THE IDENTIFICATION OF PHENOLS AS THE ESTERS OF 3,5-DINITROBENZOIC, p-NITROBENZOIC, BENZOIC AND ACETIC ACIDS

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INTRODUCTION

In analytical organic chemistry, one of the best methods of identifying a compound is to synthesize another compound from the unknown, determine its melting point and compare this with a known value. Since the known values of melting points are still lacking for a large number of compounds, the purpose of this experimentation is to prepare and characterize a number of phenolic compounds as their esters. Common reagents, that are readily available, are to be used and the method of preparation and purification is to be as simple as possible.

The phenols and phenolic compounds are being widely used in synthetical applications and also occur naturally in many forms. Therefore, simple, quick, and easy methods of identifying these substances, together with data, must be determined to be used for the identification and analysis. One of the better methods of identification is the esterification of the phenol with an acid to form a solid ester and subsequently determining the melting point of the ester.

HISTORICAL

I. EARLY ATTEMPTS OF IDENTIFICATION

As early as 1884 (9, 10, 17) and possibly even earlier, attempts were being made to devise means by which compounds, specifically phenols, could be characterized and identified. One of the first methods devised for phenols, which is known as the Schotten - Baumann reaction, was the esterification of benzoyl chloride with the respective phenol. This, however, did not always provide a useful means since the products of the reaction were often liquids. This led to devising other methods which would yield solid products instead of liquids. Of these, the first successful method, was devised by Staedel (17) in preparing the p-nitrobenzyl ethers. He accomplished this by treating the sodium or potassium salt of the phenol with p-nitrobenzyl bromide. The reaction goes to almost 100% completion and can therefore be used as a quantitative method of analysis.

Another successful method was the esterification of the phenol with 3,5-dinitrobenzoic or p-nitrobenzoic acid. Mulliken (12) first used 3,5-dinitrobenzoic acid for the characterization of alcohols. This method was later adapted to phenols after certain modifications by Brown and Kremers (5). The acid first had to be converted to the acyl halide before it could be utilized for the esterification of either the alcohol or the phenol (2, 5, 12). The phenolic esters of p-nitrobenzoic acid were prepared by Barnett and Nixon (2) using the same method of preparation. These methods of preparation involve refluxing a mixture of pyridine, phenol and acyl halide for approximately thirty minutes, then pouring the mixture into a dilute solution of acid and filtering the precipitate. The crude product was purified by recrystallization from alcohol. The method of Staedel later led to preparing several of the esters of the more unreactive phenols by treating the sodium or potassium phenolate with an acyl halide (5).

II. MODERN METHODS OF SYNTHESIS

Present day methods of preparation involve the use of pyridine as a solvent and refluxing a mixture of the solvent, the phenol and a common acyl halide (5, 6, 7, 8, 11, 13, 15, 18). One of the more novel methods for preparing the esters in the past several years, was developed by Brewster and Ciotti (4). They found that the acyl halide required for the esterification could be generated during the course of the reaction as it is used up. A mixture of the appropriate acid in 20 to 50 parts of pyridine was treated with 2 molar equivalents of phenylsulfonyl chloride. After cooling in an ice bath, the mixture was treated with one mole equivalent of alcohol or phenol, kept cold for one hour and finally poured into 3 to 4 volumes of ice water. The precipitate which forms was filtered and recrystallized. In all instances the product formed must be recrystallized before an accurate melting point can be obtained.

In the present work, the 3,5-dinitrobenzoate, p-nitrobenzoate, benzoate and acetate esters that had not been previously synthesized, of various phenols were prepared and characterized. In addition, several of those which have already been prepared were made as checks.

Several methods of preparation were attempted from which one that was suitable to the actual synthesis was chosen for the majority of the experimental work. The first, was one in which the phenol, acyl halide and pyridine as a solvent, was found not to give as high a yield as should be expected. This was the standard procedure found in most qualitative organic texts. The second involved heating the phenol and acyl halide together in the absence of a solvent, but in all trials the mixture would decompose into a tarry material. The third method utilized benzene as a solvent and required refluxing a mixture of the solvent, the phenol and the acyl halide. This method was chosen since the overall yields of the ester were generally higher. Another reason for choosing this method was the elimination of the undesirable odor of pyridine, which was used as a solvent in the first method and trapped the hydrogen chloride that was formed during the course of the reaction.

In using the selected method for preparing the esters, several undesirable features arose. One was the excessive foaming of the reaction mixture during the preparation of the p-nitrobenzoates, and another was the reactivity of the hydroxyl - hydrogen of two of the phenols; specifically, 2,4-dinitrophenol and 2,4-dinitronaphthol. The hydrogen of these phenols was sufficiently acidic that they would not react with of the acyl halides. Therefore, the method of Brown and Kremers (5) with certain modifications was used to prepare these esters. Instead of using an alkali metal, sodium carbonate was used to prepare the sodium phenolates and benzene was used as a solvent in place of xylene.

The chloride analyses of the halogenated phenolic esters was performed according to the procedure as described by Belcher and Godbert (3). Three or four determinations were made on each sample, and the average of these determinations were taken. Remainder of the analyses were made by a commercial laboratory.

EXPERIMENTAL

Materials Used

The 3,5-dinitrobenzoyl chloride, benzoyl chloride and acetyl chloride used in all preparations were obtained from the Eastman Kodak Company. The p-nitrobenzoyl chloride was obtained from the Brothers Chemical Company.

Phenols

All of the phenols used with the exceptions listed below were obtained from the Eastman Kodak Company. The exceptions, o-chlorophenol and p-nitrophenol, were obtained from the Matheson Company, Inc.

Preapration of the 3,5-Dinitrobenzoate Esters of the Phenols

One gram (approximately 6 millimoles) of each of the phenols, except for 2,4-dinitrophenol and 2,4-dinitronaphthol, and 1.5 grams (approximately 6 millimoles) of 3,5-dinitrobenzoyl chloride were added to a 50 ml. round-bottom flask equipped with a reflux condenser and a calcium chloride drying tube. To this were added 10 ml. of benzene and the mixture refluxed for one hour. The reaction mixture after sufficient cooling was then poured with stirring into 25 ml. of 5% sodium carbonate solution. After sufficient time to allow the unreacted acyl halide to react with the sodium carbonate, the mixture was filtered to remove any insoluble substances, and the benzene evaporated by stoppering the filter flask and applying suction with a water aspirator. When most of the benzene had evaporated the crude product settled out of the alkaline solution. This solid was filtered, washed well with water and air-dried. The crude ester was dissolved in boiling 95% ethanol; decolorizing charcoal was added and the solution then filtered. The pure ester crystallized from the alcohol on cooling and was filtered and dried. The recrystallization was done at least three times or until a constant melting point was obtained.

The two dinitrophenols were treated with 10% sodium carbonate solution and converted to the sodium 2,4-dinitrophenolate and 2,4-dinitronaphtholate respectively. These two compounds were relatively insoluble in water and therefore filtered and dried. One gram of the sodium derivative and 1.5 grams of 3,5-dinitrobenzoyl chloride together with 20 ml. of benzene were heated under reflux for one hour. The remainder of the procedure, which was mainly purification, was the same as the above.

In all cases the yields ranged from 0.5 grams to 1.5 grams of the purified esters, or from 25% to 80% of the theoretical yield. In some instances the esters were high boiling liquids.

Preparation of the p-Nitrobenzoate Esters of the Phenols

The same procedure as the one given for preparing the 3,5-dinitrobenzoates was used except that 20 ml. of benzene were used instead of 10 ml.

Preparation of the Benzoate and Acetate Esters of the Phenols

The same procedure was used as the one given for preparing the 3,5-dinitrobenzoates.

Melting Point Determinations

The apparatus used consisted of a U-shaped tube with a connecting tube between the two arms. The latter were wrapped with asbestos tape, then with nichrome wire for the heating element and finally with a matted asbestos. The heat was regulated using a powerstat with di-n-butyl phthalate as a heat exchanger. This was circulated with an electric stirrer. The termometer was checked against known, pure compounds and found to be accurate for the temperature range 50 to 200°C. To facilitate reading the thermometer, a magnifying eyepiece was used. The experimental melting points, known melting points and color of the crystals are given in Tables I, II III, and IV. The known values, except those with superscripts, were found in Cheronis and Entrikin (8). The values with superscripts were found in the references indicated by the superscript.

Analysis of the Esters

Five representative samples of the esters were analyzed by the Geller Microanalytical Laboratories for nitrogen content. Six of the halogenated phenols were analyzed for chloride content. The experimental values together with the calculated values are given in Table V.

TABLE I

EXPERIMENTAL AND KNOWN MELTING POINTS AND COLOR OF CRYSTALS OF THE ESTERS OF 3,5-DINITROBENZOIC ACID

Phenol	Color of Crystal	Melting Points		Molecular Formula
		Expt. °C	Known °C	
p-Phenylphenol	White	223.5 - 224.5		$C_{19}H_{12}O_6N_2$
p-Benzylphenol	White	116.5 - 116.8		$C_{20}H_{14}O_6N_2$
o-Chlorophenol	White	148.5	143	$C_{13}H_7O_6N_2Cl$
m-Chlorophenol	Light tan	158.2 - 158.8	156	$C_{13}H_7O_6N_2Cl$
p-Chlorophenol	Light tan	188.8 - 189	186	$C_{13}H_7O_6N_2Cl$
2,4,5-Trichlorophenol	Light tan	170 - 172		$C_{13}H_5O_6N_2Cl_3$
2,4,6-Trichlorophenol	White	163.1 - 163.8	136[11]	$C_{13}H_5O_6N_2Cl_3$
p-Bromophenol	Light tan	191.5 - 193	191	$C_{13}H_7O_6N_2Br$
2,4,6-Tribromophenol	Light tan	176.5 - 176.8	174	$C_{13}H_5O_6N_2Br_3$
m-Methoxyphenol	Tan	130 - 131		$C_{14}H_{10}O_7N_2$
m-Ethylphenol	White	106.5 - 107		$C_{15}H_{12}O_6N_2$
o-Cyclohexylphenol	Light tan	160.2 - 160.6		$C_{19}H_{18}O_6N_2$
o-Nitrophenol	White	154.3 - 154.7	155	$C_{13}H_7O_8N_3$
p-Nitrophenol	Light tan	184.7 - 185.3	186	$C_{13}H_7O_8N_3$
2,4-Dinitrophenol	White	154.5 - 155		$C_{13}H_6O_{10}N_4$
2,4-Dinitronaphthol	Tan	178 - 179		$C_{17}H_8O_{10}N_4$

TABLE II

EXPERIMENTAL AND KNOWN MELTING POINTS AND COLOR OF CRYSTALS OF THE ESTERS OF p-NITROBENZOIC ACID

Phenol	Color of Crystal	Melting Points		Molecular Formula
		Expt. °C	Known °C	
p-Phenylphenol	White	168.5 - 169.5		$C_{19}H_{13}O_4N$
p-Benzylphenol	White	112.5 - 113		$C_{20}H_{15}O_4N$
o-Chlorophenol	White	119 - 119.3	115	$C_{13}H_8O_4NCl$
m-Chlorophenol	White	98.5 - 99	99	$C_{13}H_8O_4NCl$
p-Chlorophenol	White	169.8 - 170	171	$C_{13}H_8O_4NCl$
2,4,6-Trichlorophenol	White	104.3 - 105	105 - 106	$C_{13}H_6O_4NCl_3$
2,4,6-Tribromophenol	White	153.5 - 154	153	$C_{13}H_6O_4NCl_3$
m-Methoxyphenol	White	123 - 123.5		$C_{14}H_{11}O_5N$
o-Cyclohexylphenol	White	97.8 - 98.5		$C_{19}H_{19}O_4N$
o-Nitrophenol	White	140 - 140.3	141	$C_{13}H_8O_6N_2$
2,4-Dinitrophenol	White	138.5 - 139	139	$C_{13}H_7O_8N_3$
2,4-Dinitronaphthol	Light tan	180 - 180.4		$C_{17}H_9O_8N_3$

TABLE III

EXPERIMENTAL AND KNOWN MELTING POINTS AND COLOR OR CRYSTALS OF THE ESTERS OF BENZOIC ACID

Phenol	Color of Crystal	Melting Points Expt. °C	Known °C	Molecular Formula
p-Phenylphenol	White	149 - 150	150	$C_{19}H_{14}O_2$
o-Chlorophenol		Liquid		
m-Chlorophenol	White	69 - 69.5	71	$C_{13}H_9O_2Cl$
2,4,6-Trichlorophenol	White	74.5 - 75	75.5	$C_{13}H_7O_2Cl_3$
m-Methoxyphenol		Liquid		
o-Cyclohexylphenol		Liquid		
p-Nitrophenol	White	142 - 142.3	142	$C_{13}H_9O_4N$
2,4-Dinitrophenol	White	120.2 - 130.5	132	$C_{13}H_8O_6N_2$
2,4-Dinitronaphthol	Tan	173.3	174	$C_{17}H_{10}O_6N_2$

TABLE IV

EXPERIMENTAL AND KNOWN MELTING POINTS AND COLOR OF CRYSTALS OF THE ESTERS OF ACETIC ACID

Phenol	Color of Crystal	Melting Points		Molecular Formula
		Expt. °C	Known °C	
p-Benzylphenol		Liquid		
m-Chlorophenol		Liquid		
2,4,6-Trichlorophenol	White	49.5 - 50	49 - 51[1]	$C_8H_5O_2Cl_3$
2,4,6-Tribromophenol	White	81.5 - 82.5	82	$C_8H_5O_2Br_3$
2,4-Dinitronaphthol	Tan	136 - 137	138 - 139[18]	$C_{12}H_8O_6N_2$

TABLE V

ANALYSIS OF THE PHENOLIC ESTERS

Ester	Nitrogen Content Calcd.	 Found
m-Ethylphenyl 3,5-dinitrobenzoate	8.86	9.00
p-Benzylphenyl p-nitrobenzoate	4.20	4.35
m-Methoxyphenyl p-nitrobenzoate	5.13	5.21
o-Cyclohexylphenyl p-nitrobenzoate	4.31	4.81
2,4-Dinitronaphthyl acetate	10.14	9.93

Ester	Chlorine Content Calcd.	 Found
o- Chlorophenyl 3,5-dinitrobenzoate	11.01	11.08
m-Chlorophenyl 3,5-dinitrobenzoate	11.01	11.06
p-Chlorophenyl 3,5-dinitrobenzoate	11.01	11.01
2,4,5-Trichlorophenyl 3,5-dinitrobenzoate	27.20	27.13
2,4,6-Trichlorophenyl 3,5-dinitrobenzoate	27.20	27.24
o-Chlorophenyl p-nitrobenzoate	12.79	13.02

DISCUSSION

The usual preparation of the ester derivatives of phenols and alcohols involves the use of pyridine as a solvent and also to act as a reagent to remove the hydrogen chloride formed during the course of the reaction. The hydrogen chloride, if any water is present, could cause a reversal of the forward reaction and thus fail to give substantial yields of the ester. However when using benzene as a solvent the hydrogen chloride formed is evolved as a gas and does not have any apparent undesirable effects on the reaction.

In the preparation of p-phenylphenyl benzoate using pyridine as a solvent, the yield of pure ester was 0.9 grams or 58% of the theoretical yield. When using benzene as a solvent though, the yield of pure ester was 1.2 grams or 78% of the theoretical yield. This increase held true in the other cases in which a comparison was made, although not as pronounced, but never was the increased yield lower than 10% over the method using pyridine.

The esters prepared from p-nitrobenzoyl chloride were a little more difficult to prepare than the others due to excessive foaming of the reaction mixture while being refluxed. This was minimized to some extent by using a larger volume of solvent than for preparing the other esters.

In several instances questionable values of the melting points for several of the chlorinated phenols were found in the literature (8, 11). In the present work the melting points were found to be several degrees higher. Analysis indicated the esters to be pure and since the melting points were sharp the reported values are questioned. In another instance, the value of one melting point was printed in error in two different editions (11).

The chlorine analyses in all except one case were a few hundredths of a percent high which corresponded to the same results obtained on a known compound. Reagent grade chloroacetic acid was used as a means of calibrating the chloride determination apparatus and the analysis of the chloroacetic acid was also a few hundredths of a percent high. Apparently this was due to the trace impurities of chlorine found in the barium carbonate used as an absorbant.

NEW COMPOUNDS SYNTHESIZED

The new compounds prepared during the course of the investigation were: p-phenylphenyl 3,5-dinitrobenzoate, p-benzylphenyl 3,5-dinitrobenzoate, 2,4,5-trichlorophenyl 3,5-dinitrobenzoate, m-methoxyphenyl 3,5-dinitrobenzoate, m-ethylphenyl 3,5-dinitrobenzoate, o-cyclohexylphenyl 3,5-dinitrobenzoate, 2,4-dinitrophenyl 3,5-dinitrobenzoate and 2,4-dinitronaphthyl 3,5-dinitrobenzoate. Also other compounds prepared were: p-phenylphenyl p-nitrobenzoate, p-benzylphenyl p-nitrobenzoate, m-methoxyphenyl p-nitrobenzoate, o-cyclohexylphenyl p-nitrobenzoate and 2,4-dinitronaphthyl p-nitrobenzoate.

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