there was obtained 11.5 g. (20%) of a product distilling at 65–90° at 15 mm.

2-Methyl-2-cyclohexen-1-one 2,4-Dinitrophenylhydrazone.—When (I) was subjected to the Mattox–Kendall dehydrobromination procedure,[3] 15 g. of (I) yielded 15.5 g. (78%) of the 2,4-dinitrophenylhydrazone, m. p. 207–208° after recrystallization from benzene–ethanol.

From 10 g. of (II) there was obtained by the same method 15 g. of the same product of m. p. 207–208°.

Anal. Calcd. for $C_{13}H_{14}O_4N_4$: N, 19.31. Found: N, 18.98.

2-Methyl-2-cyclohexen-1-one.—Pyruvic acid regeneration[3,4] of the ketone from the 2,4-dinitrophenylhydrazone in 10–15 g. lots gave the methylcyclohexenone in yields ranging from 62 to 87% in various runs. It had a boiling range of 93–97° at 25 mm. and could readily be converted to the semicarbazone m. p. 205° (literature 207°, slow heating).[6]

Anal. Calcd. for $C_8H_{13}ON_3$: N, 25.14. Found: N, 24.85.

The ketone could also be readily reconverted to the dinitrophenylhydrazone, m. p. 205°, in approximately 95% yield.

2-Methyl-2-cyclohexen-1-one (Pyridine Method).—From 7 g. of (II) after 12-hour refluxing with pyridine and working up in the usual manner there was obtained 2.5 g. of ketone (62%) b. p. 52–54° at 8 mm. After two further distillations through a column, it had the following properties: $n^{20}\text{D}$ 1.4820; $\lambda_{\text{max.}}$ 231 mμ, log ε 3.96; $\lambda_{\text{max.}}$ 327 mμ, log ε 1.58; $\lambda_{\text{max.}}$ 340 mμ, log ε 1.57 (in cyclohexane).

Anal. Calcd. for $C_7H_{10}O$: C, 76.36; H, 9.09. Found: C, 76.30; H, 9.06.

The semicarbazone m. p. 205° and the dinitrophenylhydrazone, m. p. 207°, were also prepared from this sample.

6-Methyl-2-cyclohexen-1-one.—By pyridine dehydrobromination (I) was converted to this ketone, b. p. 170–173° at 755 mm.; $n^{20}\text{D}$ 1.4727; $\lambda_{\text{max.}}$ 225 mμ, log ε 3.80; $\lambda_{\text{max.}}$ 279 mμ, log ε 2.02.

Anal. Calcd. for $C_7H_{10}O$: C, 76.36; H, 9.09. Found: C. 75.95; H, 9.05.

The semicarbazone had a m. p. of 178°, in agreement with that reported in the literature.[5]

Anal. Calcd. for $C_8H_{13}ON_3$: N, 25.14. Found: N, 25.20.

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(6) Heilbron, "Dictionary of Organic Compounds," Vol. II, Oxford University Press, New York, N. Y., 1936, p. 662.

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New Synthesis of α-Aminoadipic Acid

BY T. PHILIP WAALKES, WILLIAM S. FONES AND JULIUS WHITE

α-Aminoadipic acid has been prepared by a variety of methods.[1,2,3] In the new synthesis presented here monoethyl adipate[4] is converted to diethyl α-bromoadipate[5] from which α-aminoadipic acid is obtained both by direct amination and by condensation with potassium phthalimide followed by hydrolysis.

Experimental

α-Aminoadipic Acid: (a) By Direct Amination.—Ten sealed, glass pressure bottles (capacity 200–250 cc.), each containing 4 g. (total 40 g., 0.14 mole) of diethyl α-bromoadipate dissolved in 90 cc. of a saturated, absolute alcohol solution of anhydrous ammonia were heated at 60–65° for six days. After concentrating the contents to a small volume on a water-bath *in vacuo*, 100 cc. of water was added and evaporated to dryness. The residue was refluxed for four hours with 40 cc. of 12 *N* HCl and the acid solution removed as previously described. The solid was dissolved in water and treated with excess aniline. The precipitate resulting after 24 hours in the refrigerator was filtered and washed with cold 50% alcohol until halogen free; yield 19 g. (86% based on diethyl α-bromoadipate).

Anal. Calcd. for $C_6H_{11}NO_4$: C, 44.7; H, 6.83; N, 8.70. Found: C, 44.6; H, 6.95; N, 8.91.

(b) **By Hydrolysis of Diethyl α-Phthalimidoadipate.**—Fourteen grams (0.05 mole) of diethyl α-bromoadipate and 9.3 g. (0.05 mole) of potassium phthalimide were heated with stirring for two hours at 130–135° and 4.5 hours at 165°. The residue was washed thoroughly with hot benzene and filtered. The filtrate was washed with water, dried, and the solvent removed under reduced pressure. The crude diethyl α-phthalimidoadipate crystallized upon cooling. A sample, recrystallized from 95% alcohol, melted at 48°.

Anal. Calcd. for $C_{18}H_{21}NO_6$: C, 62.2; H, 6.05; N, 4.03. Found: C, 62.2; H, 6.04; N, 4.11.

The crude ester was converted into α-aminoadipic acid by acid hydrolysis[6]; yield 6.9 g. (84% based on diethyl α-bromoadipate).

Anal. Calcd. for $C_6H_{11}NO_4$: C, 44.7; H, 6.83; N, 8.70. Found: C, 44.8; H, 6.80; N, 8.89.

The melting point for α-aminoadipic acid has been reported as 206°[2] and 185–189°.[3] We have found it to vary from 165 to 202° depending upon the rate of heating and the bath temperature at which the sample is introduced.

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(1) Sorensen, *Compt. rend. trav. lab. Carlsberg*, **6**, 1 (1903).

(2) Dieckmann, *Ber.*, **38**, 1656 (1905).

(3) Gaudry, *Can. J. Research*, **B27**, 21 (1949).

(4) "Organic Syntheses," Coll. Vol. II, 1943, p. 276.

(5) Schwenk and Papa, THIS JOURNAL, **70**, 3626 (1948).

(6) Fink, Enns, Kimball, Silverstein, Bale, Madden and Whipple, *J. Exp. Med.*, **80**, 455 (1941).

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Preparation of 3,4-Dimethoxyphenyl- and 4-Hydroxy-3-methoxyphenylalkylcarbinols

BY PHILIP C. ROBERTI,[1] ROGER F. YORK[1] AND WARREN S. MACGREGOR

The only 3,4-dimethoxyphenylalkylcarbinol previously reported is 1-(3,4-dimethoxyphenyl)-1-propanol which was obtained by Behal and Tiffeneau[2] from the reaction of ethylmagnesium iodide with veratraldehyde and by Muller, Raltschewa and Papp[3] from hydrogenation of 3,4-dimethoxypropiophenone. Of the corresponding 4-hydroxy-3-methoxy- analogs only 1-(4-hydroxy-3-methoxyphenyl)-1-ethanol and 1-(4-hydroxy-3-methoxyphenyl)-1-pentanol have been reported.[4,5] These were prepared by treating vanillin benzoate with the appropriate Grignard reagent and saponifying the ester.

The preparation of carbinols by the direct reaction of the aldehyde group of vanillin with Grignard reagents has not been reported. Finnemore[4] demonstrated that the reaction with an equal molec-

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(1) Taken from the M. S. Theses of Philip C. Roberti and Roger F. York.

(2) Behal and Tiffeneau, *Bull. soc. chim.*, [3] **4**, 301 (1908).

(3) Muller, Raltschewa and Papp, *Ber.*, **75B**, 692 (1942).

(4) Finnemore, *J. Chem. Soc.*, **93**, 1520 (1908).

(5) Howells, Little and Andersen, THIS JOURNAL, **52**, 4076 (1930).