

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF NORTH CAROLINA]

Sulfur Studies. VII. The Preparation and Properties of Some New Thioketones

BY R. W. BOST AND B. O. COSBY

During the past several years considerable quantities of thioketones were prepared in connection with certain studies being carried on in this Laboratory. Of the various methods of preparation reported in the literature,¹⁻⁵ that of Staudinger and Freudenberg^{5b} seemed the most desirable, since good yields of a fairly pure product were given on the few thioketones prepared by this method, while most of the hazards of the other methods were eliminated.

The authors were interested in finding a procedure which would be of general application in

ried out in an atmosphere of carbon dioxide and the product dried in a vacuum.

Discussion of Results

Since thiobenzophenone is unstable and melts at a low temperature, thereby making it difficult to work with, it seemed desirable to prepare a thioketone stable under ordinary conditions and one melting high enough so as not to offer physical difficulties in purification. In phenyl diphenyl and phenyl α -naphthyl thioketones this has been realized as will be seen by their properties.

Thioketone	M. p.	Crystal form
Phenyl diphenyl	125.7	Blue plates
Phenyl α -naphthyl	110	Blue needles
Phenyl <i>p</i> -tolyl	35	Blue needles

Crystal solvent	% Yield of pure product	Sulfur analyses, %	
		Calcd.	Found
Alcohol	70	11.71	11.66
Alcohol	65	12.91	13.09
Petroleum ether	60	15.09	15.23

the preparation of various thioketones and have applied the aforementioned method^{5b} with slight modifications to the preparation of known thioketones and also to the new ones reported herein. The method has been very satisfactory except in the preparation of nitro thioketones.

Experimental

Twenty g. of the oxo ketone was dissolved in a mixture containing 60 cc. of ethyl alcohol (95%) and enough of a 50-50 mixture of ether and benzene to keep the oxo ketone in solution at -5° . (Carbon disulfide may be used as a substitute for the ether-benzene mixture.) This solution was placed in a large glass tube 5 cm. \times 35 cm. containing a three-holed stopper and a reflux condenser together with two inlet tubes leading to the bottom of the tube for the gases. The reaction tube was placed in an ice-bath where the temperature was kept between -5 and -10° . The exhaust gases from the reflux condenser were led through a gas trap as described by Marvel and Sperry.⁶ From this point the procedure for the preparation and isolation of the thioketone was identical with that of Staudinger and Freudenberg.^{5b} The crude product was finally crystallized from hot alcohol until a constant melting point was obtained. The yields and other data are given in the table above.

In the preparation of phenyl *p*-tolyl thioketone, ethyl alcohol alone was used as a solvent, the filtration was car-

The thioketones reported herein form salts with mercuric chloride and iodide. Stannous chloride forms a precipitate with phenyl *p*-tolyl thioketone but not with the others. When boiled with 10% alcoholic potassium hydroxide, they are converted into their oxo analogs. Phenyl diphenyl and phenyl α -naphthyl thioketone are very resistant to 15% hydrogen peroxide, while phenyl *p*-tolyl thioketone is easily oxidized to its oxo analog. Molecular weight measurements show that the compounds are monomers. The melting points and color of phenyl diphenyl and phenyl α -naphthyl thioketones have remained unchanged for over two years, indicating their relative stability as compared with thiobenzophenone which soon passes into the colorless oxo analog. Alcoholic solutions of each of the three thioketones show absorption bands around 5900 Å. Very little shift in the absorption band could be detected when one of the aryl groups attached to the thiocarbonyl group, such as the *p*-tolyl, was replaced by the α -naphthyl or the diphenyl group. The greatest effect of such a substitution is noted in the increased stability of the resultant compounds toward 15% hydrogen peroxide.

The authors are very grateful to Dr. E. K. Plyler and his co-workers, of the Department of Physics of the University of North Carolina, for carrying out the absorption spectra studies.

- (1) Bergreen, *Ber.*, **21**, 337 (1888).
- (2) Gattermann, *ibid.*, **28**, 2869 (1895).
- (3) Gattermann and Schulze, *ibid.*, **29**, 2944 (1896).
- (4) Schönberg, Schütz and Nickel, *ibid.*, **61**, 1375 (1928).
- (5) Staudinger and Freudenberg, *ibid.*, **61**, (a) 1577, (b) 1581 (1928).
- (6) Marvel and Sperry, "Organic Syntheses," John Wiley and Sons, Inc., New York City, 1928, Vol. VIII, p. 28.

Summary

1. Simple as well as mixed aryl thioketones were prepared in good yields by the action of hydrogen sulfide-hydrogen chloride on the corresponding oxo ketone.

2. The above method is not applicable to the preparation of nitro thioketones.

3. The substitution of a biphenyl or α -naphthyl group for a phenyl group in thiobenzophenone greatly enhances the stability of the carbon-sulfur linkage.

4. The new thioketones show the typical reactions of the thiocarbonyl group. They show absorption bands around 5900 Å.

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[CONTRIBUTION FROM THE KENT AND GEORGE HERBERT JONES CHEMICAL LABORATORIES, UNIVERSITY OF CHICAGO]

The Trihydroxybutyric Acids¹

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For a number of years, studies have been in progress in these Laboratories on the preparation and identification of the possible products of the saccharinic acid transformation of the tetroses. In the course of this work, ten of the eleven theoretically possible C₄-saccharinic (dihydroxybutyric and isobutyric) acids have been prepared and to some extent characterized.² Equally important in the program are the trihydroxybutyric (*d*- and *l*-erythronic and *d*- and *l*-threonic) acids which offer possible source material for the preparation of the tetroses whose transformations it is proposed eventually to study.

Both the optically active and the racemic forms of erythronic lactone have long been known.³ Braun⁴ has recently prepared crystalline *dl*-threonic acid (m. p. 98°). The active forms of the acid are as yet unknown. *d*-Threonic lactone⁵ has been discovered among the alkaline oxidation products of *l*-arabinose; *l*-threonic lactone⁶ similarly among the oxidation or degradation products of *d*-galactose and *d*-glucose. The latter has also been obtained by Wohl and Momber⁷ from glycerol acetal.

Perusal of the literature cited shows that while *dl*-erythronic lactone may be prepared in large quantities rather easily, all of the forms of threonic acid still remain practically unknown in

amounts larger than a few grams. The object of the work reported below was to prepare enough *dl*-threonic acid or lactone to allow a thorough study of this substance. This object was only partially achieved.

Cohen⁸ working in these Laboratories, prepared a mixture of *dl*-erythronic and *dl*-threonic acids by the oxidation of vinylglycolic ester with potassium chlorate and osmic acid. It was proposed to extend the work of Cohen in the hope that it would prove possible to set up a definite procedure for the isolation of the acid sought. This object has been accomplished.

Vinylglycolic acid, CH₂=CHCHOHCOOH, was found to be a better starting material than its ethyl ester, and silver chlorate a more satisfactory oxidizing agent than potassium chlorate. A mixture of the two acids was obtained in over 90% yield. From this mixture there was obtained (a) by a process involving differential neutralization of the two acids with barium hydroxide, 20% crystalline erythronic lactone and 7.2% threonic phenylhydrazide; and (b) by direct treatment with phenylhydrazine 4% of erythronic phenylhydrazide and 2% threonic phenylhydrazide with approximately one-half more recovered by reworking the filtrates and washings. Of the two processes, (a) is to be recommended as the better one. Because of the difficulty of the procedure and because the yield of threonic acid is so poor, other sources for its preparation are being sought.

Experimental Part

Cohen showed the presence of the threonic and erythronic acids by oxidation of the product with dilute nitric

(1) This article is abstracted from a dissertation presented by R. E. Hoen in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the University of Chicago.

(2) The last paper in this field is by Glattfeld and Chittum, *THIS JOURNAL*, **55**, 3663 (1933).

(3) For a list of the literature references on the various forms of this acid, see Glattfeld and Forbrich, *ibid.*, **56**, 1209 (1934).

(4) Braun, *ibid.*, **52**, 3176 (1930).

(5) Nef, Hedenburg and Glattfeld, *ibid.*, **39**, 1638 (1917).

(6) Anderson, *Am. Chem. J.*, **42**, 423 (1909); Glattfeld, *ibid.*, **50**, 150 (1913).

(7) Wohl and Momber, *Ber.*, **50**, 458 (1917). See also Micheel and Kraft, *Z. physiol. Chem.*, **216**, 233 (1933).

(8) Abstracts of Theses, University of Chicago Science Series, VI, 125 (1927-28).