of warming, the excess methyl iodide was distilled off. The residue (V) was recrystallized from ethyl acetate. The compound is soluble in water.

Methosulfate.—To 5.3 g. of the tertiary amine (IV) were added 2.6 g. of freshly distilled dimethyl sulfate and 4 cc. of dry benzene. The mixture was refluxed at 120° for two hours. After this time, the benzene was distilled off at reduced pressure. The residue was then dissolved in 20 cc. of methanol, treated with a little barium carbonate, and with charcoal. It was filtered and the methyl alcohol

(1) Abstracted from the thesis presented by M. I. Dexter to the Graduate School of New York University in partial fulfillment of the requirements for the degree of Master of Science, May, 1941.

(2) R. Kuhn and D. Jerchel, *Ber.*, **73**, 1100 (1940).

(3) J. B. Niederl, *Ind. Eng. Chem.*, **30**, 1269 (1938).