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).

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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.

## 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).

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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).