moplastic resins, varying in color from red through orange to brown or even gray-blue.

Another group produced small but perceptible amounts of polymer insoluble in the excess benzyl chloride. Here are to be named auric chloride, barium chloride, cobalt chloride, cupric chloride, lanthanum trichloride, nickel chloride, selenium tetrachloride and tellurium dichloride.

Chlorides that produced no solid polymer at all are antimony trichloride, arsenic trichloride, bismuth chloride, calcium chloride, ceric chloride, chromium chloride (either sublimed or dehydrated), iodine trichloride, lead dichloride, magnesium chloride, mercuric chloride, phosphorus trichloride, phosphorus pentachloride, silver chloride, strontium chloride, sulfur monochloride, tellurium tetrachloride, thallium trichloride and thorium tetrachloride.

It is surprising to find such a salt-like halide as manganese chloride so high in activity, and to note that the chlorides of tellurium are practically non-catalysts although the dioxide is active.[1b] Comparison with a similar survey of catalysts for the ketone synthesis,[3] although complicated by the difference in temperature used, shows a good but by no means perfect correlation between catalytic abilities of chlorides in the two reactions.

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(3) Dermer, Johnson, Wilson and Dermer, THIS JOURNAL, 63, 2881 (1941).

DEPARTMENT OF CHEMISTRY
OKLAHOMA AGRICULTURAL AND MECHANICAL COLLEGE
STILLWATER, OKLAHOMA

RECEIVED JULY 25, 1941

The Identification of Organic Acids by the Use of *p*-Bromobenzyl Pseudothiuronium Bromide

BY BARTLETT T. DEWEY AND HENRY G. SHASKY

In a previous paper from these laboratories,[1] some advantages of *p*-chlorobenzyl pseudothiuronium chloride as the reagent for the identification of organic acids were reported, and some precautions were suggested to prevent hydrolytic decompositions to which the salts are subject. *p*-Bromobenzyl pseudothiuronium bromide has since been prepared. This reagent offers some desirable qualities not found in the compounds previously reported.

The *p*-bromobenzyl pseudothiuronium bromide was prepared by refluxing 62.6 g. of *p*-bromobenzyl bromide with 19 g. of thiourea in 100 cc. of ethanol for one hour. After cooling, the *p*-bromobenzyl pseudothiuronium bromide was removed by filtration and recrystallized from ethanol. The melting point of the product was 213°. Analysis for nitrogen by the Kjeldahl method showed 8.62%; calculated, 8.59%.

Attempts to prepare polymorphous forms were unsuccessful. A portion of the original product was recrystallized by dissolving in ethanol and obtaining the crystals by chilling. The crystals obtained melted at 213°. Another portion was dissolved in 30% hydrobromic acid. The crystals obtained by slow and by rapid cooling melted at 213°. Microscopic examination revealed that the crystals obtained by all the methods were similar in form. Hydrobromic acid is not a satisfactory solvent for recrystallization because of the limited solubility of the *p*-bromobenzyl pseudothiuronium bromide.

The salts of the organic acids were obtained by adding a hot alcoholic solution of *p*-bromobenzyl pseudothiuronium bromide to an aqueous solution of the sodium or potassium salt of the acid. If the acid was used, sodium or potassium hydroxide was added to neutralize the acid. An excess of alkali did not produce rapid decomposition. The *p*-bromobenzyl pseudothiuronium salts precipitated at once in the pure state. When recrystallization was necessary, alcohol was found to be a satisfactory solvent. Boiling the alcoholic solutions for as long as one hour produced no appreciable evidence of decomposition. The salts were removed from the mother liquor by filtration. They were dried in air and over sulfuric acid for twenty-four hours. Weighed samples were then dried at 85° in a vacuum oven. No loss of weight indicative of the decomposition of hydrates was observed. The purity of the salts was established by analysis for nitrogen by the Kjeldahl method.

The high molecular weight of the reagent and the low solubility of the salts make it possible to obtain a large yield of the salt from small amounts of the acid. The formate was the only one of the thirty-seven salts prepared which did not precipitate at once. To obtain this compound, it was necessary to remove a portion of the solvent and cool to induce precipitation.

The melting points were determined in an electrically heated Thiele tube. The melting points of twenty-one aliphatic and sixteen aromatic salts are listed in the table. The melting points of the fatty acid series are not well dispersed. The salts of dibasic acids have well distributed melting points. Those containing an even number of car-

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(1) B. T. Dewey and R. B. Sperry, THIS JOURNAL, 61, 3251 (1939).

bon atoms are higher than those containing an odd number. Aromatic position isomers can be distinguished readily with the exception of the *o*-toluate and the *m*-toluate. Mixed melting points of salts with identical or nearly identical melting temperatures are from six to twelve degrees lower than those of the pure compounds.

I. ALIPHATIC SALTS

	M. p., cor., °C.		M. p., cor., °C.
Acetate	149	Monochloroacetate	154
Butyrate	142	Oleate	133
Caprate	145	Oxalate	194
Caproate	146	Palmitate	135
Caprylate	147	Propionate	146
Diethylacetate	141	Stearate	135
Formate	148	Succinate	167
Glutarate	149	Trichloroacetate	146
Heptylate	147	Valerate	146
Laurate	142	Isovalerate	148
Malonate	139		

II. AROMATIC SALTS

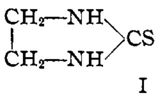
Benzoate	154	*o*-Iodobenzoate	154
o-Bromobenzoate	163	*m*-Iodobenzoate	152
m-Bromobenzoate	154	*p*-Iodobenzoate	181
p-Bromobenzoate	173	Phthalate	166
Cinnamate	170	Salicylate	168
o-Chlorobenzoate	168	*o*-Toluate	151
m-Chlorobenzoate	150	*m*-Toluate	151
p-Chlorobenzoate	163	*p*-Toluate	165

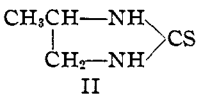
DEPARTMENT OF CHEMISTRY
NORTH PACIFIC COLLEGE OF OREGON
PORTLAND, OREGON
RECEIVED AUGUST 14, 1941

A Qualitative Test for Ethylene and Propylene Thioureas

BY C. O. EDENS AND TREAT B. JOHNSON

The 2-thio-4,5-dihydroglyoxalines have not received the attention that they deserve. It is possible that some of the simple representatives of this series may prove to be substances of biochemical interest, and it is desirable to acquire a better knowledge of their chemistry. During the course of some investigations in this series, the authors have found very useful a spot-test for detecting small amounts of the two simple reduced 2-thioglyoxaline derivatives I and II in reaction products.


I


II

The procedure is very simple and consists of adding a few drops of the unknown to 1 ml. of the spot reagent.[1] A positive test is indicated by the immediate formation of a characteristic colorless and gelatinous precipitate composed of extremely small fiber-like crystals. These fibers are visible by a high-powered microscope.

20 drops of reagent + 1 ml. of ethylene-thiourea which is	Result
0.01 *M*	Precipitate at once
.005	Slight precipitation
.0025	Precipitate after one minute
.0010	After cooling to 5° for four minutes became slightly opalescent

The lowest dilution giving a precipitate is 0.001 *M*. One ml. of this solution gives a distinct opalescence. Thus the sensitivity of the tests permits detection of 0.102 mg. per ml. of ethylene-thiourea in pure aqueous solution.

The test may be used as a semi-quantitative method by diluting a known volume of liquid until precipitation is no longer observed. The free thiol group appears to be necessary for the formation of the characteristic precipitate. Interaction of the thioldihydroglyoxaline with chloroacetic acid prevents the formation of a precipitate with the spot-reagent. The test has proved very convenient in our work, and has given reliable results. Much is yet to be learned, however, about interfering substances. The test was also applied to 2-thio-5-methylglyoxaline, and with formation of a gelatinous precipitate. It is very possible that this reagent may serve not only for detection, but also for developing a technique for the isolation of these sulfur cycles from mixtures of biological products.

(1) The reagent is a mixture of equal volumes of saturated aqueous copper sulfate and concentrated hydrochloric acid.

DEPARTMENT OF CHEMISTRY
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The Use of Amalgamated Aluminum as a Catalyst in the Friedel and Crafts Reaction

BY L. I. DIUGUID

It has been shown by the writer[1] that a series of alkylbenzenes could be prepared via Friedel and Crafts procedure using amalgamated aluminum catalyst. Isolated examples of the use of amalgamated aluminum or aluminum have been reported but no systematic investigation under

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(1) Research work completed under the supervision of Dr. W. T. Miller, Cornell University, in partial fulfillment of the requirements for the degree of Master of Science (Thesis, 1939).