

### Experimental Conditions Influencing the Rearrangement of the Pyrimidine Thiocyanate I

A.—Heating of the thiocyanate I at 115–120° for four hours and at 100° for eight hours did not give any detectable amount of the isothiocyanate modification.

Digestion of the pyrimidine thiocyanate I in toluene did not produce a rearrangement but the change was brought about by refluxing in xylene solution.

B. Rearrangement of the Thiocyanate I by Heating with Alcohol.—At the boiling point of ethyl alcohol the pyrimidine thiocyanate I undergoes no change and can be recrystallized repeatedly from this solvent without structural alteration. On the other hand, when heated in alcohol solution at 100° for six hours (55° below its boiling point), the thiocyanate is transformed completely into the isothiocyanate II, and the latter combines with the alcohol, giving the corresponding thionurethan. The yield is excellent, and the thionurethan melts sharply after one crystallization at 97–98°.

### Summary

1. 2-Ethylmercapto-4-methyl-6-thiocyanopyrimidine is formed by interaction of potassium thiocyanate with 2-ethylmercapto-4-methyl-6-chloropyrimidine in boiling ethyl alcohol solution.

2. This thiocyanate distills at 155–158° at 5 mm. and is rearranged to its isomeric form, the isothiocyanate, (1) by heating with alcohol at 100° and (2) by digestion in boiling xylene.

3. 2-Ethylmercapto-4-methyl-6-isothiocyanopyrimidine cannot be distilled without decomposition. It is slowly transformed into a polymeric modification.

4. The thiocyanate does not react with alcohols, ammonia or aniline. The isothiocyanate interacts with these same reagents to form the corresponding thionurethans and thioureas, respectively.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF MARYLAND]

## THE PARA-PHENYLPHENACYL ESTERS OF CERTAIN ORGANIC ACIDS<sup>1</sup>

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The advantages of *p*-phenylphenacyl bromide as a reagent for identifying organic acids have been previously described by Bronitsky and one of us.<sup>2</sup> We have made frequent use of the reagent in this Laboratory in research and in a course in organic qualitative analysis, and because of the success we have experienced in its use, we have deemed it desirable to report the melting points and solubility behavior of certain *p*-phenylphenacyl esters not prepared in the earlier work.

<sup>1</sup> From a thesis submitted to the Graduate School of the University of Maryland by J. P. Sweeney in partial fulfillment of the requirements for the degree of Master of Science.

<sup>2</sup> Drake and Bronitsky, *THIS JOURNAL*, **52**, 3715 (1930).

Judefind and Reid<sup>3</sup> found that *p*-bromophenacyl bromide did not yield esters smoothly with dibasic acids; however, from phenacyl bromide, Rather and Reid<sup>4</sup> were able to prepare satisfactorily the esters of succinic and glutaric acids. They did not attempt to prepare esters of any of the other dibasic acids.

*p*-Phenylphenacyl bromide, was found to yield esters smoothly with all the members of the  $\alpha,\omega$ -dibasic acid series from malonic acid to sebacic acid.

### Experimental

**Preparation of the Reagent.**—The reagent was prepared as previously described.<sup>2</sup> In order to obtain a colorless *p*-phenylacetophenone with a minimum of effort, it has been found essential to wash the crude ketone obtained from the decomposition of the Friedel-Crafts addition product very carefully until entirely free from acid. If this precaution is taken, one or two crystallizations from alcohol are sufficient to give a colorless product with the correct melting point. Similarly in the preparation of the bromide, it is essential that *all* the acid be washed out of the crude material before recrystallization. One recrystallization from hot 95% alcohol is then sufficient to yield a pure colorless product. If these simple precautions are not observed, much difficulty will be encountered in obtaining a satisfactory reagent.

TABLE I

Acid	RESULTS OBTAINED		Solvent for recrystallization
	Melting or decomposition point of <i>p</i> -phenylphenacyl ester		
Malonic	175	(dried at 100°C.)	Alcohol
Glutaric	152		Acetone
Adipic	148		Acetone
Pimelic	145-148	dec.	Alcohol
Suberic	151		Acetone
Azelaic	141		Acetone
Sebacic	140		Acetone
Phenylacetic	63	dec.	Alcohol
Hydrocinnamic	95		Alcohol
Isocaproic	70		Alcohol
Tartaric	203-204	dec.	Alcohol
<i>p</i> -Nitrobenzoic	182		Benzene
3,5-Dinitrobenzoic	154		Benzene
<i>o</i> -Bromobenzoic	98		Alcohol
Salicylic	148	(dried at 100°C.)	Alcohol
<i>p</i> -Hydroxybenzoic	240		Acetone
<i>o</i> -Methoxybenzoic	131		Alcohol
Anisic	160		Alcohol
Gallic	195-198	dec.	Aq. alcohol
<i>o</i> -Phthalic	167.5		Alcohol
4-Nitrophthalic	120		Benzene
Tetrachlorophthalic	193		Acetone
Benzilic	122		Alcohol

<sup>3</sup> Judefind and Reid, *THIS JOURNAL*, **42**, 1043 (1920).

<sup>4</sup> Rather and Reid, *ibid.*, **41**, 75 (1919).

**Preparation of the Esters.**—The method used was similar to that employed in the former work, but it was found more convenient to use a solution of 1 *N* sodium hydroxide for neutralization of the acid, taking care to have the final salt solution slightly acid to prevent formation of colored by-products. The neutral equivalent of an unknown acid may thus be obtained with no additional effort.

The sodium salts of some of the dibasic acids were found to be insoluble in aqueous alcohol, and caused trouble. Mere substitution of the ethyl ammonium salt for the sodium salt did not obviate the difficulty. If, however, the acid was dissolved in a little water and neutralized with ethylamine, alcohol could be added until the salt started to come out of solution. By use of salts prepared in this way it was possible to obtain the di-esters satisfactorily; 0.0025 mole of acid and 0.005 mole of reagent were used in the experiments with dibasic acids.

Many of the esters listed below were found to be sparingly soluble in 95% alcohol, and accordingly their solubility was tested in acetone, ether and benzene.

Melting points were taken in a small beaker containing concd. sulfuric acid which was well stirred during the determination. No corrections were applied to the melting points, but the thermometer used was calibrated, and registered correctly at 0, 100 and 121.25°, the melting point of pure benzoic acid.

With but two acids were we unable to obtain satisfactory results. The ester of methylantranilic acid was a gum which could not be induced to crystallize, and the ester of trinitrobenzoic acid was a red colloid which could not be filtered. It was also found that under the conditions used in this work, no esters were obtainable from sulfonic acids.

### Summary

A number of common acids have been characterized by the preparation of their *p*-phenylphenacyl esters.

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[CONTRIBUTION FROM THE PEARSON MEMORIAL LABORATORY OF TUFTS COLLEGE]

## PENTHAZOLINES. I. THE ACTION OF HALOGENS ON THE DIMETHYL MALONATE ADDITION PRODUCT OF ALLYL MUSTARD OIL<sup>1</sup>

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It has been shown previously that the aromatic isothiocyanates react smoothly with certain esters<sup>2</sup> containing an active methylene group, forming substituted thioamides that have been found useful for the preparation of heterocyclic ring compounds. The aliphatic derivatives have been much less studied. Ruhemann was unable to obtain a tractable<sup>3</sup> substance from the action of allyl mustard oil on malonic ester. Methyl isothiocyanate, however, and its homologs have been observed to form

<sup>1</sup> Original manuscript received July 3, 1931.

<sup>2</sup> Worrall, *THIS JOURNAL*, **44**, 1551 (1922); **45**, 3092 (1923); **46**, 2832 (1924).

<sup>3</sup> Ruhemann, *J. Chem. Soc.*, **93**, 621 (1908).