keto-succinic acid is readily explained by the fact that this acid is a β-ketonic acid and suffers, on treatment with dil. alkali, the loss of one molecule of carbon dioxide: $HOOC.CO.C(CH_3)OH.COOH = HOOC.CO.CHOHCH_3. + CO_2$.

Obviously no attempt has as yet been made at the isolation either of the complete or the partial degradation products of hydroxy-methyl-keto-succinic acid themselves. For the purpose of this particular research identification of the simplest and most readily isolated derivatives of these products has sufficed.

Summary

1. A method for the preparation of methyltartaric acid has been outlined.

2. A preliminary study of the behavior of methyltartaric acid toward hydrogen peroxide has been carried out.

3. A mechanism, based on the decomposition of the oxidation product of methyltartaric acid, for the decomposition of dihydroxymaleic acid has been suggested.

ROCKEFELLER INSTITUTE FOR
MEDICAL RESEARCH
NEW YORK, N. Y.

[CONTRIBUTION FROM THE GEORGE WASHINGTON UNIVERSITY]

THE CONDENSATION OF THE ISOMERIC TOLYL-2-THIO-4-KETO-THIAZOLIDINES (RHODANIC ACIDS) WITH SUBSTITUTED VANILLINS

BY RAYMOND M. HANN

RECEIVED APRIL 10, 1925 PUBLISHED JULY 3, 1925

The aldehyde condensation products of the rhodanic acid series are dyes, the majority of them being of slight value due to their fading by the action of light. It has been pointed out, however, that hydroxy-benzal-rhodanic acids when coupled with diazo compounds yield derivatives which dye silk or wool directly fast yellow or orange-yellow colors.[1]

The object of the present investigation was to prepare a series of halogen aldehyde condensation products of the isomeric tolyl-rhodanic acids in order to study the effect of the relative positions of the methyl group in the tolyl residue, as well as the halogen substitution effect in such a series of compounds upon their spectrophotometric behavior. Vanillin was selected as the parent aldehyde for two reasons: its mono-halogen substitution products are known (except chlorovanillin, which was prepared for this investigation), and it contains an hydroxy group in the *para* position to the aldehyde grouping, which should accentuate its dyeing

[1] Zipser, *Monatsh.*, **23**, 958 (1902).

properties. The investigation was later extended to include a nitro aldehyde, 5-nitrovanillin being selected on account of its constitutional similarity to other members of the series.

The 2-thio-4-thiazolidones, more commonly known as rhodanic acids, a misnomer since they are in reality the cycle anhydrides of the dithiocarbamo-glycolic acids, were prepared by general methods.[2]

One of the marked characteristics of the 2-thio-4-thiazolidones is their reactivity with aldehydes due to the methylene grouping in the $CO–CH_2–S$ linkage. Wheeler and Jamieson[3] have remarked upon the activity of such a methylene grouping in their study of the condensation of pseudo thiohydantoin (2-imino-4-thiazolidone) with ethyl oxalate, while Johnson and Guest[4] have extended the condensation to the acyclic series, showing that the methylene hydrogen of ethylbenzyl thioglycolate reacts with ethyl formate to yield α-benzyl-mercapto-β-hydroxyacrylate.

Tolyl-2-thio-4-thiazolidones have been previously prepared by Jäger,[5] Andreasch and Zipser,[6] Stuchetz,[7] Andreasch,[8] Holmberg[9] and Holmberg and Psilanderhielm.[2]

o- And *p*-vanillal-tolyl-2-thio-4-thiazolidones have been prepared, but the *meta* isomer has not been previously described.

Experimental Part

Preparation of Aldehydes

5-Bromovanillin—This aldehyde has been prepared by Tiemann and Haarmann,[10] Brady and Dunn[11] and Dakin.[12] The method of Dakin with slight modification gave quantitative yields of a pure white product which may be used without further purification.

5-Nitrovanillin.—Nitration of vanillin with fuming nitric acid according to the method of Bentley[13] gave excellent yields. The compound may be conveniently recrystallized from alcohol or glacial acetic acid.

---

[2] Delépine, *Bull. soc. chim.*, **29**, 48 (1903). Nägele, *Monatsh.*, **33**, 941 (1912). Andreasch and Zipser, *ibid.*, **24**, 499 (1903); **25**, 159 (1904); **26**, 1191 (1905). Holmberg, *J. prakt. Chem.*, **81**, 451 (1910). Miolati, *Ann.*, **262**, 82 (1891). Dixon, *J. Chem. Soc.*, **71**, 628 (1897). Holmberg, *Ber.*, **39**, 3068 (1906). Holmberg and Psilanderhielm, *J. prakt. Chem.*, **82**, 440 (1910). Berlinerblau, *Ber.*, **19**, 124 (1886). Fredyl, *Monatsh.*, **10**, 82 (1889).

[3] Wheeler and Jamieson, THIS JOURNAL, **25**, 366 (1903).

[4] Johnson and Guest, *Am. Chem. J.*, **42**, 271 (1909).

[5] Jäger, *J. prakt. Chem.*, [2] **16**, 17 (1877).

[6] Andreasch and Zipser, *Monatsh.*, **26**, 1191 (1905).

[7] Stuchetz, *ibid.*, **26**, 1209 (1905).

[8] Andreasch, *ibid.*, **29**, 399 (1908).

[9] Holmberg, *J. prakt. Chem.*, [2] **81**, 451 (1910).

[10] Tiemann, *Ber.*, **32**, 3408 (1899).

[11] Brady and Dunn, *J. Chem. Soc.*, **107**, 1859 (1915).

[12] Dakin, *Am. Chem. J.*, **42**, 493 (1909).

[13] Bentley, *ibid.*, **24**, 172 (1900).

5-Iodovanillin.—This derivative was prepared by the previously described[14] modification of the procedure of Carles.[15] The compound melts at 180°[16] instead of 174° as reported by Carles. It crystallizes in the rare monoclinic domatic class and the axial ratio is a:b:c = 1.014:1:0.8161 with $\beta = 87° 30'$. Upon examination under the petrographic microscope it is observed to belong to the biaxial class, showing readily the indices $\alpha = 1.505$ and γ above 1.740. The optical sign is +, the sign of elongation — and the optic axial angle is approximately 22°. The needles are pleochroic, appearing yellow when light vibrates crosswise and colorless when lengthwise.

5-Chlorovanillin.—The available chemical literature does not include a description of a chlorinated 3-methoxy-4-hydroxybenzaldehyde. It is easily prepared by direct chlorination of vanillin in glacial acetic acid in the presence of fused sodium acetate.

5-Chlorovanillin crystallizes readily from acetic acid in brilliant, colorless, tetragonal plates, possesses a slight appreciable odor and melts at 165° to a clear oil.

Anal. Subs., 0.2080: AgCl, 0.1599. Calcd. for $C_8H_7O_3Cl$: Cl, 19.00. Found: 18.97.

Ammonium Tolyl-dithiocarbamates

Primary amines react with molecular proportions of concd. aqueous ammonia and carbon disulfide to yield ammonium salts of substituted dithiocarbamic acids. $RNH_2 + NH_4OH + CS_2 = HNRCSSNH_4 + H_2O$. The reaction is markedly exothermic; in certain cases it becomes necessary to cool the reaction mixture to prevent loss of its volatile constituents. The ammonium salt crystallizes on cooling or upon standing overnight; it should be used as soon as possible since the dithiocarbamates are subject to rapid decomposition.[17] The ammonium, barium and nickel salts of the tolyldithiocarbamic acids have been prepared by Losanisch,[18] but experimental details and yields are not reported.

Ammonium *o*-Tolyl-dithiocarbamate.—Thirty g. of *o*-toluidine, 45 cc. of concd. aqueous ammonia, and 25 g. of carbon disulfide were mixed and the mixture was vigorously agitated. The first effect was that of cooling, but the liquid became heated and its components combined to give a clear red solution. Upon standing overnight clear prismatic crystals separated. These were filtered off by suction and used without further purification; yield, 75%.

Ammonium *m*-Tolyl-dithiocarbamate.—The corresponding *meta* and *para* salts were prepared in a similar manner and were obtained in 95% and quantitative yields, respectively.

2-Thio-3-Tolyl-4-Thiazolidones

These compounds have been prepared by Andreasch and Zipser[6] and by Andreasch[8] from chloro-ethyl acetate. Ethyl bromo-acetate has been substituted in the present investigation because of its more vigorous reaction and the decrease in the amount of intermediate tolyl-dithiocarbamino-acetate formed. No attempt was made to purify the cyclic derivatives, since a preliminary observation showed that the reaction mixture used in the subsequent condensation changed any of this intermediate acyclic ester directly into the thiazolidone. The yields of *ortho*, *meta* and *para* isomers were, respectively, 76, 90 and 96%.

[14] Hann, *J. Washington Acad. Sci.*, **14**, 79 (1924).

[15] Carles, *Bull. soc. chim.*, **17**, 14 (1872).

[16] See also Bougault and Robin, *Compt. rend.*, **172**, 452 (1921).

[17] Sebrell and Boord, THIS JOURNAL, **45**, 2393 (1923).

[18] Losanisch, *Ber.*, **24**, 3026 (1891).

2-Thio-3-tolyl-4-keto-5-(3-methoxy-4-hydroxy-5-halogen benzal) Thiazolidines

The halogen vanillal-tolyl-rhodanic acids are formed by the condensation of the isomeric tolyl-rhodanic acids with substituted vanillins. They were all prepared by one general procedure. Three g. of the tolyl-thiazolidone, a molecular equivalent of the required aldehyde, 5 g. of fused sodium acetate, and 50–100 cc. of glacial acetic acid were refluxed together for 2.5 hours. To the cooled solution (or at times solid and liquid mixture) an excess of water was slowly added in a fine stream to prevent coagulation of the precipitated condensation product and subsequent difficulty in washing and purification. The precipitated mass was filtered off by suction, washed thoroughly with water, dried and recrystallized once or twice from glacial acetic acid. The yield of reaction product was quantitative.

The 5-halogeno vanillal-tolyl-thiazolidones are all crystalline compounds, for the most part forming beautiful needles. The chloro and

TABLE I

COMPOUNDS FORMED

Thiazolidine 2-Thio-	Melting point °C.	Nitrogen, % Found	Calcd.	Remarks
3-*o*-tolyl-4-keto-5-(5-bromovanillal)	207 Slight decomposition	3.11	3.21	Iridescent, yellow-brown, cubic crystals
3-*o*-tolyl-4-keto-5-(5-chlorovanillal)	196	3.48	3.57	Brilliant yellow, acicular needles
3-*o*-tolyl-4-keto-5-(5-iodovanillal)	213	2.82	2.89	Orange-red, microcrystalline powder
3-*o*-tolyl-4-keto-5-(5-nitrovanillal)	205 decomposition	6.92	6.96	Golden-brown leaflets
3-*m*-tolyl-4-keto-5-(vanillal)	210	3.98	3.92	Deep yellow, microcrystalline powder
3-*m*-tolyl-4-keto-5-(5-bromovanillal)	Melts to clear oil at 201°, solidifies, remelts at 223–4°	3.12	3.21	Light yellow needles
3-*m*-tolyl-4-keto-5-(5-chlorovanillal)	210	3.45	3.57	Brilliant yellow needles
3-*m*-tolyl-4-keto-5-(5-iodovanillal)	190–1 decomposition	3.18	2.89	Yellow-brown powder
3-*m*-tolyl-4-keto-5-(5-nitrovanillal)	220 decomposition	6.81	6.96	Brown, crystalline aggregate
3-*p*-tolyl-4-keto-5-(5-bromovanillal)	223	3.12	3.21	Brilliant, light yellow needles
3-*p*-tolyl-4-keto-5-(5-chlorovanillal)	224	3.57	3.57	Brilliant yellow needles
3-*p*-tolyl-4-keto-5-(5-iodovanillal)	243	2.82	2.89	Deep yellow, crystalline powder
3-*p*-tolyl-4-keto-5-(5-nitrovanillal)	214–5 decomposition	7.22	6.96	Golden-brown plates

bromo compounds are brilliant yellow, the iodo derivatives are somewhat deeper in color and the nitro substitution products are yellow to golden-brown. They are insoluble in water, slightly soluble in alcohol and most organic solvents, but are easily purified by recrystallization from acetic acid. They dissolve readily in concd. sulfuric acid with the production of brilliant red colors. Melting points were determined with short-scale thermometers and the mercury column totally immersed.

Measurements of the absorption of these compounds in acetic acid by Walter C. Holmes indicate that the maximum absorption occurs too far in the red end of the spectrum to allow use of direct absorption measurement methods.

Summary

5-Bromo-, 5-chloro-, 5-iodo- and 5-nitrovanillins have been condensed with the isomeric 2-thio-3-tolyl-4-thiazolidones.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

A QUALITATIVE COLOR TEST FOR THE GRIGNARD REAGENT

BY HENRY GILMAN AND F. SCHULZE[1]

RECEIVED APRIL 13, 1925 PUBLISHED JULY 3, 1925

In connection with studies involving the Grignard reagent a need was felt for a sensitive qualitative test which could be carried out in a short time. When organomagnesium halides are treated with such reagents as carbon dioxide and isocyanates a smooth reaction occurs and the products obtained lend themselves to ready identification. However, the preparation of these and other derivatives has inherent disadvantages, in particular, the tediousness and time involved in testing for small quantities.

The idea of the color test which is described here is not novel. It was suggested by experiments made by Ehrlich and Sachs[2] on the preparation of triphenylmethane dyes from *p*-dimethylamino-phenylmagnesium bromide. Furthermore, F. and L. Sachs[3] proposed the use of Michler's ketone (tetramethyl-diaminobenzophenone) as the best reagent for the detection of phenylmagnesium bromide, because of the ready formation of malachite green.

The test as finally developed is readily made as follows. One-half to 1 cc. of the solution to be tested is treated, at room temperature, with an

[1] This paper is an abstract of a part of a thesis presented by F. Schulze in partial fulfilment of the requirements for the degree of Master of Science in Chemistry at Iowa State College.

A report of this work was made at the Spring Meeting of the American Chemical Society held at Baltimore, Md., in April, 1925.

[2] Ehrlich and Sachs, *Ber.*, **36**, 4296 (1903). Baeyer, *Ann.*, **354**, 152 (1907). Votocek and Matejka, *Ber.*, **46**, 1755 (1913). Holt and Reid, THIS JOURNAL, **46**, 2329 (1924).

[3] F. and L. Sachs, *Ber.*, **37**, 3088 (1904).