verted to the chloride.[7] Nine grams of 4-chlorosalicylic acid was obtained, m. p. 211° after crystallization from water. No depression in m. p. was observed when this product was mixed with the substance prepared below. *Anal.* Calcd. for $C_7H_5O_3Cl$: C, 48.71; H, 2.92; Cl, 20.54. Found: C, 48.52; H, 3.04; Cl, 20.69.

A mixture of 6 g. of 2,4-dichlorobenzoic acid, 20 g. of barium hydroxide hydrate, 60 ml. of water and 0.5 g. of copper-bronze was heated in a sealed tube for six hours at 160–170°. The product was filtered and then suspended in water and decomposed with hydrochloric acid. Crystallized from hot water, the chlorosalicylic acid, 2.9 g, melted at 211–212°. 4-Chlorosalicyclic acid is reported to melt at 211°; 2-chloro-4-hydroxybenzoic acid at 159°.[8]

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[7] The procedure described in "Org. Syn.," Coll. Vol. I, p. 163, 1st ed., was followed except that threefold volumes of acid were employed to facilitate the reaction of the insoluble acid hydrochloride and its insoluble diazonium salt. In addition, chlorobenzene was added during the decomposition of the diazonium salt, to extract the product as formed.

[8] Hodgson and Jenkinson, *J. Chem. Soc.*, 1740 (1927).

DIVISION OF MEDICINAL CHEMISTRY
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The Preparation of Phthalaldehyde

BY S. WAWZONEK AND R. E. KARLL[1]

Varying yields have been reported for the preparation of phthalaldehyde from *o*-xylene.[2] It has been found that, by using all-glass apparatus and the procedure described below, *o*-xylene and *o*-methylbenzyl bromide can be brominated in 64% yield to $\alpha,\alpha,\alpha',\alpha'$-tetrabromo-*o*-xylene. Under similar conditions *o*-methylbenzyl chloride gives the same yield of a mixture of $\alpha,\alpha,\alpha',\alpha'$-tetrabromo-*o*-xylene and $\alpha,\alpha,\alpha',\alpha'$-chlorotribromo-*o*-xylene. *o*-Methylbenzyl chloride is the most suitable starting material since the best commercially available *o*-xylene is only 90% pure while *o*-methylbenzyl bromide is a powerful lachrymator.

The tetrahalo-*o*-xylenes can be hydrolyzed to phthalaldehyde of melting point 55.5° in a 90% yield by the method of Thiele.[2a] The only modification made in this procedure was to saturate the aqueous solution of the aldehyde with sodium chloride instead of sodium sulfate.

Experimental[3]

$\alpha,\alpha,\alpha',\alpha'$-Tetrahalo-*o*-xylene.—*o*-Methylbenzyl chloride[4] was brominated according to the directions given in "Organic Syntheses"[5] with the following modifications. All-glass equipment was used together with a Trubore glass stirrer. From 132.6 g. of *o*-methylbenzyl chloride, 245 g. of product was obtained by taking up the reaction mixture in hot chloroform (300 ml.) and cooling; m. p., 106°. Repeated recrystallizations from ethanol gave a white crystalline compound melting at 110–111°. A mixture with tetrabromo-*o*-xylene (m. p., 115.5°) melted at 112°.

Anal. Calcd. for $C_8H_6ClBr_3$: Br, 63.6. Calcd. for $C_8H_6Br_4$: Br, 78.20. Found: Br, 72.89, 72.97.

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[1] Abstracted from a thesis by R. E. Karll presented to the Graduate College of the State University of Iowa in partial fulfillment of the requirements for the M.S. degree, June, 1947.

[2] (a) Thiele and Gunther, *Ann.*, **347**, 106 (1906); Thiele and Weitz, *ibid.*, **377**, 8 (1910); (b) Sandstrom and Lillevik, *Ind. Eng. Chem., Anal. Ed.*, **13**, 781 (1941); (c) Fieser and Pechet, THIS JOURNAL, **68**, 2577 (1946).

[3] Melting points are corrected.

[4] Smith and Spillane, THIS JOURNAL, **62**, 2640 (1940).

[5] "Organic Syntheses," Vol. 20, John Wiley and Sons, Inc., New York, N. Y., p. 92.

DEPARTMENT OF CHEMISTRY
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IOWA CITY, IOWA
RECEIVED NOVEMBER 13, 1947

Ethyl Acetamidoacetoacetate

BY RICHARD H. WILEY AND OLIN H. BORUM

The reduction of oximinoacetoacetic ester over palladium catalyst in acetic anhydride gives a product, m. p. 46–47.5°, which has been characterized as acetamidoacetoacetic ester, $CH_3CONHCH(COCH_3)CO_2C_2H_5$. The only known previous reference[1] to this compound describes a less convenient method of preparation and reports a melting point of 141°.

Experimental

Ethyl Oximinoacetoacetate.—This compound was prepared by the method of Adkins and Reeve.[2]

Ethyl Acetamidoacetoacetate.—Thirty-two grams of ethyl oximinoacetoacetate and 6.9 g. of palladium catalyst[3] were shaken in 50 ml. of acetic anhydride at room temperature under 30 lb. hydrogen pressure for ten hours. After separating from the catalyst and removing the excess acetic anhydride, 35 g. of acetamidoacetoacetic ester b. p. 128–140° (3–4 mm.) was obtained. Refractionation gave 25.7 g. b. p. 125–132° (3–4 mm.) which solidified on standing, m. p. 46–47.5°.

Anal. Calcd. for $C_8H_{13}O_4N$: C, 51.33; H, 7.0; N, 7.48. Found: C, 51.13; H, 7.0; N, 7.50.

This solid gave qualitative tests for carbonyl with 2,4-dinitrophenylhydrazine reagent and for enol with alcoholic ferric chloride. Reaction with phenylhydrazine in ether, according to the procedure of Michael[4] for the preparation of the phenylhydrazone of acetoacetic ester, gave a yellow precipitate of the phenylhydrazone, m. p. 131.5–132.5°.

Anal. Calcd. for $C_{14}H_{19}O_3N_3$: C, 60.63; H, 6.9; N. 15.15. Found: C, 60.43; H, 6.96; N, 15.10.

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[1] Cerchez and Colesiu, *Compt. rend.*, **194**, 1954 (1932).

[2] Adkins and Reeve, THIS JOURNAL, **60**, 1328 (1938).

[3] R. Mozingo, *et al.*, *ibid.*, **67**, 2093 (1945). Washed free of chloride.

[4] A. Michael, *Am. Chem. J.*, **14**, 519 (1892).

VENABLE CHEMICAL LABORATORY
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The Decomposition of *o*-Methoxybenzene Diazonium Chloride

BY H. E. WOODWARD AND A. A. EBERT, JR.

M. L. Crossley and others[1] have reported that the decomposition of *o*-methoxybenzene diazonium chloride can be assumed to consist of two de-

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[1] THIS JOURNAL, **69**, 1160 (1947).

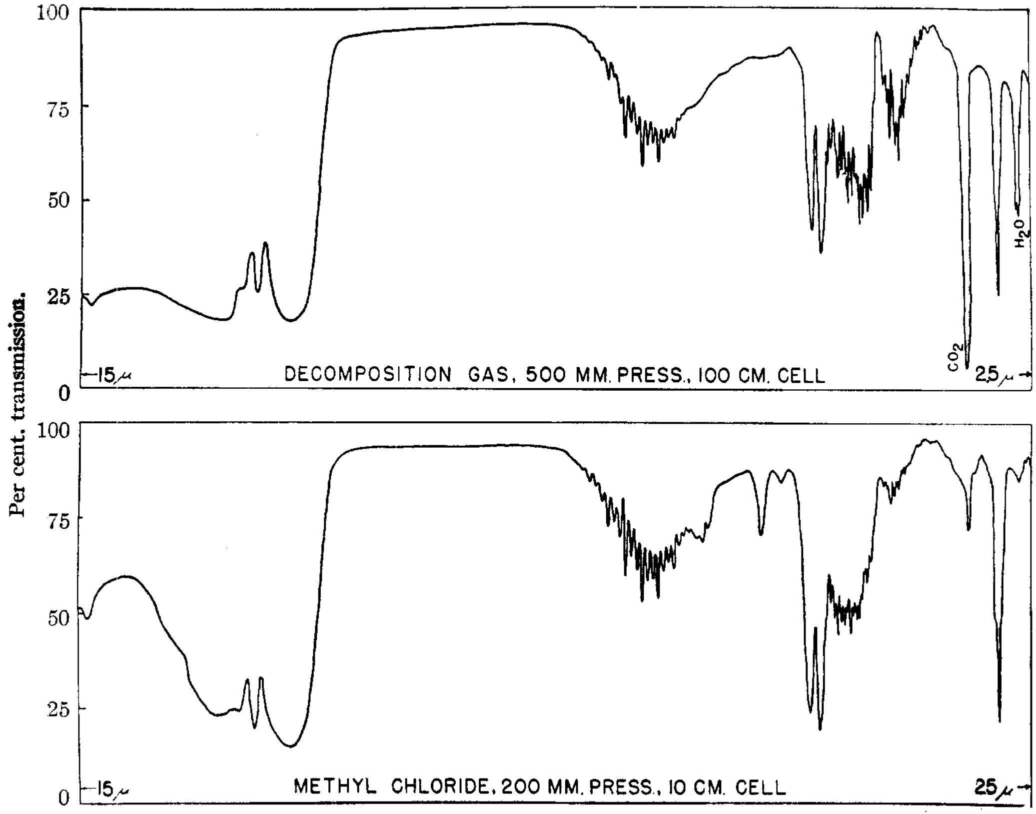

Fig. 1.—Comparison of spectra of methyl chloride and gas sample obtained from decomposition of *o*-methoxybenzene diazonium chloride.

composition reactions occurring simultaneously, one a slow single-step reaction to give guaiacol, and the other a pair of consecutive reactions to give catechol. They regretted that they did not find methyl chloride or methyl alcohol to substantiate their hypothesis.

We have obtained some evidence that their hypothesis is correct by infrared spectral analysis of the evolved nitrogen in the following manner: A solution of the diazonium salt was prepared from *o*-anisidine with 2.5 equivalents of hydrochloric acid and 1 equivalent of sodium nitrite. This solution was heated for about six hours at 90–95° and the evolved gas was passed through Drierite and soda-lime (to remove carbon dioxide used in sweeping air out of the apparatus) and collected over mercury. The gas was transferred to an infrared absorption cell which had an optical path length of one meter. With the gas at a pressure of 500 mm. the spectrum was recorded between 2.5 and 15 microns. The characteristic absorption spectrum of methyl chloride clearly was evident as shown in Fig. 1. A quantitative determination showed that the mole fraction of methyl chloride was 0.026. No other products were detected.

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2-Substituted-thiazolidine-4-carboxylic Acids

BY HAROLD SOLOWAY,[1] FRANK KIPNIS, JOHN ORNFELT AND PAUL E. SPOERRI

Schubert[2] has reported on the interaction of a number of aldehydes with cysteine to produce substituted thiazolidine carboxylic acids. Other workers[3] have extended the reaction and Ratner and Clarke[4] found that the mechanism consisted in hemimercaptal formation, followed by dehydration and cyclization.

Recently, with the discovery that penicillin contained a thiazolidine moiety within the molecule, interest was revived in this class of heterocyclics, and further syntheses have been announced.[5]

The present work reports on the interaction of a representative group of aldehydes with cysteine to produce thirteen new 2-substituted-thiazolidine-4-carboxylic acids. The new compounds form

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[1] Abstracted from a thesis by Harold Soloway submitted to the Polytechnic Institute of Brooklyn in partial fulfillment of the requirements for the degree of Master of Science in Chemistry.

[2] Schubert, *J. Biol. Chem.*, **111**, 671 (1935); **114**, 341 (1936); **121**, 539 (1937); **130**, 601 (1939).

[3] Génévois and Cayrol, *Bull. soc. chim.*, [5] **6**, 1223 (1939); Woodward and Schroeder, THIS JOURNAL, **59**, 1690 (1937); Micheel and Emde, *Ber.*, **72**, 1728 (1939).

[4] Ratner and Clarke, THIS JOURNAL, **59**, 200 (1937).

[5] British Patent 584,918 (1947); Neher, Wettstein and Miescher, *Helv. Chim. Acta*, **29**, 1815 (1946); Brack, *ibid.*, **30**, 1 (1947).