tially, this procedure involves the slow addition of isoamyl nitrite to the appropriate aniline salt suspended in cold glacial acetic acid. In order to precipitate the benzenediazonium salt in a crystalline form, dry ether must be added dropwise to the solution over a period of three to four hours.

This, and analogous, methods not only have the disadvantage of being tedious and time-consuming, but also it not infrequently happens that an oil, instead of a crystalline precipitate, is produced. Further, the yields obtained by these methods are rather poor.

The following method has been found to be rapid (fifteen to thirty minutes), to always produce good crystalline precipitates, and to give yields which approach the theoretical.

Preparation.—Five grams of aniline hydrochloride is suspended in a mixture of 30 ml. of glacial acetic acid and 30 ml. of anhydrous, peroxide-free dioxane. The mixture is cooled in an ice–salt-bath and ethyl nitrite bubbled in until all the solid material is dissolved. It has been previously established that the complete diazotization of the hydrochloride coincides with the disappearance of the solid phase and the first appearance of an excess of ethyl nitrite. Hence, the instantaneous coloration of starch iodide paper produced by a drop of the solution gives evidence that diazotization is complete. 150 ml. of dry dioxane at room temperature is then added in one portion to the completely diazotized solution, and benzenediazonium chloride immediately precipitates in a fine, white crystalline form. The solid is filtered on a Büchner funnel and washed twice with two 25-cc. portions of dry dioxane to remove any last traces of acetic acid.

The yield of dry benzenediazonium chloride from seven different preparations was, in all cases, calculated to be better than 95% of the theoretical.

It was previously found[2] that benzenediazonium chloride could be stored under anhydrous ether in an icebox for several weeks without deterioration. We now find that the salt may be kept in good condition for at least a month by merely placing it in a stoppered bottle, at room temperature, under dry dioxane. During the course of time the supernatant liquid gradually changed color, going from water-white to amber. The salt, however, retained its original white, crystalline properties. It appears, then, that any decomposition products which are formed under these conditions are readily soluble in the dioxane and hence their contamination of the solid material is prevented to a large extent.

The rates of decomposition, in water, of freshly prepared benzenediazonium chloride, and of that which had been stored for one month, were compared. The rates were identical ($k_{30} = 1.04 \times 10^{-4}$ sec.$^{-1}$) within the limits of experimental error. In both cases, the nitrogen evolved at 30° was 98% of the theoretical.

The method described here has been found equally successful in the preparation of benzenediazonium sulfate. It is reasonable to assume that this method should give equally good yields of high purity for diazo salts from all acids.

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[2] Waring and Abrams, THIS JOURNAL, **63**, 2757 (1941).

The Use of Phenylhydrazine to Characterize Organic Acids[1]

BY G. H. STEMPEL, JR., AND GERSON S. SCHAFFEL

Most of the common methods for the preparation of derivatives for the identification of organic acids require the use either of the acid chloride or of a solution of the sodium salt of the acid. A chance observation of the ease with which acetic acid reacts with phenylhydrazine in benzene solution suggested the possible use of phenylhydrazine as a reagent for characterizing organic acids. A search of the literature revealed the application of this reagent by Latimer and Bost[2] to the identification of aliphatic sulfonic acids. We have investigated the reaction of phenylhydrazine with a number of carboxylic and sulfonic acids and have found that in most cases a white, crystalline material suitable as a derivative is formed readily. The procedure developed utilizes a reagent which is readily available and requires less time than most methods commonly used to identify organic acids. We have also worked out a simple method for obtaining derivatives of monobasic aliphatic acids formed in the saponification of esters.

The general method used in preparing these derivatives was to boil a solution of the acid in phenylhydrazine for thirty minutes. When the solution was cooled, the solid product either separated in good yield or was precipitated out by the addition of benzene. It was then recrystallized from benzene or from an alcohol–water mixture. In a few cases precipitation occurred immediately upon mixing the acid and phenylhydrazine in the cold. By this procedure weaker acids, in general, form phenylhydrazides, while the stronger acids, such as chloroacetic and various sulfonic acids, form salts. The dibasic acids investigated yield a bis-phenylhydrazide when

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[1] Presented before the Division of Organic Chemistry of the American Chemical Society at its 102nd meeting at Atlantic City, New Jersey, in September, 1941.

[2] P. H. Latimer and R. W. Bost, THIS JOURNAL, **59**, 2500 (1937).

heated with phenylhydrazine alone; but when heated with phenylhydrazine in benzene solution, a phenylhydrazine salt is formed with each carboxyl group. A few acids, including crotonic, salicylic, and halogen substituted benzoic acids, fail to react, while many halogen substituted aliphatic acids, such as α-bromopropionic, α-bromo-*n*-caproic, β-bromopropionic, bromoacetic, and β-bromoisobutyric acids, merely split off hydrogen halide to yield a precipitate of the corresponding phenylhydrazine hydrohalide.

In Table I are listed the melting points and elementary analyses of the derivatives with phenylhydrazine not previously reported. The melting points which we have found for the derivatives which have been previously reported, together with the melting points as given in Beilstein[3] (these enclosed in parentheses) are as follows: formic, 143° (145°); acetic 129° (129°); propionic 157° (157°); isobutyric 140° (140°); *n*-butyric 102° (103°); *n*-caproic 98° (96.5°); isocaproic 144° (144°); heptoic 103° (103°); *n*-caprylic 106° (104°); lactic 115° (114.5°); adipic 209° (207°); succinic 210° (209°); benzoic 168° (168°).

TABLE I

MELTING POINTS OF DERIVATIVES OF ACIDS FORMED WITH PHENYLHYDRAZINE

	M. p., °C.	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
n-Valeric	109	68.72	68.75	8.38	8.39
Capric	105	73.24	73.03	9.99	9.99
Undecanoic	110	73.90	73.54	10.21	9.93
Diethylacetic	145	69.91	69.83	8.80	8.79
Undecylenic	97	74.44	74.60	9.55	9.43
Chloroacetic	111[b]	[a]			
α-Chloropropionic	95[b]	49.89	49.75	6.05	6.07
Trichloroacetic	123[b]	35.36	35.79	3.31	3.53
Sebacic	194	69.12	68.63	7.91	7.89
Malonic	194	63.42	63.67	5.67	5.71
Benzene sulfonic	179[b]	50.69	50.70	5.67	5.74
p-Toluene sulfonic	188[b]	55.71	55.38	5.71	5.71

[a] Molecular weight found by titration with standard base: calcd. 202.6; found 204.7. [b] This indicates that the derivative obtained was a salt.

Experimental

Two general procedures were used in preparing derivatives of the acids examined, the choice depending upon the kind of acid.

Procedure 1.—One gram of the acid was dissolved in 2 cc. of phenylhydrazine, and the solution boiled gently for thirty minutes. The crystalline product which separated when the solution cooled was filtered off with suction and washed with small quantities of benzene or ether until the crystals were completely white. When a large excess of phenylhydrazine was used, it was sometimes necessary to dilute the mixture with benzene in order to bring about precipitation of the product. It was found that the derivatives of the lower monobasic acids were best recrystallized from hot benzene, while those of the higher acids and dibasic acids were best recrystallized from alcohol or alcohol–water mixtures. The derivatives obtained from dibasic acids by this method proved to be bis-β-phenylhydrazides.

Procedure 2.—One gram of the acid was mixed with 2 cc. of phenylhydrazine dissolved in 5 cc. of benzene. In some cases a white solid precipitated immediately and was recrystallized from alcohol. If no solid separated, the mixture was refluxed for thirty minutes, and the product which precipitated upon cooling was filtered, washed with ether, and recrystallized from benzene or alcohol. Sulfonic acids, halogen substituted aliphatic acids, and aliphatic dibasic acids yielded salts by this procedure.

Phenylhydrazides were obtained from the aliphatic monobasic acids, formed in the saponification of esters, in the following manner.

The ester was saponified in the usual way. The solution of the salt of the acid was evaporated nearly to dryness, acidified with a slight excess of dilute phosphoric acid, and extracted with ether. A large excess of phosphoric acid must be avoided to prevent the precipitation of the phosphoric acid salt of phenylhydrazine. The acid obtained after the evaporation of the ether was treated with phenylhydrazine in the same manner as indicated in Procedure 1 to obtain the derivative.

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[3] Beilstein, "Handbuch der organischen Chemie," Vol. XV.

Steryl Sulfates. III. Preparation of 3,5,6-Cholestantriol-I

BY ALBERT E. SOBEL,[1] IRVING ALLAN KAYE AND PAUL E. SPOERRI

The unusual stability of the ester linkage of steryl sulfates in alkaline media makes this derivative valuable for the study of the reactions of sterols in basic solutions while protecting the hydroxyl group. This is especially so because such derivatives are water soluble and form in quantitative yields.[2] The present paper deals with the result of such studies in which a new method for the preparation of 3,5,6-cholestantriol I was found by treating pyridonium dibromocholesteryl sulfate with aqueous potassium carbonate at room temperature as indicated below.

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[1] Partially from the dissertation submitted to the Polytechnic Institute of Brooklyn in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1940. Previous paper, THIS JOURNAL, **64**, 361 (1942).

[2] A. E. Sobel and P. E. Spoerri, *ibid.*, **63**, 1259 (1941).