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: $n^{20}D$ 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
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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).

TABLE I

4-HYDROXY-3-METHOXYPHENYLALKYLCARBINOLS

Alkyl group	Yield, %	M. p., °C.	Methoxyl, % Calcd.	Found	Diacetyl derivatives B. p.,[a] °C.	M. p., °C.	Methoxyl, % Calcd.	Found	Acetyl, % Calcd.	Found
Ethyl	68	84–85	17.0	17.0	116–118	48–49	11.7	11.5	32.4	31.9
n-Propyl	50	61.5–62.5	15.8	15.8	120–121	1.5054[d]	11.1	11.1	30.7	30.7
Isopropyl	46	86.5–87	15.8	15.7	117–119	52–53	11.1	10.9	30.7	31.2
n-Butyl	57	80.5–81[b]	14.7	14.8	128–131	1.5023[d]	10.5	10.6	29.2	29.2
s-Butyl	30	64.5–65	14.7	14.9	122–124	1.5041[d]	10.5	10.3	29.2	30.2
t-Butyl	67	73–73.5	14.7	14.6	118–120	82–83	10.5	10.4	29.2	29.0
Isobutyl	32	51–53	14.7	15.0	122–123	1.5020[d]	10.5	10.7	29.2	29.6
n-Amyl	51	76.5–77.5	13.8	13.7	135–137	1.4998[d]	10.1	10.3	27.9	27.9
Ethyl[e]	88	89.5–90[e]	11.9	11.8						

[a] At 0.2 mm. [b] Reported value: 81.5°.[5] [c] 5-Bromo-4-hydroxy-3-methoxyphenylethylcarbinol, reported m. p., 88–89°. [d] $n^{20}D$.

ular quantity of methylmagnesium iodide involved only the phenolic hydrogen. Recently Cartwright and Haworth[6] prepared 1-(5-bromo-4-hydroxy-3-methoxyphenyl)-1-propanol by treating a fivefold excess of ethylmagnesium iodide with 5-bromovanillin. Duplication of their procedure led to an 88% yield.

The alcohols listed in Table I were prepared by treating vanillin with approximately six equivalents of the appropriate alkylmagnesium bromide in the usual manner. The presence of two hydroxyl groups (one on the phenyl residue and one on the side chain) was shown by the preparation of the diacetyl derivative. When three equivalents of alkylmagnesium bromide was used the yields were about 5% lower than those given in the Table.

The 1-(3,4-dimethoxyphenyl)-1-alkanols shown in Table II were obtained from the treatment of veratraldehyde with 2 equivalents of the corresponding alkylmagnesium bromides. Analysis of the products for hydroxyl gave low results and several attempts to obtain crystalline esters or urethans were unsuccessful. The principal reaction with excess phenyl isocyanate at 100° was dehydration evidenced by the formation of diphenylurea in good yields.

TABLE II

3,4-DIMETHOXYPHENYLALKYLCARBINOLS

Alkyl group	Yield, %	B. p.,[a] °C.	$n^{20}D$ or m. p., °C.	Methoxyl, % Calcd.	Found
Ethyl	62	102–103	1.5525	31.7	31.6
n-Propyl	63	110	64–65	29.6	29.6
Isopropyl	75	103	63–64[b]	29.6	29.5
n-Butyl	52	120–123	1.5395	27.6	27.4
s-Butyl	48	110–112	47–48[c]	27.6	27.4
Isobutyl	46	114–116	1.5355	27.6	27.8

[a] At 0.2 mm. [b] $n^{20}D$ 1.5403. [c] $n^{20}D$ 1.5357.

Experimental

The Grignard reactions were run in the usual manner. The preparation of 1-(4-hydroxy-3-methoxyphenyl)-1-propanol is typical. Magnesium turnings (9.5 g., 0.39 mole) and a crystal of iodine were placed in a dry 3-necked flask. Seventy-five cc. of absolute ether and 5 g. of ethyl bromide were added. When the reaction commenced a solution of 37.5 g. of ethyl bromide (0.39 mole total) in 75 cc. of ether was added dropwise with stirring during one hour and stirring was continued an additional one-half hour. The yield of ethylmagnesium bromide, determined by titration,[7] was 0.36 mole (94%). A solution of 10.0 g. (0.066 mole) of vanillin in 200 cc. of ether was then added dropwise during 1.25 hours, the resulting suspension was stirred an additional 1.75 hours and allowed to stand overnight. Saturated ammonium chloride solution (300 cc.) was then added and the mixture stirred until decomposition of the bromomagnesium salt was complete. After separating the ether layer, the aqueous layer was washed three times with ether. The ether solutions were combined, dried over magnesium sulfate and evaporated at aspirator pressure to approximately 50 cc. When this solution was poured into 300 cc. of petroleum ether, an oil separated and crystallized upon standing. Filtering and drying gave 8.2 g. (68%) of crude product, m. p. 79–84°. Purification was effected by recrystallizing from benzene or benzene–petroleum ether mixtures. The diacetates were obtained using excess acetic anhydride in pyridine solution at room temperature.

The 3,4-dimethoxyphenylalkylcarbinols were prepared in similar manner. The bromomagnesium salt (from 0.6 mole magnesium, 0.6 mole alkyl bromide and 0.3 mole veratraldehyde) was decomposed by pouring the reaction flask contents into a mixture of 500 g. of ice and 40 ml. of concentrated sulfuric acid. The *n*-propyl- and isopropylcarbinols were obtained crystalline from the ether–petroleum ether precipitation and were purified either by recrystallization or distillation. The other carbinols were oils and were purified by distillation at 0.2 mm. pressure.

(6) Cartwright and Haworth, *J. Chem. Soc.*, 535 (1944).

(7) Gilman, Zoellner and Dickey, THIS JOURNAL, **51**, 1580 (1929). The yields in the other cases were also in close agreement with those reported by these authors.

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The Infrared Spectrum and Structure of Tungsten Carbonyl

BY RAYMOND K. SHELINE

X-Ray diffraction studies[1] of the solid hexacarbonyl of tungsten and electron diffraction studies[2] of its vapor indicate with reasonable certainty that the six carbonyl groups are arranged octahedrally around the central tungsten atom as shown in Fig. 1. This structure can also be inferred from the fact that $W(CO)_6$ is a complex with a coördination number of 6 which hybridizes two 5d, one 6s and three 6p orbitals, the d^2sp^3 hybrid being an octahedron.

(1) W. Rüdorff and U. Hofmann, *Z. physik. Chem.*, **B28**, 351 (1935).

(2) L. O. Brockway, R. V. G. Ewens and M. W. Lister, *Trans. Faraday Soc.*, **34**, 1350 (1938).