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

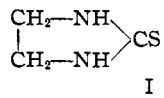
Benzoate	154	*o*-Iodobenzoate	154
o-Bromobenzoate	163	*m*-Iodobenzoate	152
m-Bromobenzoate	154	*p*-Iodobenzoate	181
p-Bromobenzoate	173	Phthalate	166
Cinnamate	170	Salicylate	168
o-Chlorobenzoate	168	*o*-Toluate	151
m-Chlorobenzoate	150	*m*-Toluate	151
p-Chlorobenzoate	163	*p*-Toluate	165

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

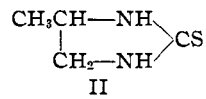
A Qualitative Test for Ethylene and Propylene Thioureas

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 ethylenethiourea 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
YALE UNIVERSITY
NEW HAVEN, CONNECTICUT RECEIVED SEPTEMBER 23, 1941

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

(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).

TABLE I

SYNTHESIS OF ALKYLBENZENES[a]

Reactants and catalysts	Principal products obtained	Yield, %	M. p., °C.	B. p. °C.	Mm.	d^{20}_4	$n^{20}D$	Derivatives
Ethyl chloride and benzene	Ethylbenzene	76	−93	132 −134.7	732	0.8667	1.4953	
n-Propyl chloride and benzene	*n*-Propylbenzene	15.2		154 −157	735	.8618	1.4922	
	Isopropylbenzene	52.2	−94	152 −153	735	.8617	1.4918	
Isopropyl chloride and benzene	Isopropylbenzene	83.3	−94	150.5–151.5	740	.8614	1.4919	
n-Butyl chloride and benzene	*s*-Butylbenzene	36.6	−80	172.0–172.5	744	.8616	1.4900	*p*-Acetamino-*n*-butylbenzene, m. p. 103.5
	n-Butylbenzene			179.3–180.8	744	.8614	1.4909	
s-Butyl Chloride	*t*-Butylbenzene	59.9	−60	167.5–168.5	735		1.4934	*p*-Acetamino-*s*-butylbenzene m. p. 124
t-Butyl chloride and benzene	*t*-Butylbenzene	74.5	−60.2	168 −169	731.3	.8664	1.4934	
s-Butyl chloride and naphthalene	*s*-Butyl-α-naphthalene	48		180 −190	20–30		1.5780	

s-Butyl-α-naphthalene was prepared by the same general method using 138 g. of naphthalene dissolved in 275 cc. of anhydrous chlorobenzene as solvent and one mole of *s*-butyl chloride.

[a] Physical constants above agree with physical constants cited in literature.

carefully controlled conditions in which the structure and yields of products were carefully established has been carried out.[2] The identity and yields of principal products obtained were carefully established and by using this catalyst in the alkylation type reaction it was shown that the alkylbenzenes could be prepared in general with less rearrangement, formation of tars, disproportionation and dimerization than by the use of aluminum chloride in the usual Friedel and Crafts alkylation reaction.

The following series of alkylbenzenes and also *s*-butyl-α-naphthalene were prepared in good yields: ethylbenzene, isopropylbenzene, *s*-butylbenzene, *t*-butylbenzene, and *s*-butyl-α-naphthalene.

Synthesis of Alkylbenzenes

Six hundred cc. of thiophene free-benzene was placed in a liter round-bottom flask and 100 cc. distilled off to thoroughly dry the benzene and the flask. One hundred cc. of the dry benzene was mixed with 1 mole of the alkyl chloride and set aside in a stoppered bottle until ready for use. The liter flask was fitted with a 250-cc. graduated dropping funnel and a reflux condenser with a hydrogen chloride absorption device[3] connected to the top of the condenser through a calcium chloride tube. The activated aluminum catalyst[4] was added to the benzene in the reaction flask, the dropping funnel and condenser placed in position and the chloride–benzene mixture poured into the dropping funnel. A calcium chloride tube was inserted in the top of the funnel and about 25 cc. of the chloride solution allowed to run into the flask at room temperature. The reaction ordinarily began immediately. After the evolution of hydrogen chloride began to subside, the addition of the chloride solution was continued at the rate of 1 cc. per min. This maintained a fairly vigorous evolution of gas. About four hours were required for the addition after which the reaction mixture was allowed to stand overnight. If any moisture was present a flocculent precipitate of aluminum hydroxide formed and heating was necessary to start the reaction. After the completion of the reaction the solution was a reddish brown color and a small brown oily layer about the thickness of the catalyst was present in the bottom of the flask. After the decomposition with dilute hydrochloric acid approximately one-half of the unreacted aluminum catalyst was present.

After standing overnight, the reaction was heated to gentle refluxing for five to ten minutes, cooled and washed with a 5% solution of hydrochloric acid and with water twice. The benzene layer was separated and dried over calcium chloride for distillation.

Separation and purification of the alkylbenzenes was accomplished by means of fractional distillation using a highly efficient column 60 × 1 cm. inside dimensions. The column was packed with glass helices, and fitted with a partial take off type distillation head. A column[5] with a similar packed section 41 × 1 cm. has been found by

(2) Böeseken and Bastet, *Rec. trav. chim.*, **32**, 184 (1914); von Korczynski, *Ber.*, **35**, 868 (1902); Radziewanowski, *ibid.*, **28**, 1135 (1895).

(3) H. Gilman, "Organic Syntheses," Vol. 14, p. 2.

(4) The amalgamated aluminum catalyst was prepared by washing 2 g. of granulated aluminum metal (30 mesh) with dilute sodium hydroxide and water, then treating with 10 cc. of a 5% solution of mercuric chloride in a test-tube for two to three minutes. Small globules of mercury were visible on the surface of the aluminum after this treatment. The supernatant liquid was poured off and the catalyst washed with water, two 5-cc. portions of ethyl alcohol, and several portions of dry benzene. Alternately, the benzene could be distilled from the catalyst to ensure absolutely anhydrous conditions. To activate this amalgam 3 cc. of an equal volume of the alkyl chloride to be used in the preparation was added to the amalgam in a test-tube, warmed if necessary to start the reaction and allowed to react until the gas evolution slowed down, then added quickly to the reaction flask. The activated catalyst must be used immediately.

(5) Fenske, *Ind. Eng. Chem.*, **26**, 1213 (1934).

Fenske to have an efficiency of 11–12 plates. The inner tube containing the packings was surrounded by an electric heater which was in turn enclosed in a Pyrex vacuum jacket.

Solid *p*-acetamino derivatives of some of the alkylbenzenes were prepared according to the procedure of Ipatieff and Schmerling.[6]

In conclusion, amalgamated aluminum has been shown to have certain decided advantages over aluminum chloride in alkylation reactions of aromatic hydrocarbons. (a) Higher yields of the desired product are obtained in most cases than those cited in literature using aluminum chloride.[7] (b) The reaction proceeds smoothly with the formation of smaller amounts of rearranged products and tars.[8] (c) The use of this catalyst affords certain manipulative advantages.

1. Temperature remains fairly constant during the entire reaction and the use of the catalyst simplifies experimental procedures. 2. Reaction may be allowed to proceed overnight without observation.

(6) Ipatieff and Schmerling, *J. Chem. Soc.*, **59**, 1056 (1937).

(7) Schreiner, *J. prakt. Chem.*, **81**, 558 (1910); Bert, *Ber.*, **36**, 3086 (1903); Radziewanowski, *ibid.*, **28**, 1137 (1895); **33**, 439 (1900); Boedtker, *Bull. Soc. Chim.*, **45**, 647 (1929); **25**, 844 (1901); **31**, 966 (1904); *Chem. Zentr.*, VIII, **12**, 1112 (1904).

(8) Calloway, *Chem. Rev.*, **17**, 327 (1935); Read, THIS JOURNAL, **49**, 3153 (1927); **48**, 1606 (1926); Wagner, *Ber.*, **11**, 1251 (1878).

DEPARTMENT OF CHEMISTRY
AGRICULTURAL MECHANICAL AND NORMAL COLLEGE
PINE BLUFF, ARKANSAS RECEIVED AUGUST 4, 1941

Simplified Method for the Preparation of Aromatic Sulfuric Acid Esters

BY J. FEIGENBAUM AND C. A. NEUBERG

The aromatic sulfuric acid esters are found in normal and especially in pathological urine. Since the discovery of pheno-sulfatase, which splits the aromatic sulfuric acid esters, the preparation of the esters has become significant.[1] The procedure generally used and improved by Neuberg and collaborators[2] is that according to Czapek.[3]

Analogous to this method chlorosulfonic acid is added to an ice-cooled solution of pyridine in chloroform and then a solution of phenol in pyridine. The chloroform is first distilled off *in vacuo*. The mixture is then made alkaline with strong aqueous potassium hydroxide and the pyridine is removed by a second distillation *in vacuo*. The ester potassium salt is obtained from the residue by extraction with hot alcohol, from which it separates in crystalline form upon cooling.

It should be remarked that, in view of the situation caused in some countries by the war, there is great difficulty in procuring pure pyridine. We, therefore, in the above-mentioned procedure, substituted for pyridine dimethylaniline, which is cheaper. As an immediate result we obtained bright, pure white crystals, whereas with the former method the substance sometimes remained colored even after several recrystallizations.

Therefore, in order to find a quicker and simplified method, we looked for a substitute for chloroform as a solvent that would enable us to maintain alkalinity without having to distill off the solvent as in the case of chloroform. With solvents such as petroleum ether, benzine, carbon disulfide, carbon tetrachloride and benzene (which itself reacts with chlorosulfonic acid), we obtained the pure ester salt, but the yield was rather poor.

We have therefore tried the reaction of chlorosulfonic acid directly in the solution of the phenol in dimethylaniline, and have not only obtained the pure white crystals of the potassium salt of the aromatic sulfuric acid esters, but also have succeeded in getting a better yield (average 90% instead of 70%) than by the former procedure. Thus, in this manner, we are *able to avoid all distillations in vacuo*. We only need to filter the separated substances and to wash them, preferably with ether. Petroleum ether, benzine, benzene, etc., may also be used.

Procedure.—Fifteen grams of technical chlorosulfonic acid is added drop by drop with constant stirring to an ice-cooled solution of 10 g. of phenol in about 40 cc. of dimethylaniline. The mixture is then made alkaline with strong aqueous potassium hydroxide (1:1). The solid portion is filtered off by suction and washed thoroughly with ether. The ester salt is extracted from the residue with hot alcohol (95%) and the alcoholic solution filtered through a heated funnel. The separated crystals thus obtained from the alcoholic filtrate are filtered with suction and washed with cold alcohol. By recrystallization from a minimum of hot water we get a pure sulfuric acid ester potassium salt, free from any chlorine and sulfate ions.

Further ester salt can be gained by evaporating on a water-bath the water-layer of the first filtrates. This no longer contains any tertiary amine, because it is present in the ether layer. The same can be done with the alcohol of the second filtrate. (The ether and dimethylaniline used in the preparation are recovered by simple distillation.)

By substituting in this simplified procedure pyridine for dimethylaniline the resulting substance was also white and well crystallized.

It seems that when working with this method the yield with some phenols, as α- and β-naphthol, is better if dimethylaniline is used, while with phenol itself, cresols and polyalkylated phenols better results are obtained with pyridine.

By the same simplified method we obtained good results with phenol when substituting quinoline for dimethylaniline or pyridine.

(1) C. Neuberg and E. Simon, *Ergeb. Physiol.*, **34**, 896 (1932).

(2) Neuberg, *et al.*, *Biochem. Z.*, **156**, 368 (1925).

(3) Czapek, *Monatsh.*, **35**, 635 (1914).