mination of boiling points and other physical properties. Figures 1 and 2 were drawn from boiling points determined with a recently described alembic type tensimeter-still.[9] The temperature coördinates of these figures (Cox charts) were laid off as linear functions of $1/(t° + 223)$. This was easily achieved[10] by adding 50° to each calibration mark on a Cox chart graduated according to $1/(t° + 273)$.

Boiling points of the esters at 1 mm. pressure were taken from Figs. 1 and 2 and plotted *vs.* the normal boiling points of the alcohols ROH. These points fell approximately on a straight line, the equation of which was $B_E = 0.67\ B_A + 115$, where B_E = b. p. of the ester at 1 mm. and B_A = b. p. of ROH at atmospheric pressure. The maximum deviation from this line was 8° and the average was 4°. This equation is convenient for the estimation of the boiling points of lactate adipates for which data are not available.

Acknowledgment.—We are grateful to C. O. Willits, C. L. Ogg and their associates for analytical data; to E. I. du Pont de Nemours and Company, Inc., for 3,5,5-trimethylhexanol, and to Carbide and Carbon Chemicals Corporation for 2-ethylhexyl, butoxyethyl, hexyloxyethyl and butoxyethoxyethyl alcohols.

Experimental

Lactates.—Ethyl and butyl lactates are available commercially. All the others except those in Table II have been reported previously[11] and were prepared by direct esterification[11d] of lactic acid or by the alcoholysis[6a] of methyl or ethyl lactate.

Ethyl and butyl lactyllactates (Table II) have been reported by Claborn[12] who made them by the reaction of lactide with the appropriate alcohol. We prepared these esters by the self-alcoholysis[13] of the corresponding lactate. Briefly, the lactate, containing about 0.2% of sulfuric acid, was refluxed in a still while approximately the theoretical amount of alcohol was distilled out. The catalyst was then neutralized, and the product was distilled at the lowest practicable temperature.

Reaction of Adipyl Chloride with Lactates.—One mole of lactate and one mole of pyridine were dissolved in 200 to 300 cc. of anhydrous ether. This solution was stirred and maintained at 0–10°, while one-half mole of adipyl chloride was added dropwise. After being left for several hours at room temperature, the reaction mixture was washed with water, dried and distilled. For the distillation, a short Vigreux column or an alembic type still[9] was most suitable. The latter was used exclusively for determination of boiling points.

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PHILADELPHIA 18, PENNSYLVANIA RECEIVED JULY 17, 1950

(9) Ratchford and Rehberg, *Anal. Chem.*, **21**, 1417 (1949).

(10) Rehberg, *Ind. Eng. Chem.*, **42**, 829 (1950).

(11) (a) Smith and Claborn, *ibid.*, **32**, 692 (1940); (b) Fein, Ratchford and Fisher, THIS JOURNAL, **66**, 1201 (1944); (c) Fein and Fisher, *ibid.*, **68**, 2631 (1946); (d) Rehberg, *Org. Syntheses*, **26**, 4 (1946).

(12) Claborn, U. S. Patent 2,350,388, June 6, 1944.

(13) Filachione, Costello and Fisher, "Plasticizers from Lactic Acid. Esters of Polymeric Lactic Acid," presented before the Division of Paint, Varnish and Plastics Chemistry, American Chemical Society, 112th Meeting, New York, Sept. 1947.

New Methods of Preparation of 2-Methy cyclohexen-1-one[1]

BY WALTER W. RINNE, H. R. DEUTSCH, MAX I. BOWMAN AND IRVING B. JOFFE

In investigating the preparation of 2-methyl-2-cyclohexene-1-one,[2] it occurred to us to try a number of methods previously unreported. One method which appears to be very satisfactory is bromination of 2-methylcyclohexanone, followed with dehydrobromination with 2,4-dinitrophenylhydrazine,[3,4] a method previously used only with steroidal compounds.

Bromination of 2-methylcyclohexanone with bromine in acetic acid gives a bromoketone fraction (I) which is different from that (II) obtained by the N-bromosuccinimide method as shown by differences in chemical behavior. (II) was converted virtually quantitatively to the 2,4-dinitrophenylhydrazone of 2-methyl-2-cyclohexen-1-one by the Mattox–Kendall procedure,[3] whereas (I) gives the same product but only in 68% yield. Pyridine dehydrobromination of (II) gave 2-methyl-2-cyclohexene-1-one in good yield, whereas (I) under the same conditions yielded 6-methyl-2-cyclohexen-1-one.[5] This difference could be explained either on the assumption that (I) contains both the 2-bromo and 6-bromo derivatives or that a rearrangement occurs in one of the dehydrobromination steps.

2-Methyl-2-cyclohexen-1-one could also be prepared from the Oppenauer oxidation of 1-methyl-1,2-cyclohexandiol to give 2-methyl-2-hydroxycyclohexanone, which, as has previously been shown,[2] can be readily dehydrated by various methods. Because of the difficulty of purification of the product, this method is less satisfactory than the others.

Bromination of 1-methylcyclohexene with N-bromosuccinimide gave a bromo derivative which could also be converted to this ketone by the Sommelet procedure, but in rather low yield.

Experimental

Bromomethylcyclohexanone (I).—To 20 g. of 2-methylcyclohexanone in 150 ml. of glacial acetic acid kept at 5°, was added with constant stirring 14 g. of bromine dissolved in 50 ml. of acetic acid containing 0.5 ml. of 4 *N* HBr. The bromo compound was separated by addition of water and extraction with ether. After washing with sodium bicarbonate solution, the ether solution was dried over anhydrous calcium sulfate, the ether removed by distillation and the residual liquid distilled. The fraction boiling at 65–97° at 10 mm. was collected as a viscous oil. The yield was 13 g. The bromo compound was not further purified but was used in subsequent reactions as soon as possible to avoid polymerization to a tarry material.

Bromomethylcyclohexanone (II).—From 33.5 g. of 2-methylcyclohexanone, brominated with 53 g. of N-bromosuccinimide in carbon tetrachloride in the usual manner,

(1) This work was carried out under contract N8onr76201 between the Navy Department, Office of Naval Research and the University of Louisville.

(2) Butz, Davis and Gaddis, *J. Org. Chem.*, **12**, 122 (1947).

(3) Mattox and Kendall, THIS JOURNAL, **70**, 882 (1948).

(4) Djerassi, *ibid.*, **71**, 1004 (1949).

(5) Kotz and Steinhorst, *Ann.*, **379**, 1 (1911).

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,[5] 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: $n^{20}D$ 1.4820; $\lambda_{max.}$ 231 mμ, log ε 3.96; $\lambda_{max.}$ 327 mμ, log ε 1.58; $\lambda_{max.}$ 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.; $n^{20}D$ 1.4727; $\lambda_{max.}$ 225 mμ, log ε 3.80; $\lambda_{max.}$ 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.

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

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF LOUISVILLE
LOUISVILLE, KENTUCKY

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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.

(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-

(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).

(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).